

Assessment of Heavy Metal Concentration and Fractionation in Selected Dumpsite Soils within Ibadan Metropolis, Nigeria

Abstract

Dumpsites are gradually turning into farm land with the belief that they must have accumulated necessary nutrient element required for plant growth and thus making some farmers to use refuse dumpsite material for composting not minding the type of waste that are involved and what they are actually made up off. This study therefore investigated the concentrations of heavy metals in selected dumpsite soils and various forms to determine their mobility with the view to crystallize their extent of contamination to the soil when used for farming activities. Two dumpsites (Bodija dumpsite (BD) and Olukunle dumpsite (OD) were randomly selected from Ibadan South Western Nigeria based on different waste distributions at the depth of 0-20cm. The metals investigated include: Cd, Pb, Cu, Zn, As, Cr and Ni. Sequential extraction method was used to assess the redistribution of heavy metals from which total heavy metals were earlier determined by acid digestion with aqua regia solution. Treatments were laid out in a completely randomized design with four replicates. Data collected from the laboratory and were analyzed using descriptive statistics and ANOVA at $p \leq 0.05$. The mean concentrations (mg/kg) of total HM were 100.9, 48.9, 57.8, 16.6, 49,022.0 and 3,627.3 for As, Cr, Cu, Ni, Pb and Zn respectively with coefficient of variance ranging from 1.31% for Ni to 141.2% for Pb. There was no significant difference ($T \text{ stat}=1.70$ at $P= 0.107$) in metal concentration in both BD and OLD soil. The residual fraction was the most predominant in the soils with the exception of Pb and Zn. The average metal concentration over soil samples were 307.6, 2,390.8, 1,666.8 and 4,448.8 for the exchangeable, reducible, oxidizable and residual fractions respectively. Only Zn had an appreciable amount (54.3%) associated with the exchangeable fractions while the oxidizable fraction was highest for Pb (79.1%) in soil BD and Zn (78.4%) in soil OD. It is therefore paramount to create awareness on the health hazard inherent in planting on refuse dumpsite soil without ascertaining its metal status, so that metals in them do not end up in the edible parts of crops.

Keywords: Dumpsite, Heavy metals, Fractionation, contaminated soils, sequential extraction

1.0 INTRODUCTION

Heavy metal pollution is a major problem across the globe due to its great consequence on human health, plant and the ecosystem. Increase in population and urbanization had contributed to enormous generation of both industrial and municipal waste in urban centers in Nigeria. An estimate of 7.6 million tons of municipal solid waste was dumped per day in developing countries as reported by [1]. Furthermore, some of these wastes contain heavy metals which eventually are adsorbed onto soil surface and found their ways into plant and finally end up in the human system [2]. Heavy metals can accumulate in human cells and disrupt the functions of vital organs and glands like the heart, brain, kidney, and bone and the liver. They also in addition displace vital nutritional minerals from their origin, hindering their biological functions [3]. Heavy metal in plant induces oxidative stress which causes cellular damage and disturbance of cellular ionic homeostasis [4].

Investigation had shown that some of these dumpsites are gradually turning into farm land for the cultivation of vegetable for the cities dwellers [5-6]. In an attempt to avoid the exorbitant price being charged for the purchase of fertilizer, some farmers have recourse to the use of composted material to fertilize their soils to improve crop production thereby introducing heavy metals into their crops not knowing that heavy metal are embedded in their compost. Plant on the other hand takes up these metals via the root into the harvestable parts. This becomes possible because metals come in the ionic form which makes it easy for uptake through plant root and easy translocation into the stem and the aerial parts of the plant.

The mobility and bioavailability of heavy metal depend absolutely on their speciation or chemical forms. These forms are determined by sequential extraction technique, this method give vivid information about metal affinity to the soil components together with the strength to which they are bound to the soil matrix [7]. Also the metal fractions give detail about soil origin, biological and physicochemical availability, their mode of occurrence, mobility and transportation of trace metals[8]. Several extraction scheme had been employed and described in literature but the Tessier et al., 1979 has been widely used. This procedure has been able to identified six chemical or geochemical forms of heavy metals [9-11]. This method however had given way to a method that only involved four chemical or geochemical forms using the modified Community Bureau of Reference (BCR) as described by [12]. Three different extraction procedures were used to establish the extractability and to predict the phytoavailability of heavy metals in the soils. The following fractions were identified with the BCR methods;

Exchangeable and acid extractable, reducible form (Fe/Mn oxide bound), the oxidizable forms (organic matter and sulphur bound) and the residual form (residual/silicate).

This study therefore aimed at determining the concentration of Ni, Cr, Pb, Zn, Cd, Cu and As in selected dumpsite in Ibadan and investigate their environmental contamination risk between the different chemical speciation forms.

2.0 Material and Methods

2.1 Description of Study Site

This study was carried out at two locations: Agronomy Department, University of Ibadan, Oyo State, Nigeria and Purdue University, West Lafayette, Indiana State, United State of America. Four soil samples were collected for this study from dumpsites located in Ibadan. Ibadan has a mean annual rainfall of 1289 mm and mean annual temperature of 26.3 °C [13]. Sampling site description is shown in Figure 1.

2.2 Soil sampling and preparation

A total of four surface polluted soils (0-20cm) were purposively sample at different locations within Ibadan municipal area in the central region of South Western Nigeria. Sampling was done with the aid of soil auger and spade. Triplicate soil samples were collected randomly from each location at different points, mixed and bulked to form a composite sample, out of which representative samples were air-dried, crushed and sieved through a 2 mm sieve and for each location after which they were bagged in clean polythene containers to prevent further contamination. Samples were further ground and passed through a 0.5 mm sieve for organic carbon and total nitrogen analysis

.

2.3 Routine soil analysis

All glassware used in this study were pre-washed with HNO₃ and rinsed with deionize water and all the chemicals used were of analytical grade purchased from Sigma Aldrich, USA Chemical analyses were carried out using the recommended chemical soil test. Procedures for the North Central Region, U.S.A [14] were used. The pH and electrical conductivity of soil samples were measured with a soil: water ratio of 1:2 using pH meter. Total Nitrogen was measured by an automated carbon and Nitrogen analyzer using the principles of oxidative combustion-

chemiluminescence. Concentrations was then determined by comparing to known standards. Total carbon was determined by combusting the sample and converting all carbon to carbon dioxide. The carbon dioxide is measured using a non-dispersive infrared gas analyzer. Available P was extracted with Melich III and regressed to weak bray P data. Exchangeable cations were extracted with IM NH_4OAC and CEC was obtained by summing the meq exchangeable bases per 100kg (cmol/kg) and meq exchangeable acidity per 100g (cmol/kg). Exchangeable acidity may be estimated from. The SMP buffer pH measurement:
meq acidity per 100 g = 12 (7.0 - SMP buffer pH) .
Particle size analysis was determined using Bouyoucos technique as outlined by [15]

100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116

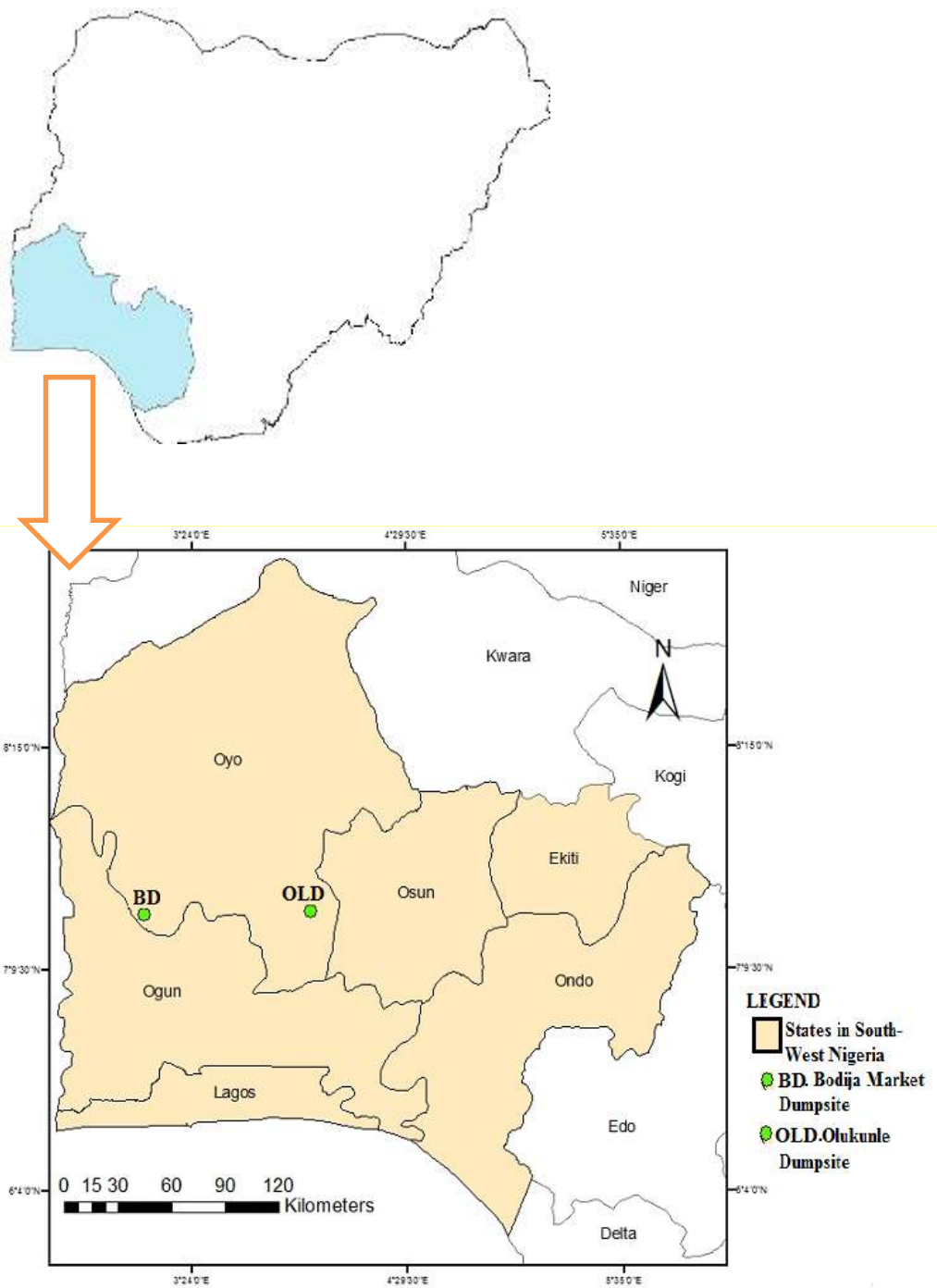


Figure 1: Map of South-western Nigeria showing polluted soil sample site in Ibadan metropolis.

2.4 Total heavy metals (Pb, Cd, Ni, Cr, Cu and Zn) and Fractionation experiment

Acid digestion with aqua regia solution (Hydrochloric acid and Nitric acid in ratio 3:1) was used to evaluate the total heavy metal content of the soil [16]. Inductive couple plasma –Mass spectrophotometer was used to read the total metal concentration. The acid digested soil-metal analysis was performed in triplicates.

Metal fractions in the soils were determined using sequential extraction technique by [12] with a little modification in the volume of the aqua regia reagent used. The following fractions were determined ; (Fractions A) Exchangeable and acid extractable- (0.11M CH₃COOH-extractable); (Fraction B) Reducible form – (0.1M NH₂OH-HCl-extractable) ; Fraction C the oxidizable forms – (8.8M H₂O₂)/ 1M CH₃COONH₄-extractable) of the metals and the residual form (Fraction D) which was be computed as the sum of fractions A,B& C and subtracted from the total content. Heavy metal contents in the digests were analyzed using ICP-MS.

2.5 Statistical analysis

The data collected were evaluated using excel to calculate mean, standard deviation and coefficient of variance for each sets of values.

3.0 RESULT AND DISCUSSION

3.1 Physical and chemical properties of the experimental soils

The physical and chemical properties as well as the heavy metal concentrations of the soil used for the study are contained in Tables 2 and 3. The pH of Bodija refuse dumpsite (BD) soil was 7.7, while that of Olukunle dumpsite (OLD) soil was 6.3. Cation exchange capacity (CEC) was greater in BD (23.1cmol/kg) soil than in OLD (1.5cmol/kg). Soil organic matter was high across the soil samples. Total Nitrogen in OLD (3.7g/kg) soil was more than in OLD (0.6g/kg). The exchangeable bases in the soil varied, with (BD) soil having the highest Potassium (K),Ca and Mg with the following values respectively; 3.53, 17.3 and 2.3 cmol/kg while Olukunle soil had these values in same order; 0.2, 0.3

and 0.2cmol/kg. Available phosphorus (P) was 1mg/kg in soil (OLD) and 197mg/kg in soil BD. The soils are generally in the sandy loam textural class.

3.2 Total heavy metal concentrations in experimental soils

The soils were analyzed for the following metals: As, Cd, Cr, Cu, and Ni, Pb and Zn as shown in Table 3. Some of their concentrations were higher than the FAO and USEPA critical levels. The concentration of the Arsenic was highest in soil OLD (157 mg/kg) and the least were recorded in soil BD (44.65mg/kg).

Chromium concentration was 38.78mg/kg in BD soil and 58.97mg/kg in soil OLD. Copper (Cu) was 37.60 mg/kg in soil BD and 77.91mg/kg in soil OLD. Nickel in both soils was almost in same concentration with soil BD (16.80mg/kg) **slightly higher** than values obtained in soil OLD (16.47mg/kg). Lead (Pb) concentration was extremely high in soil OLD (97,951mg/kg) than in soil BD (92.25mg/kg) Zinc concentration was very high in soil BD (6,708 mg/kg) when compared to its concentration in soil OLD (546.11mg/kg) . There was no significant difference ($T=1.70$ at $P= 0.107$) in metal concentration in both BD and OLD soil.

Table 2 Some basic chemical and physical properties of the experimental soils

Soils		Locations
Soil BD (Bodija market dump site)		Soil OD (Olukunle dumpsite)
Soil properties		Values
pH(H ₂ O)	7.5	6.3
CEC(cmol/kg)	23.1	1.5
OM(g/kg)	35	31
N(g/kg)	3.7	0.6
Ca (cmol/kg)	17.25	1.0
Mg(cmol/kg)	2.33	0.29
K(cmol/kg)	3.53	0.2
Available P (mg/kg)	197	1
Particle Size distribution (g/kg)		
Sand	753	649
Clay	69	55
Silt	178	296
Textural class	Sandy loam	Sandy Loam

168 Table 3. Total heavy metal concentrations (mg/kg) in the experimental soil samples

Heavy metals	Soil BD	Soil OD
As	44.65±1.64	157.08±27.64
Cr	58.97±2.71	38.78±2.47
Cu	37.60±1.78	77.91±4.38
Ni	16.80±1.0	16.49±2.00
Pb	92.25±8	97951.73±9156.70
Zn	6708.12±635	546.11±34.77
	T stat = 1.70	
	P= 0.107	NS

169 Key

170 **Soils**

171 BD- Bodija refuse dump site

172 OD- Olukunle Dumpsite

173

174

175

176

177

178

179

180

3.3 Heavy metal Fractions ($\mu\text{g/g}$) in the experimental soils

The chemical fractions of Arsenic (As) Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb) and Zinc (Zn) shown in Tables 4 and 5 were similarly dominated by the residual and the reducible fractions, except for Chromium which only had the exchangeable and acid extractable form in the least proportion and its reducible forms were not detected in all the Soil Samples.

3.4 Exchangeable Fractions/acid extractable.

The exchangeable fractions of all the metals were low as shown in Table 4. However Zn had about 55% of its concentration associated with this fraction in soil (BD). There were no detectable level of Cr in this fraction in soils OLD

3.5 Reducible Form (Fe/Mn oxide bound).

The reducible fractions of sampled metals in the two soils were below 50% of all the total metal content. However, about 30% of total Zn total in soil BD was associated with this fractions while minimal concentrations of As, Cr, Cu and Pb were recorded in same soil. In soil OLD, Cu concentration found in the reducible form was more than the other metals having about 38% of its total value. Chromium had about 30% of its total in this fractions and Pb about 27% of its total concentration as shown in Table 4.

3.6 Oxidizable form (organically bound +Sulphur bound).

The oxidizable fractions of Arsenic, Chromium and Nickel were not detected in all the soil samples. In BD soil, Pb had the highest concentration (79%) of its total content associated with the oxidizable fractions; the least was recorded for Zn (8%). Even though Zn in soil OLD was predominantly associated with the oxidizable fraction with 78% of its total value. Lead was followed with 49% of its total contents and Cu had the least of about 29% of its concentration associated with the oxidizable fraction (Table 5).

206 **Table 4: Exchangeable and Reducible fractions (Fe/Mn oxide bound) of metals in soil samples**

Metals	Exchangeable metal fractions		Reducible fractions (Fe/Mn oxide bound)	
	BD	OLD	BD	OLD
As	0.35±0.02 (0.79%)	ND	0.88±0.84 (1.97%)	36.07±2.21 (22.96%)
Cr	1.14±0.17 (1.93%)	ND	ND	ND
Cu	1.14±0.17 (1.93%)	1.78±0.40 (2.28%)	ND	30.32±5.76 (38.92%)
Ni	2.41±0.25 (14.35%)	ND	ND	1.74±0.68 (10.55%)
Pb	1.14±0.30 (1.24%)	ND	8.78±3.7 (9.5%)	26447.57±737.8 (27.00%)
Zn	3677.55±53.4 (54.82%)	5.86±1.21 (1.07%)	2061.19±117 (30.73%)	103.34±2.83 (18.92%)

207 Key

208 **ND- Not detected**

209 **BD- Bodija dumpsite,**

210 **OLD- Olukunle dumpsite**

211

212

213 **3.7 Residual fractions in soil samples**

214 Arsenic, Cr and Ni had larger portion of their total concentration associated with the
215 residual fraction in BD soil. The least concentration was about 7 % of total Zn while Pb had 10%
216 of its total in this fraction. In OLD soil, Chromium was predominantly associated with the
217 residual fractions. Appreciable amount of As (74%), Ni (89%) and Pb (54%) were in the residual
218 fractions, notwithstanding, Zn had the least value associated with this fraction.

219 **Table 5. Oxidizable and Residual fractions of metals in soil samples**

Metals	Oxidizable fractions		Residual fractions	
	BD	OLD	BD	OLD
As	ND	ND	43.41 (97.22%)	34.20 (74.30%)
Cr	ND	ND	57.83 (98.06%)	38.78 (100%)
Cu	ND	22.64±20.6 6(29.06%)	57.83 (98.06%)	23.17 (29.73%)
Ni	ND	ND	14.39 (85.65%)	14.75 (89.45%)
Pb	72.98±2.10 (79.11%)	18942.18±81.0 (19.34%)	9.35 (10.14%)	52561.98 (53.66%)
Zn	529.87±103.57 (7.90%)	433.51±148.58 (78.38%)	439.51 (6.55%)	3.40 (0.62%)

220 Key

221 **ND- Not detected**

222 **BD- Bodija dumpsite,**

223 **OLD- Olukunle dumpsite**

224

225 **4.0 DISCUSSION**

226 The physico-chemical properties of soils characteristics show that BD soil was slightly alkaline
227 while that of OLD was slightly acidic. An alkaline soil may not favor metal mobility due to high
228 sorption of these metals in them while low pH condition may enhance metal solubility and
229 possible movement into water column and subsequent leaching into underground water. The
230 chemical properties of metals in the soil and their retention in soil solid phase are affected by pH.
231 Metals become soluble and available with increase in the pH of the soil and are therefore
232 available for plant uptake [17-18]. The pH of these soils also falls within the optimum range for
233 soil nutrient availability for plant uptake according to [19].

234 The organic matter content of the soils was high according to [20] which is an indication that
235 these soils could have a great impact on the sorption of metals that are present in them. Also
236 organic matter is important because of its relationship with metals most especially Copper. Soil
237 organic matter had been reported to be a major soil property that greatly affects sorption of heavy
238 metal because they contain functional groups that are capable of complexing metals [21-22].
239 Higher Organic matter content had been reported to be peculiar characteristics of waste
240 contaminated soil [23]. The high total nitrogen content in soil BD is probably because of the
241 nature of the various wastes in this dumpsite which comprises mainly of municipal and domestic
242 wastes. However, Total N from OLD dumpsite is low as a result of the industrial waste
243 deposited over a long period of time which may have an adverse effect on the soil Nitrogen.
244 More so this element is one of the limiting nutrient elements in tropical soils. Soil BD could
245 have greater ability to hold and retain both metals and nutrient elements because of its high CEC
246 (23.1) (cmol/kg) than OLD soil that is characterized with low CEC.

247 The high P values in soil (BD) could be attributed to excessive burning of the wastes on the
248 dumpsite which is a normal practice for dumpsite in that area. Another reason for the high P
249 could also be attributed to the high organic matter content of the soil that had been earlier
250 reported for this soil. In soil OLD the P content was low. The high K content recorded for BD
251 Soil could be as a result of the nature of the parent rock basement complex characteristics of the
252 soil that may be rich in K bearing minerals and the large quantity of ashes deposited on the soil

through burning can also be a source of soluble K [24]. The value of K recorded for soil OLD was also above the critical level for K according to [25]. Magnesium is also essential for photosynthesis in plants and its value in soil BD is above the critical value reported by [25] and that of OLD soil is within the critical values for South-Western soils in Nigeria. Calcium content in BD soil was high while that of OLD soil was low. The texture of the soils were sandy loam, these soil had higher sand content than silt and clay, reflecting the parent material from which they were formed. [26] reported that loamy and clay textured soils as those that have high moisture holding capacity and loamy sands and sand have low moisture holding capacity. Therefore, they could also have the potential to leach heavy metals as they will not be able to hold them as reported by [27].

The concentration of heavy metals in the experimental soil varies considerably probably because of the source and the years of contamination. The concentration of As in both soils exceeded the limit range for soils recorded for UK (20mg/kg) and Canada (37mg/kg) [28]. This could be a problem due to the probability of plant uptake of this metal.

Cadmium concentration in BD soil is below the USEPA recommended threshold limit while that of OLD soil was above this limit as reported by [29]. This is an indication that Cd is a major pollutant from industrial waste. Cadmium had been listed by [30] as one of the major pollutants and the injection of high level can irritate the stomach causing diarrhea and vomiting. Copper concentration in soil OLD was above the (50mg/kg) permissible level based on USEPA recommendation while that in BD soil was below this range. The critical permissible level for chromium in soil by USEPA and Great Britain according to [29] is 50mg/kg and only BD soil exceeded this limit while OLD soils fall below it. This could be as a result of the waste containing colored polythene bags, and discarded plastic wastes [31] which were the major waste from BD being very close to a very big market in the city.

Copper a micronutrient is good for plant but high concentration can have an adverse effect on plant growth. Its higher concentrations in OLD soil could be as a result of biodegradable waste introducing metallic copper into the dumpsite according to [32]. The concentration of Nickel was below the permissible value from USEPA. Lead concentration was extremely high in soil OLD. This value was higher than the permissible value proposed Pb value by [33] and [34]

282 NEPCA, 2010 for agricultural soils. The reason could be attributed to waste from the defunct
283 battery industries dumped at this site; however, Lead in BD soil was below this limit.

284 The very high concentration of Zn in BD soils (6708mg/kg) could be due to the fact that the
285 categories of waste in this dumpsite may be high in pollutants of Zn origin. High concentration
286 of Zn is enough to cause phyto-toxicity in plant with symptoms such as chlorosis, reduction in
287 leaf production due to wilting of plant leaves and stunted growth. Zinc from OLD soil was also
288 higher (300mg/kg) than the permissible level recommended by USEPA.

289 The potential of migration of metals in soil system depends on the chemical form of the metals.
290 Chromium and Arsenic concentrations were found mostly in the residual fractions in all the soil
291 samples. [35-36] had reported that metals found mostly in residual fractions could be due to the
292 sandy nature of the soil which resulted in the co-precipitation of the metals with various silicate
293 species consequent to their adsorption into the mineral lattice. This fraction can be used as a
294 guide to the degree of pollution of the soil. The smaller the percentage of metals found in these
295 fractions, the greater the pollution that will be generated [37]. There was also no detectable level
296 of Cr in the Fe and Mn oxide fractions. This implies that Cr in this fraction was tightly held and
297 its release into the soil solution will be slow and as such may not pose any problem of pollution
298 to the environment and groundwater [38].

299 Most species of Cu like Cr was found in the residual fractions of BD and 100% of Cr in OLD
300 soil, while the same soil only had a little portion of Cu associated with it. This is in consistence
301 with the findings of [39&40]. They reported that Cu was found in the soil in the residual forms.
302 Copper usually have high affinity for soluble organic ligand and this may result in complex
303 formation which will greatly increases its mobility in soil. This may be responsible for its
304 associated with the Iron and Manganese oxide in the reducible fractions and oxidizable form in
305 the organic fractions in soil OLD. [41&40] had also reported that Cu was the most abundant
306 metal in the organic matter fractions. As pH increases more Cu are complexed with organic
307 matter and become unavailable. That could be the reason why very low concentration of this
308 metal was found in the exchangeable / acid extractable fractions in all soils.

309 Nickel was present in all the fractions except in the organic forms. Large amount of Ni was
310 mostly found in the residual form in all the soil types. Earlier report by [42, 11, 43- 44] had

indicated that Ni in its natural origin form is mainly associated primarily in soil with the residual fractions. Although, only soil OLD was associated with the Fe/Mn oxide fractions and this oxide has been reported to control the mobility of Ni in polluted soils according to [11]

The high organic matter Pb bound to BD soil could be attributed to the fact that Pb has a strong affinity for organic matter and the formation of its complexes may greatly increase the mobility of Pb in soil as reported by [41-45]. Furthermore, the pH above 6 makes Pb to either be adsorbed on clay surfaces or form Pb carbonate. The residual form of Pb was highest in soil OLD (53.66%), while BD was very low (10.14%). The observed result shows that most of the Pb in this study existed in the non-residual fraction of Fe-Mn oxide and organic matter than the residual fraction. The slow release of Pb into the environment can be a potential hazard to human health and the environment through ingestions as those in the non-residual fraction can be released slowly.

High percentages of Zn were not associated with the residual fraction like it was the case with some of the metals reported in this study. The association of Zinc with the reducible fraction has been reported earlier by several other scientists [9&46]. Appreciable amount of Zn in the oxide form was recorded in soil samples BD and OLD. The dominance of the Fe/Mn oxide bound Zn have also been reported earlier by [9&47]. Zinc associated with organic matter fractions were fairly small (<9%) in all the soil samples except for OLD (78.38%). Metal bounded to the organic matter are temporarily inaccessible but can be solubilized by chemical oxidation. The fractions bounded to the exchangeable/acid extractable forms were not negligible and they followed this order: BD>OLD. Metals associated with the exchangeable fractions are however bioavailable and mobile, while a change in the pH of the soils can also release this fraction into the environment

5.0 Summary and conclusion

The concentration of heavy metals from the various dumpsite examined in this study exceeded the normal level in soil according to [48] and USEPA. Furthermore, all the metals have their higher concentrations in the residual fractions which posed no problem to the ecosystem except when the soil undergo reduction reaction which is the only condition that makes them available . Arsenic also has appreciable concentrations in the reducible form which could be released when

the soil undergoes reduction reactions while low concentrations were associated with the exchangeable fractions just like Chromium. Chromium concentrations were not detected in the oxidizable and reducible forms. Highest Cu concentration associated with the reducible fraction was found in OLD soil while other soil types also recorded substantial concentration in these fractions. However all the soils had low concentrations in the exchangeable fractions except Zn and can be easily available for plant uptake. Lead and Zinc were also associated with the reducible fractions. This fraction (reducible) with time could also be available for plant uptake.

It is therefore paramount to desist from the habit of planting on refuse dumpsite soil, knowing that metals in them bio accumulate and can be taken up by the plant ending up in the food chain and finally in the human system causing serious problem. Further policies which will prevent the indiscriminate disposal of both industrial and municipal waste should be enacted. There is also the need to test for the physiochemical parameter of dumpsite material to be used as compost that will be applied to the soil to enhance its fertility.

REFERENCES

- 1 Nagendram R, Joseph K, Esakku S, Visvanatha C, Norbu T (2006). Municipal Solid Waste Dumpsites to Sustainable Landfills. Development Insight October – December. Pp. 65-68
2. Benson NU, Ebong GA (2005). Heavy metals in vegetables commonly grown in a tropical garden ultisol. J. Sustainable Trop. Agric. Res., 16: 77-80.
- 3 Singh, R., Gautam, N., Mishra, A and Gupta, R. 2011 Heavy metals and living system: An overview. Indian Journal of Pharmacology 43(3): 246-253.
- 4 Singh MR. Impurities-heavy metals: IR perspective. 2007. Available from: <http://www.usp.org/pdf/EN/meetings/asMeetingIndia/2008Session4track1.pdf>
5. Okorokwo NE, Igwe JC, Onwuchekwe EC (2005). Risk and health implication of polluted soils for crops production. Afr. J. Biotechnol., 4(13): 1521-1524
6. Ebong GA, Akpan MM, Mkpene VN (2008). Heavy metal contents of municipal and rural dumpsite soils and rate of accumulation by *Carica papaya* and *Talinum triangulare* in Uyo, Nigeria. E-J. Chem., 5(2): 281-290.
7. Kotoky P, Bora BJ, Baruah NK, Baruah J, Baruah P and Borah GC (2003). Chemical fractionation of heavy metals in soils around oil installation, Assam. Chem. Spec. Bio. 15(4): 115- 125.

-
- 374
375 **8.** Tessier A and Campbell PGC. 1987. Partitioning of trace metals in sediments: relationship
376 with bioavailability. *Hydrobiologia*, 149: 43-52.
377
- 378 **9.** Ramos L, Hernandez LM and Gonzalel MJ . 1994. Sequential fractions of Copper, Lead,
379 Cadmium, and Zinc in soils from Domana Natural Park. *Journal of Environmental Quality*
380 23:50-57.
- 381 **10.** Abollino O, Giacomino A, Malandrino M, Mentasti E, Aceto M. and Barberis, R.
382 (2006) Assessment of metal availability in a contaminated soil by sequential extraction. *Plant*
383 *Soil*, 265(1 – 2), 243 –252.
384
- 385 **11.** Hickey MG and Kittrick JA. (1984) Chemical partitioning of cadmium, copper, nickel, and
386 zinc in soils and sediments containing high levels of heavy metals. *J. Environ. Qual.*, 13, 372 –
387 376.
388
- 389 **12.** Quevauviller P. 1998. Operationally defined extraction procedures for soil and sediment
390 analysis I. Standardization. *Trends in Analytical Chemistry* 17:289–298.
- 391 **13.** Alabi RT and Ibiyemi AG. 2000. Rainfall in Nigeria and food crop production.. *Agronomy*
392 *in Nigeria* , M.O. Akoroda,. Eds. 63-67pp
393
- 394 **14.** Brown JR. 1998. Recommended Chemical Soil Test Procedures for the North Central
395 Region, North Central Regional Research Publication No. 221: 31-58 (Revised)
- 396 **15.** Gee GW and Or D. 2002: Particle size analysis. In: *Methods of soil analysis. Part 4. Pyhsical*
397 *methods.* J.H Dane and G.C.P Topp (eds.) pp. 255-293. American society of Agronomy,
398 Madison,WI
399
- 400 **16.** Mench MJ, Didier VL , Loffler M, Gomez A. and Masson P. 1994. A mimicked - situ
401 remediation of metal-contaminated soils with emphasis on Cadmium and Lead. *Journal .of*
402 *Environmental Quality* 23: 58 – 63.
- 403 **17.** Oliver DP, Tiller K G, Alston AM, Cozens G.D and Merry RH (1998). Effect of soil pH
404 and applied cadmium on cadmium concentration in wheat grain. *Aust. J. Soil Res.* 36:571-583.
405
- 406 **18.** Salam AK and Helmke PA (1998). The pH dependence of free ionic activities and total
407 dissolved concentrations of copper and cadmium in soil solution. *Geoderma* 83:281-291
- 408 **19.** Isirimah NO , Igwe C and Iwegbue CMA (2003). Important Ions in Soils Environment; In:
409 *Introductory Soil Chemistry and Biology for Agric and Biotech.* Osia In'l Pub. Lt. Port Hacourt.
410 pp. 34-97
- 411 **20.** FMANR, 1990. Literature review on soil fertility investigations in Nigeria (in five volumes).
412 Federal Ministry of Agriculture and Natural resources, Lagos .pp:32-48
-

-
21. Neagoe A, Virgil I, and Ileana C F (2003) The Role of Organic Matter in the Mobility of Metals in Contaminated Catchments E. Kothe and A. Varma (eds.), Bio-Geo-Interactions in Metal Contaminated Soils, Soil Biology 31, DOI 10.1007/978-3-642-23327-2_15, # Springer-Verlag Berlin Heidelberg 2012
22. Saar R A and Weber JH. (1982) Fulvic acid: Modifier of metal-ion chemistry. Environmental Science and Technology, 16: 510–517.
23. Shuman LM. 1991. Chemical forms of micronutrients in soils. In J. J. Mortvedt (ed.). Micronutrients in agriculture. Soil Soc. Soc. Amer. Book Series #4. Soil Sci. Soc. Amer., Inc., Madison, WI
24. Ayodele OJ and Omotosho SO. (2008) Nutrient management for maize production in soils of the savannah zones of South-Western, Nigeria. *International Journal of Soil Science* 3(1): 20-27
25. Agboola AA and O.J Ayodele , 1985, Prospects and problems of using Soil Testing for adoption of fertilizers use in Ekiti-Akoko Agricultural development Project Area. In proceeding of workshops on appropriate Technologies for farmers in Semi-Arid, West Africa. Ohm, H.W and J.G Nagy (Eds). Purdue University, West Lafayette USA, pp123-136
26. Brady NC (1996). The Nature and Properties of Soils, 11th ed.; McMillan: New York. p. 621
27. Nyles CB, Ray RN (1999). The Nature and Properties of Soils. 12th Ed. United States of America. pp. 743 – 785
28. Papapreponis, P., Robertson, R., Roworth, M., Oston, F.L.R. and Williams, S.A. 2006. Levels of Inorganics and organics in soil; when it is, high? *Environment and Health International* 8.1: 4-12.
29. Chipso M. (2011); Assessment of Heavy Metal Accumulation in Wastewater Irrigated Soil and Uptake by Maize Plants (*Zea Mays* L) at Firle Farm in Harare; *Journal of sustainable Development* 4. 6:132- 137 Published by the Canadian Centre of Science and Education available online www.ccsenet.org/jsd
30. Environmental Protection Agency EPA: (1991, 1998, 1999). Facts Reports on Health and Environmental Safety U.S.A.
31. Jung CH , Matsuto T and Tanaka N. (2006). Flow analysis of metals in a municipal solid waste management system. *J. Waste Manage.* 26: 1337-1348.
32. Dara, S.S. (1993). A textbook of Environmental Chemistry and Pollution Control. S. Chad and Company Ltd. Ram. Nagar. P 120..
33. World Health Organization (WHO) (1993). Standard maxima for metals in Agricultural soils.

-
34. National Environment Protection Council of Australia (NEPCA) (2010). Limits of heavy metals in soils. Available online at www.newzealand.govt.nz
35. Manceau A, Boisset M, Sarret G, Hazemann J, Mench M, Cambier, P and Prost, R. 1996. Direct determination of lead speciation in contaminated soils by EXAFS Spectroscopy. *Environmental Science Technology* 30: 1540-1552.
36. Asagba EU, Okieimen FE, and Oospore J. 2007. Screening and speciation of heavy metal contaminated soil from an automobile spare-part market. *Chemical speciation and Bioavailability*, 19.1: 9-15.
37. Horsfall M (Jnr.) and Spiff A (2005). Speciation and bioavailability of heavy metals in Sediment of Diobu River, Port Harcourt, Nigeria. *European Journal of Science Resource* 6.3: 20-36.
38. Ogundiran MB and Osibanjo O. 2009. Mobility and speciation of heavy metals in soils impacted by hazardous waste. *Chemical Speciation and Bioavailability* 21:2.
39. Kashem MA, Singh BR, Huq SMI, Kawai S. (2008). Cadmium phytoextraction efficiency of aurum (*Colocasia antiquorum*), radish (*Raphanus sativus* L.) and water spinach (*Ipomea aquatica*) grown in hydroponics. *Water Air Soil Pollution.*, 192, 273-279.
40. Wuana RA, Okieimen FE and Imborvungu JA. 2010. Removal of heavy metals from a contaminated soil using organic chelating acids. *International Journal Environmental Science Technology* 7.3: 485-496
41. McLean, J.E and Bledsoe B.E. 1992. Behavior of Metals in Soils. United States Environmental Protection Agency, EPA/540/S-92/018.
42. Ma LQ and Rao N (1997). Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. *J. Environ. Qual.* 26: 259-264.
43. Iwegbue CMA .2007. Metal fractionation in soil profiles at automobile mechanic waste dumps. *Waste Management Resources* 25: 1-9.
44. Abeh T, Gungshik J and Adamu MM. 2007. Speciation Studies of trace elements levels in sediments from Zaramagada stream in Jos, Plateau State, Nigeria. *Journal of Chemical Society of Nigeria* 32.2: 218-225
45. Kabata-Pendias A and Pendias H. 1992. Trace elements in soils and extractability of cadmium in soils naturally high in metals at and plants. 2nd ed. CRC Press, Boca Raton, FL.
46. Obasi NA, Akubugwo EI, Ugbogu OC and Glory O. 2012. Assessment of Physico-chemical Properties and Heavy Metals Bioavailability in Dumpsites along Enugu-port Harcourt Expressways, South-east, Nigeria. *Asian Journal of Applied Sciences*, 5: 342-356

-
- 499 .
- 500 **47.** Ahumada I, Mendoza J and Ascar L . 1999. Sequential extraction of heavy metals in soil
- 501 irrigated with wastewater. *Communication in Soil Science and Plant Analysis* 30: 1507-1519.
- 502
- 503 **48.** FAO. 1985. Water quality for irrigation for agriculture. Irrigation and Drainage Paper 29: 1-
- 504 130.
- 505