

Research paper **Levels of Heavy Metals in and Around Scrap Car Dumpsite at Uwelu, Nigeria**

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ABSTRACT

Soil contaminated with heavy metals can result to very serious environmental hazard. As a result of this problem, this research was carried out to investigate the concentration of heavy metals (Fe, Zn, Pb, Cu and Cr) in and around Uwelu scrap car dumpsite in Benin City, southern Nigeria. In carrying out this research, soil samples were collected at various depths at the dumpsite, and at various horizontal distances from the dumpsite including human settlements close to the dumpsite, in order to ascertain the levels of toxic heavy metal concentration on human living habitat around the dumpsite. The heavy metals in the waste soils samples were sequentially extracted and measured using atomic absorption spectrometry (AAS). The results show that Fe had the highest concentration of 515mg/kg, followed by Zn, 236.8mg/kg, Cu, 78.61mg/kg and Cr, 0.94mg/kg at the dumpsite surface, where all the metals recorded their highest concentration. The level of Fe and Pb were above the Federal Environmental Protection Agency (FEPA) minimum acceptable limit. Besides, the concentrations of these heavy metals decreased with increased vertical depth at the dumpsite and with increased horizontal distance from the dumpsite. Similar trends were observed for the various soil pH.

Keywords: Heavy metals, dumpsites, scrap car, soil, horizontal distance, vertical depth

1. INTRODUCTION

Presently, in most cities in Nigeria scrap car dumpsites are located in and around human settlements, very close to motor mechanic workshops and fairly used motor spare parts markets [1]. The absence of metals recycling systems in most cities in Nigeria have resulted to gradual accumulation of scrap motor parts as well as scrap motors (which can either be cars, lorries and motor cycles), which later becomes heaps, known as scrap car dumpsites [2]. The presence of used/worn-out scrap car parts and scrap motor vehicles at the

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32 dumpsites causes soils, underground water and surface water contamination. The pollutants
33 are mainly toxic heavy metals such as Fe, Pb, Zn, Cu, and Cd. The sources include motor
34 vehicle parts, scrap tyres/rubber. After corrosion these metals gets leached into the
35 environment causing serious pollution. Scrap cars pollution from heavy metals is a major
36 environmental concern worldwide [3]. The presence of heavy metals in high levels can
37 endanger the ecosystem, plants and animals and cause severe health problems in humans,
38 animals and plants [4]. However, some heavy metals (trace elements) such as copper,
39 selenium and zinc are essential to maintain the metabolism of the human body [5].
40 Nevertheless, at higher concentrations they can lead to poisoning [5]. Heavy metals are
41 dangerous because they tend to bioaccumulate, that is, build up within the biological
42 systems over time. Trace elements accumulate in living beings any time they are taken up
43 and stored faster than they are broken down (metabolized) or excreted. Studies have
44 revealed that various factors such as presence or absence of other ions, pH, temperature
45 and residence time can affect the sorption/desorption process of heavy metals from soils,
46 soil clay fractions, and other soil components [6,7].

47 The awareness of this fact has led to increased scientific and public attention to level of
48 toxicity exerted by these metals in the environment. This has resulted in governments the
49 world over, funding research in new methods of analytical determination of concentrations of
50 heavy metals in soil at waste dumpsites in particular, and the methods of treating industrial
51 effluents so as to reduce the effect of these metals on the environment. The effects include:
52 destruction of eco system, destruction of marine biota, hindering of fisheries and other
53 aquacultural operations, poisoning of sea food, contamination of surface and underground
54 water, disturbances of soil function, reduction of plants productivity and chance of survival
55 etc.

56 The aim of the study was to ascertain the concentration of heavy metals in soil, and the
57 extent contamination of human living habitant in and around a scrap car dumpsite in Benin
58 City in order to assess the human health and ecological risks associated with the dumpsite.

59 60 **2. MATERIAL AND METHODS**

61 62 **2.1 Description of the dumpsite**

63
64 The Uwelu scrap car dumpsite is located in the Uwelu area of Benin City, the capital of Edo
65 State in Southern Nigeria. The site is geographically situated as follows: Latitude 6° 23' 00"
66 N and Longitude 5° 35' 00" E. The map indicating the location of the dumpsite is shown in
67 Figure 1. The area is the residence of a number of activities ranging from auto mechanic
68 workshops (automobiles repairs), auto spare parts sales, used automobiles sales and other
69 related activities. The congestion of the area with these activities involving the use of metals
70 resulted from the directive from the state government that all auto mechanic workshops,
71 metal works, scrap vehicle recycling and the like should vacate the mainstream of the city.
72 This prompted the mass migration of these businesses to the area. The heavy
73 anthropogenic activities and the corresponding huge amount of metallic wastes generated
74 and discarded on daily basis (this has been ongoing for over two decades) led to the choice
75 of the Uwelu scrap car dumpsite for this study. In addition, the site is the major scrap metal
76 dumpsite in Benin City.

77 78 **2.2 Sample collection and preparation**

79 Soil samples were collected using polythene bags from in and around Uwelu scrap car
80 dumpsite, Benin City, Nigeria in triplicate. The samples were collected at various vertical
81 distances (depths) up to 1.6 m at the dumpsite and 18 m from the dumpsite. Also, at various

82 horizontal distances from the dumpsite up to 18 m. The soils were air-dried at laboratory
83 temperature ($30 \pm 2^\circ\text{C}$) for 6 days and then ground and passed through 2 mm sieve to
84 obtain the soil fraction used. The samples were stored in polythene bottles in desiccators at
85 room temperature before extraction.

86 All the reagents were of analytical grade and were obtained from Chemical Engineering
87 laboratory store, University of Benin, Benin City, Nigeria. Double distilled-deionized water
88 was used. Glassware and polythene sample bottles were washed with liquid soap, rinsed
89 with water, soaked in 10% HNO_3 for 24 h, cleaned thoroughly with double distilled de-
90 ionized water and dried.

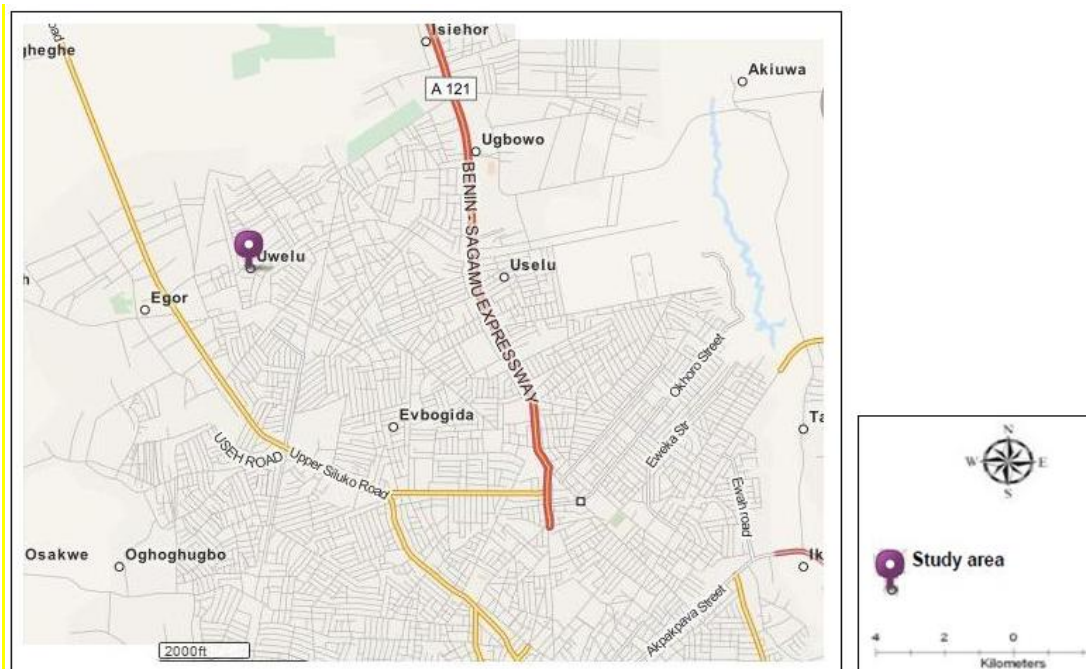


Fig. 1. Map of Benin City showing the study area (Uwelu)

2.3 Heavy metals extraction and determination

The collected soil samples were analysed for the following heavy metals; Fe, Zn, Pb, Cu and Cr. These metals were chosen because of the human health and ecological risks associated with them when living being are exposed to them. In order to make the metals accessible for analysis, they were extracted from the soil samples. The extraction was carried out with an initial mass of 1.0 g air dried waste soil samples in polypropylene centrifuge tube of 50 ml capacity. The conventional method developed by Page [8] was used in the extraction. However, $\text{Mg}(\text{NO}_3)_2$ was use instead of MgCl_2 to avoid an increase in the solubility of heavy metals within the soil solution. The extractions were carried out on three sub-samples. Each sample was shaken at room temperature with 16 ml of 1M $\text{Mg}(\text{NO}_3)_2$ at pH 7.0 for 1 h, centrifuged and supernatant decanted and made up to 40 ml with double distilled-deionsed water after which 25 ml of 0.05 M Na_2EDTA was added, shaken for 6 h and centrifuged. The supernatant was decanted and made up to 40 ml with distilled water prior to analysis. Residue from the previous stage was combined with 17.5 ml $\text{NH}_2\text{OH}.\text{HCl}$ 0.1M and 17.5M $\text{CH}_3\text{COONH}_4$, shaken for 1 h, centrifuged, and the supernatant decanted and made up to 40 ml with distilled water prior to analysis. The resulting residue was digested by using $\text{HCl} - \text{HNO}_3$ (0.35:12w/v soil solution ratio) in acid digestion Teflon cup. It was dry ashed for 2 h

111 and evaporated to dryness. The residue was diluted to 40 ml with distilled water prior to
 112 analysis. After each successive extraction, the sample was centrifuged at 4500rpm for
 113 15min. The supernatant was removed with Whatman No.42 filter paper. The residue was
 114 washed with de-ionized water followed by vigorous handshaking and then 15 min
 115 centrifugation before the next extraction. The volume of the rinsed distilled water used was
 116 kept to a minimum. The extracts were analysed using Atomic Absorption
 117 Spectrophotometer. The pH of the soil was measured in water at ratio 1:1 soil/water.

118 3. RESULTS AND DISCUSSION

119

120 Figure 2 shows the variation of pH with vertical distance at the dumpsite and at 18 m from the
 121 dumpsite. It can be seen that the pH values decreased with increased vertical distance.
 122 This might be as a result of the fact that soil acidity was produced by mineral leaching from
 123 the corroded metal parts, industrial wastes, acid rain and certain forms of micro-biological
 124 activity as previously reported by Xin, [9].

125 Figure 3 shows the variation of pH with horizontal distance from the dumpsite. The pH was
 126 5.9 at the dumpsite and 4.7 at 18 m from the dumpsite. The decrease in pH might be as a
 127 result of decrease in alkalinity due to the decreasing concentration of heavy metals with
 128 horizontal distance. Comparing the pH values at the dumpsite with pH values at 18 m from
 129 the dumpsite (in and around human settlement), it was found that at a depth of 1.2 m the pH
 130 values have the same value of 5.1. Federal environmental protection agency FEPA, [10]
 131 reported that Nigeria soil pH is usually between 5 and 9. This implies that the soils at the
 132 dumpsite and in the neighborhood (within 18 m from the dumpsite) were within the
 133 acceptable soil pH limit. Ogundiran and Osibanjo [2] reported pH values in the range of 5.8
 134 to 7.6 for soils obtained from a deserted slag dumpsite in Ibadan, a state in western Nigeria.
 135 Uba et al, [1] reported pH values in the range of 7.8 to 9.2 for soils obtained from municipal
 136 refuse dumpsites in Zaria a state in northern Nigeria. The difference in values obtained
 137 compared with that reported in this work could be as a result of the difference in the activities
 138 leading to the wastes in these dumpsites.

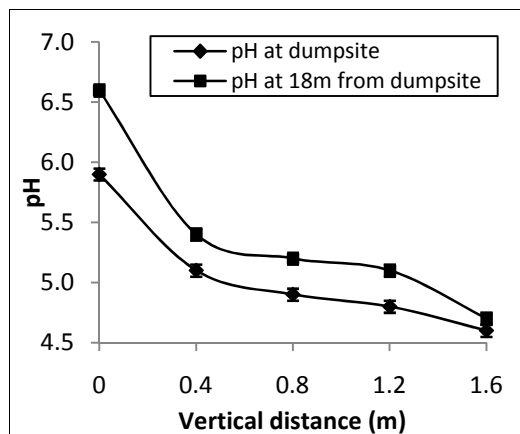


Fig. 2. Variation of pH with vertical depth at the dumpsite and at 18m from the dumpsite

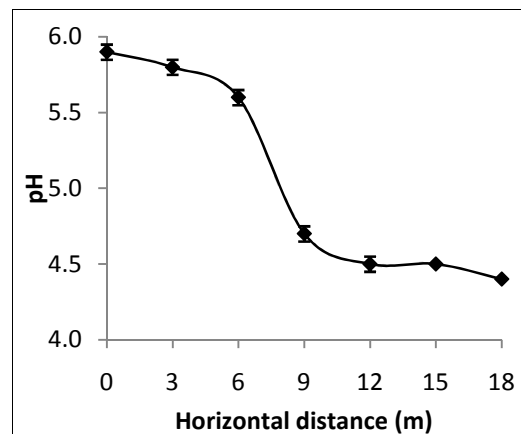


Fig. 3. Variation of pH with horizontal distance from the dumpsite

139 Figure 4 shows the variation of Fe concentration with horizontal distance from the dumpsite.
 140 The Fe concentration was highest (515mg/kg) at the dumpsite surface. This was above the
 141 FEPA maximum acceptable limit of 400 mg/kg [10]. This might be due to the fact that most
 142 motor vehicle parts, and scrap vehicles dumped at the dumpsite are mainly made of iron,
 143 which corrode very fast when exposed to environment conditions. The results also show that
 144 there was a sharp decrease in Fe concentration from 515mg/kg at the surface of the

145 dumpsite to a value of 84.9mg/kg within 0.4 m depth. This is because iron is strongly
 146 adsorbed and retained by soil [9,11]. Thus, with this high retention and adsorption, Fe could
 147 not be effectively leached down the soil profile, hence the low Fe concentration at depths
 148 below the surface. Some researchers have reported that soil with coarse texture has a
 149 higher infiltration rate than soil with fine texture [12]. The visual inspection of the soil around
 150 the dumpsite shows that the soil has fine texture. This can also explain the low concentration
 151 of Fe down the surface of the dumpsite. The variation of Fe concentration with increased
 152 depth at 18 m from the dumpsite was similar to that at the dumpsite. Between the depths of
 153 0.8 m to 1.6 m, the concentration of Fe was found to be almost constant at both the
 154 dumpsite and at 18m from the dumpsite. This might be as a result of very little or no leaching
 155 process taking place between this depths. The relatively high levels of Fe recorded are in
 156 agreement with the results of other researchers who reported that Nigerian soils typically
 157 contain high levels of Fe [13-15].
 158 Figure 5 shows the variation of Fe concentration with horizontal distance from the dumpsite.
 159 The Fe concentration decreased with increasing horizontal distance from the dumpsite.
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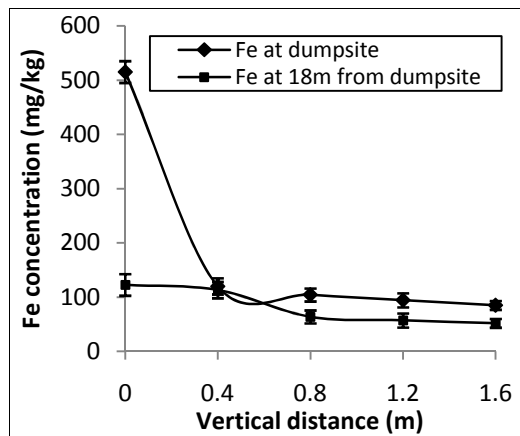


Fig. 4. Variation of Fe concentration with vertical depth at the dumpsite and at 18m from the dumpsite

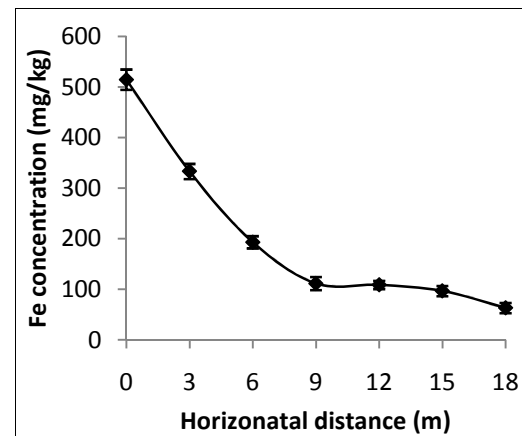


Fig. 5. Variation of Fe concentration with horizontal distance from the dumpsite

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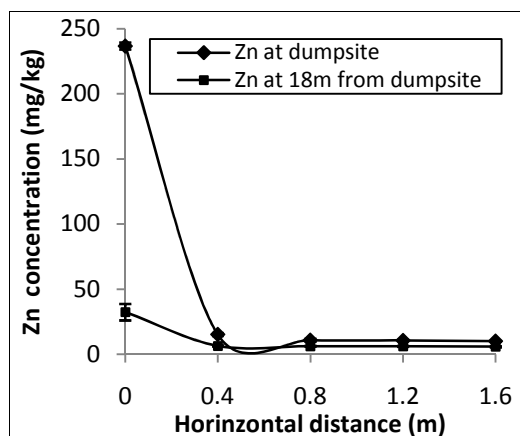


Fig. 6. Variation of Zn concentration with vertical depth at the dumpsite and at 18m from the dumpsite

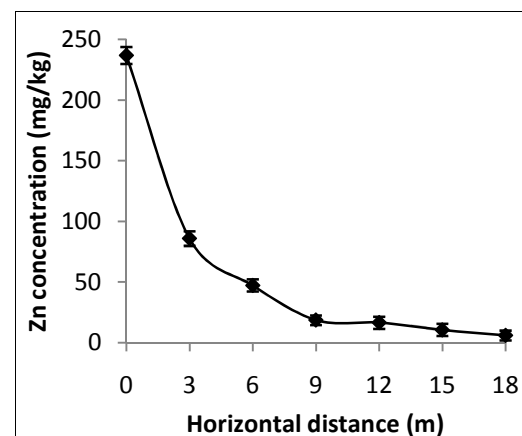


Fig. 7. Variation of Zn concentration with horizontal distance from the dumpsite

164 The concentration of Zn was significantly high at the surface of the dumpsite as indicated in
 165 Figure 6. The Figure shows that the concentration of Zn at the surface of the dumpsite was
 166 236.8mg/kg and this value decreased to 9.89mg/kg at a depth of 1.6 m. This implies that soil
 167 toxicity decreased with depth. The values recorded were however within the maximum
 168 acceptable limit of 300-600 mg/kg set by FEPA [10]. Similar trend was observed at 18 m
 169 from the dumpsite, around the neighbourhood. The high concentration of Zn at the surface of
 170 the dumpsite might have resulted from the corroded Zn plated materials, from car scrap
 171 dumped at the dumpsite. Förstner and Wittmann, [16] reported that Zn is an adsorbing
 172 metal, whose mobility depends strongly on the pH value and the concentration of humic
 173 substance. Also, Zn has a high affinity to clay materials. Besides, Xin, [9] reported that metal
 174 adsorption increases with the concentration of dissolved heavy metals as long as the
 175 corresponding surface sites are available. The studies reported by Fic and Schroter, [17]
 176 indicated that there were significant differences in mobility among heavy metals. They
 177 classified Zn and Cd as relatively mobile and Cu and Cr as relatively immobile. Thus, the
 178 high retention nature of Zn to the surface soil with little leached down the subsurface could
 179 be explain. This is the reason for the sharp decline seen in Figure 5.

180
 181 Below 0.4 m depth, the concentration of Zn was found to be almost constant. This might be
 182 as a result of very little or no leaching process taking place below this depth. Along
 183 horizontal distance, the variation of Zn concentration with distance from the dumpsite gave a
 184 similar trend as shown in Figure 7. Ogundiran and Osibanjo [2] reported similar trend in the
 185 distribution of Zn for soils obtained from a deserted slag dumpsite in Ibadan, a state in
 186 western Nigeria. They reported a decrease in the levels of Zn and other metals they studied
 187 with an increase in distance from the dumpsite.

188
 189 Figure 8 shows that the concentration of Pb at the surface of the dumpsite was 36.85mg/kg.
 190 It decreased to 11.17mg/kg at a depth of 1.6 m. The entire Pb concentration was above
 191 FEPA maximum acceptable limit of 1.6 mg/kg [10]. This implies that there was Pb toxicity in
 192 soil in and around the dumpsite. The trend observed might be because metallic Pb is only
 193 stable in a very low redox potential condition [18]. The rate of Pb oxidation and the resulting
 194 corrosion products are highly variable and site specific. In general, Pb is much more soluble
 195 under acidic (low pH) conditions than at neutral or alkaline (high pH) conditions [9].

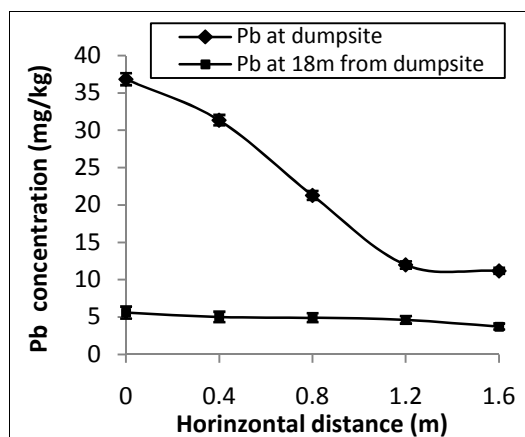


Fig. 8. Variation of Pb concentration with vertical depth at the dumpsite and at 18m from the dumpsite

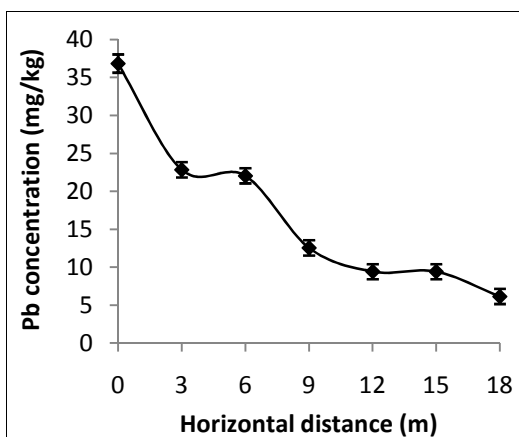


Fig. 9. Variation of Pb concentration with horizontal distance from the dumpsite

196 Pb sorption in clay usually increases with increasing pH, decreasing soil/solution ratio, and
 197 decreasing ionic strength [19]. It can be seen from the soil pH results in Figure 2 that as the

198 soil depth increases, the soil becomes more acidic hence, the increasing solubility of Pb.
 199 Similar trend was observed in the variation of Pb concentration with horizontal distance from
 200 the dumpsite as shown in Figure 9.

201 Figure 10 shows that the concentration of Cu at the surface of the dumpsite was 78.61mg/kg
 202 and this value decreased to 2.97 mg/kg at a depth of 1.6 m. The concentration of Cu was
 203 high at the surface of the dumpsite and just about fell within the maximum acceptable limit of
 204 70-80 mg/kg set by FEPA [10]. This could have been as a result of corrosion and leaching of
 205 Cu metal from the scrap car and vehicle parts at the dumpsite. Besides, the concentration of
 206 Cu decreased sharply within a depth of 0.4 m at the dumpsite. This concentration was within
 207 the FEPA acceptable limit. This indicates that soil toxicity decreased with depth, because Cu
 208 mobility was low. Awokunmi et al, [20] reported levels of Cu in the range of 18.00 - 133.10
 209 mg/kg for soils taken from some dumpsites in Ekiti State of Nigeria.

210 The results also show that Cu concentration at the dumpsite was much lower than that of Fe
 211 and Zn. This might be due to its relatively low corrosion rate. Borg and Johansson [21]
 212 reported that copper is largely retained in the soil. They noticed that the mobility increased
 213 with decreased pH. They suggested that the mobility of Cu was associated with the transport
 214 of organic material since the Cu was highly adsorbed by them. Cu is a strongly adsorbing
 215 metal, it can bound very strongly to humus substances, Fe/Al-oxides and other variable-
 216 charge particle surfaces due to its large tendency to form complexes, so theoretically it
 217 should be well retarded in most type of soils and thus being prevented from leaching to
 218 further soil profiles. Xin, [9] and Igloria et al., [12] reported that the possibility of formation of
 219 complexes between heavy metals and organic matter colloids in solutions, as well as those
 220 attached to soil surfaces. Sposito [22], on the other hand, claimed that the effect of these
 221 colloids might retard metals transport. Ma et al. [23] suggested that the chemical speciation
 222 of the metals determined metal behaviour and mobility in the environment. These reasons
 223 explained the sharp decreased in Cu concentration. At 18 m from dumpsite, the
 224 concentration of Cu was very low and it has an approximate constant value of 1.98mg/kg
 225 irrespective of the depth. The concentration of Cu also decreased with horizontal distance
 226 from the dumpsite as shown in Figure 11.

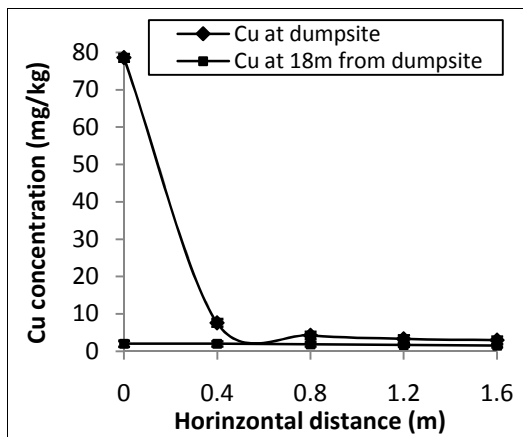


Fig. 10. Variation of Cu concentration with vertical depth at the dumpsite and at 18m from the dumpsite

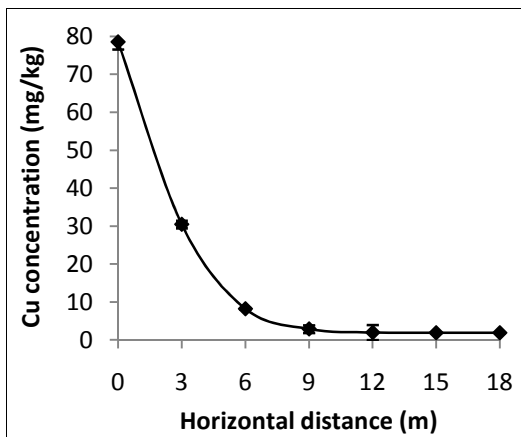


Fig. 11. Variation of Cu concentration with horizontal distance from the dumpsite

Figure 12 shows that the concentration of Cr at the surface of the dumpsites was 0.94mg/kg and this value decreased 0.14mg/kg at a depth 1.6m. The concentration of Cr was relatively low at the dumpsite when compared with other heavy metals. Also, it was within the FEPA acceptable limit [10]. The low concentration of Cr might be as a result of Cr strong resistant to corrosion and also because it is only few car parts actually contain Cr as it is less used in car metallic parts. This explanation was supported Xin, [9] report that low concentration of Cr was as a result of the ability of Cr to resist corrosion; hence the leaching process is very limited. At 18 m from the dumpsite, the concentration was 0.14mg/kg at the surface as shown in Figure 12. Cr the mostly naturally occurs as chromium (VI) which is toxic at low concentration. However, the toxicity associated with Cr in soil might be very low, since the dumpsite has a large Fe concentration, which according to some researchers, will largely reduce chromium (VI) to chromium (III) [24,25]. The Cr present in the dumpsite will most likely be the less toxic form (chromium (III)). Amadi and Nwankwoala [26] reported levels of Cr in the range of 0.02-2.78 mg/kg for soils taken from the Enyimba Dumpsite in Aba, Southeastern Nigeria.

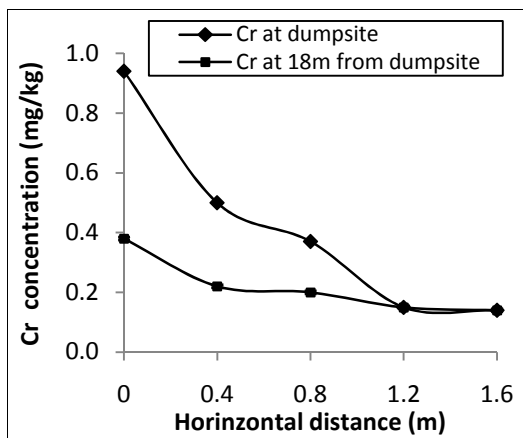


Fig. 12. Variation of Cr concentration with vertical depth at the dumpsite and at 18m from the dumpsite

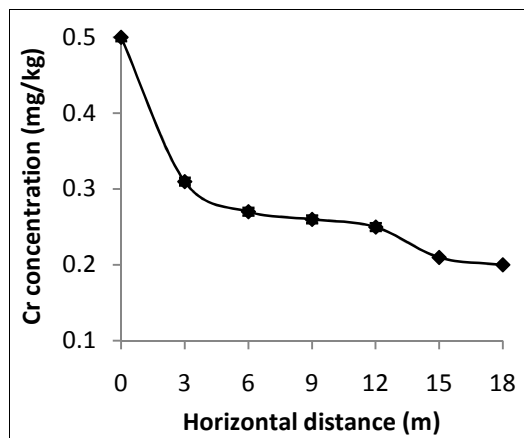


Fig. 13. Variation of Cr concentration with horizontal distance from the dumpsite

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244 4. CONCLUSION

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The conclusions made from this research study are as follows:

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- The soil in and around the scrap car dumpsite was contaminated with toxic heavy metals such as; Fe, Pb, Cu, Zn, and Cr.
- At the dumpsites, the FEPA limit for metals concentration in soil was exceeded by Fe, Zn, and Pb, hence the soil was polluted with heavy metals.
- Around the neighbourhood of the dumpsite (10 m to 18 m from the dumpsite) the soil was mainly polluted with Pb.
- It was found that for all the heavy metals, the concentrations were highest at the surface of the dumpsite. Fe had the highest concentration of 515mg/kg, the order was Fe > Zn > Cu > Pb > Cr.
- The metals concentration and pH values decreased with increased vertical depth and with increased horizontal distance from the dumpsite.

In the light of the conclusions drawn above, some recommendations have been made as follows:

260 A well designed sanitary landfill that takes into consideration, the local geology, prevalent
261 climatic condition, type of waste generated, nature of settlement should be encouraged. This
262 will mitigate the infiltration of the metal leachate into the soil and shallow groundwater
263 system. The use of the Uwelu scrap car dumpsite should be discontinued. Although no
264 severe pollution problems are currently apparent apart from Fe and Zn, the continuous
265 dumping of waste at the dumpsite may lead to the enrichment of the soil with other metals
266 that are presently at uncontaminated levels. The separation and recycling of wastes as well
267 should be encouraged. As a result of the toxicity of heavy metals, the use of manure from
268 the dumpsite for agricultural purposes should be discouraged as plants and vegetables can
269 easily absorb them.

270 **COMPETING INTERESTS**

271 Authors have declared that no competing interests exist.

273 **AUTHORS' CONTRIBUTIONS**

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275 Author FAA, in collaboration with author IGO, designed the study. Author IGO performed the
276 experiments, and wrote the first draft of the manuscript. Authors FAA and IGO managed the
277 literature searches while author ETA provided analytical advise and manuscript correction.
278 All authors read and approved the final manuscript.

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