

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, a total of 36 soil samples were taken for laboratory analysis. The 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 2. MATERIALS AND METHODS

60 2.1 Description of the dumpsite

61
62 The Uwelu scrap car dumpsite is located in the Uwelu area of Benin City, the capital of Edo
63 State in Southern Nigeria. The site is geographically situated as follows: Latitude 6° 23' 00"
64 N and Longitude 5° 35' 00" E. The map indicating the location of the dumpsite is shown in
65 Figure 1. The area is the residence of a number of activities ranging from auto mechanic
66 workshops (automobiles repairs), auto spare parts sales, used automobiles sales and other
67 related activities. The congestion of the area with these activities involving the use of metals
68 resulted from the directive from the state government that all auto mechanic workshops,
69 metal works, scrap vehicle recycling and the like should vacate the mainstream of the city.
70 This prompted the mass migration of these businesses to the area. The heavy
71 anthropogenic activities and the corresponding huge amount of metallic wastes generated
72 and discarded on daily basis (this has been ongoing for over two decades) led to the choice
73 of the Uwelu scrap car dumpsite for this study. In addition, the site is the major scrap metal
74 dumpsite in Benin City.

75 2.2 Sample collection and preparation

76
77 Soil samples were collected using polythene bags from in and around Uwelu scrap car
78 dumpsite, Benin City, Nigeria in triplicate. A total of 36 soil samples were taken for laboratory
79 analysis. The samples were collected at various vertical distances (depths) up to 1.6 m at
80
81

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

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

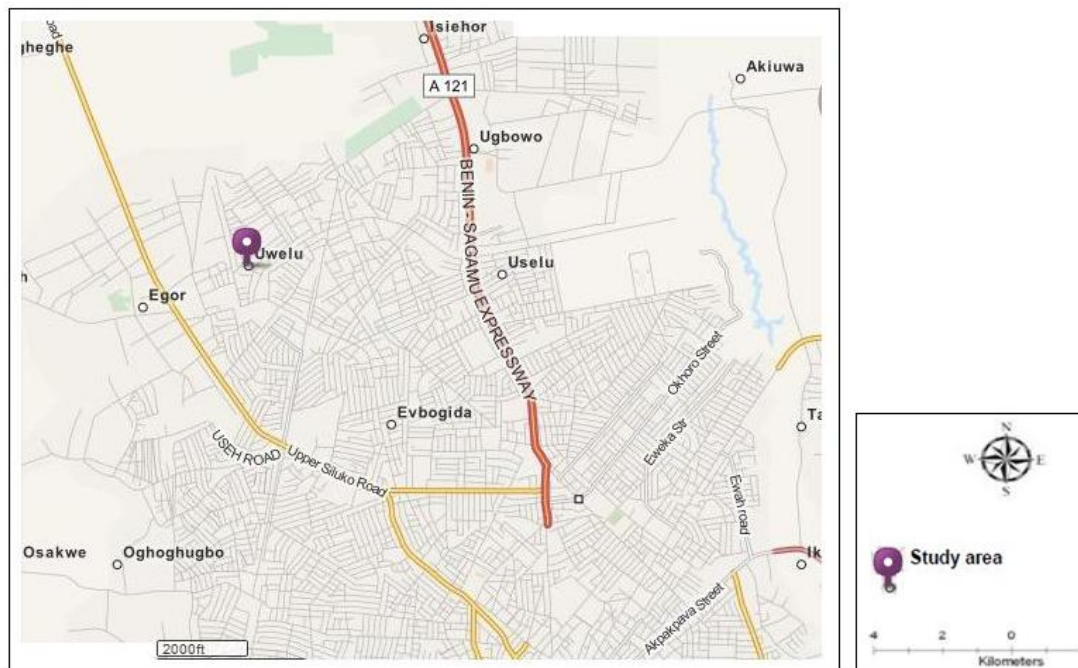


Fig. 1. Map of Benin City showing the study area (Uwelu)

94 2.3 Heavy metals extraction and determination

95
96 The collected soil samples were analysed for the following heavy metals; Fe, Zn, Pb, Cu and
97 Cr. These metals were chosen because of the human health and ecological risks associated
98 with them when living being are exposed to them. In order to make the metals accessible for
99 analysis, they were extracted from the soil samples. The extraction was carried out with an
100 initial mass of 1.0 g air dried waste soil samples in polypropylene centrifuge tube of 50 ml
101 capacity. The conventional method developed by Page [8] was used in the extraction.
102 However, $\text{Mg}(\text{NO}_3)_2$ was use instead of MgCl_2 to avoid an increase in the solubility of heavy
103 metals within the soil solution. The extractions were carried out on three sub-samples. Each
104 sample was shaken at room temperature with 16 ml of 1M $\text{Mg}(\text{NO}_3)_2$ at pH 7.0 for 1 h,
105 centrifuged and supernatant decanted and made up to 40 ml with double distilled-deionised
106 water after which 25 ml of 0.05 M Na_2EDTA was added, shaken for 6 h and centrifuged. The
107 supernatant was decanted and made up to 40 ml with distilled water prior to analysis.
108 Residue from the previous stage was combined with 17.5 ml $\text{NH}_2\text{OH} \cdot \text{HCl}$ 0.1M and 17.5M
109 $\text{CH}_3\text{COONH}_4$, shaken for 1 h, centrifuged, and the supernatant decanted and made up to 40
110 ml with distilled water prior to analysis. The resulting residue was digested by using HCl –

HNO₃ (0.35:12w/v soil solution ratio) in acid digestion Teflon cup. It was dry ashed for 2 h and evaporated to dryness. The residue was diluted to 40 ml with distilled water prior to analysis. After each successive extraction, the sample was centrifuged at 4500rpm for 15min. The supernatant was removed with Whatman No.42 filter paper. The residue was washed with de-ionized water followed by vigorous handshaking and then 15 min centrifugation before the next extraction. The volume of the rinsed distilled water used was kept to a minimum. The extracts were analysed using Atomic Absorption Spectrophotometer. The pH of the soil was measured in water at ratio 1:1 soil/water.

2.4 Quality Control

The efficiency of the digestion procedure employed was tested by carrying out recovery studies (analyzing spiked samples that were made from previously analyzed samples). Replicate analyses were performed on the spiked soil to yield a mean which was used to determine standard deviation of the mean to measure precision.

124

3. RESULTS AND DISCUSSION

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The percent recovery of metals obtained from sequential extractions is presented in Table 1. For all metals, except Pb, recovery ranged from 100 to 105%, which is within the acceptable range. This variation may be attributed to the differences in leaching time, reagents and the total volume of extractant [9]. Similar ranges have already been reported in literature for sequential extraction [10].

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Table 1: Percentage recovery of heavy metals during extraction

Metals	Recovery
Fe	100.98±0.89
Zn	102.21±0.27
Pb	98.23±0.81
Cu	105.33±0.11
Cr	104.13±0.77

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Figure 2 shows the variation of pH with vertical distance at the dumpsite and at 18 m from the dumpsite. It can be seen that the pH values decreased with increased vertical distance. This might be as a result of the fact that soil acidity was produced by mineral leaching from the corroded metal parts, industrial wastes, acid rain and certain forms of micro-biological activity as previously reported by Xin, [11].

Figure 3 shows the variation of pH with horizontal distance from the dumpsite. The pH was 5.9 at the dumpsite and 4.7 at 18 m from the dumpsite. The decrease in pH might be as a result of decrease in alkalinity due to the decreasing concentration of heavy metals with horizontal distance. Comparing the pH values at the dumpsite with pH values at 18 m from the dumpsite (in and around human settlement), it was found that at a depth of 1.2 m the pH values have the same value of 5.1. Federal environmental protection agency FEPA, [12] reported that Nigeria soil pH is usually between 5 and 9. This implies that the soils at the dumpsite and in the neighborhood (within 18 m from the dumpsite) were within the acceptable soil pH limit. Ogundiran and Osibanjo [2] reported pH values in the range of 5.8 to 7.6 for soils obtained from a deserted slag dumpsite in Ibadan, a state in western Nigeria. Uba et al, [1] reported pH values in the range of 7.8 to 9.2 for soils obtained from municipal refuse dumpsites in Zaria a state in northern Nigeria. The difference in values obtained compared with that reported in this work could be as a result of the difference in the activities leading to the wastes in these dumpsites.

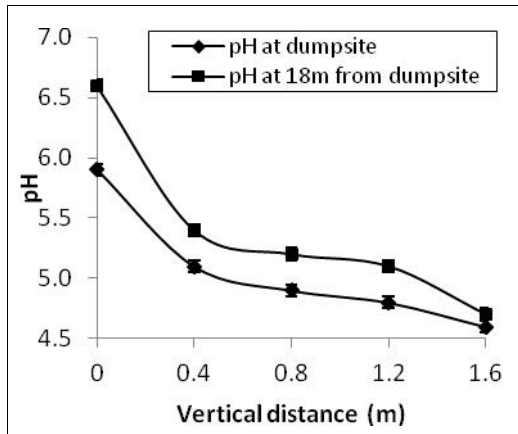


Fig. 2. Variation of pH with vertical depth at the dumpsite and at 18m from the dumpsite

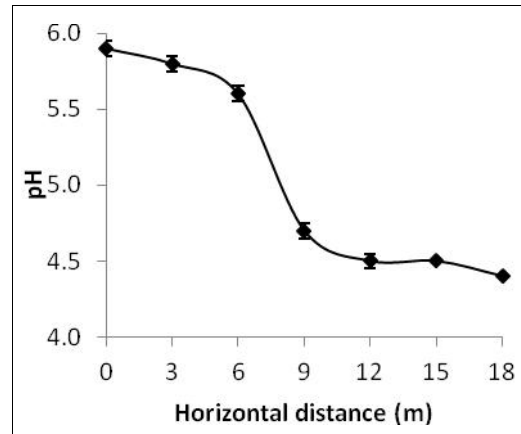


Fig. 3. Variation of pH with horizontal distance from the dumpsite

Figure 4 shows the variation of Fe concentration with horizontal distance from the dumpsite. The Fe concentration was highest (515mg/kg) at the dumpsite surface. This was above the FEPA maximum acceptable limit of 400 mg/kg [12]. This might be due to the fact that most motor vehicle parts, and scrap vehicles dumped at the dumpsite are mainly made of iron, which corrode very fast when exposed to environment conditions. The results also show that there was a sharp decrease in Fe concentration from 515mg/kg at the surface of the dumpsite to a value of 84.9mg/kg within 0.4 m depth. This is because iron is strongly adsorbed and retained by soil [11,13].

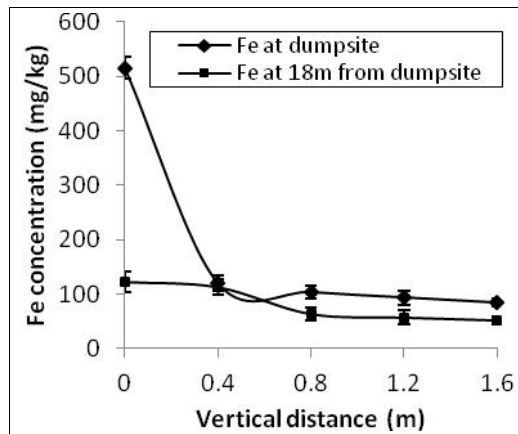


Fig. 4. Variation of Fe concentration with vertical depth at the dumpsite and at 18m from the dumpsite

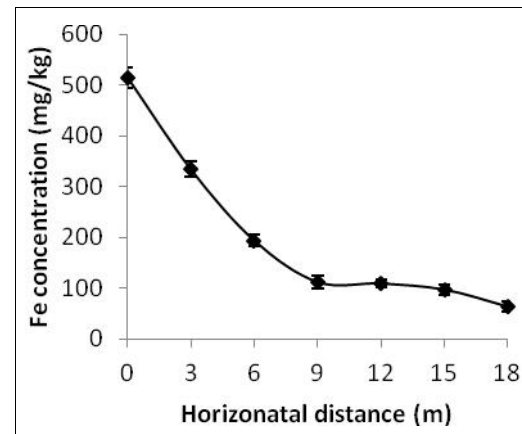


Fig. 5. Variation of Fe concentration with horizontal distance from the dumpsite

Thus, with this high retention and adsorption, Fe could not be effectively leached down the soil profile, hence the low Fe concentration at depths below the surface. Some researchers have reported that soil with coarse texture has a higher infiltration rate than soil with fine texture [14]. The visual inspection of the soil around the dumpsite shows that the soil has fine texture. This can also explain the low concentration of Fe down the surface of the dumpsite. The variation of Fe concentration with increased depth at 18 m from the dumpsite was similar to that at the dumpsite. Between the depths of 0.8 m to 1.6 m, the concentration of Fe was found to be almost constant at both the dumpsite and at 18m from the dumpsite. This might be as a result of very little or no leaching process taking place between this

depths. The relatively high levels of Fe recorded are in agreement with the results of other researchers who reported that Nigerian soils typically contain high levels of Fe [15-17]. Figure 5 shows the variation of Fe concentration with horizontal distance from the dumpsite. The Fe concentration decreased with increasing horizontal distance from the dumpsite.

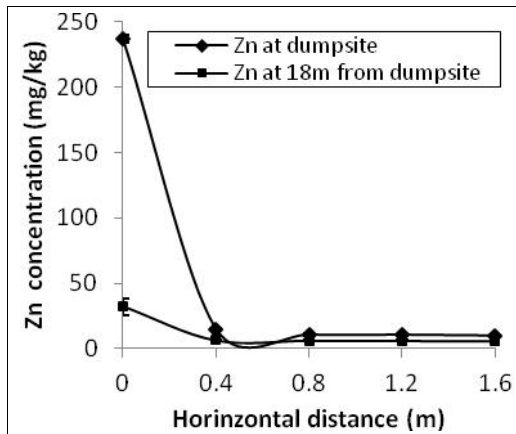


Fig. 6. Variation of Zn concentration with vertical depth at the dumpsite and at 18m from the dumpsite

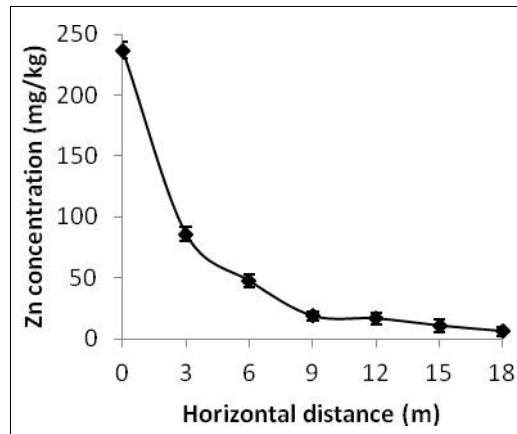


Fig. 7. Variation of Zn concentration with horizontal distance from the dumpsite

The concentration of Zn was significantly high at the surface of the dumpsite as indicated in Figure 6. The Figure shows that the concentration of Zn at the surface of the dumpsite was 236.8mg/kg and this value decreased to 9.89mg/kg at a depth of 1.6 m. This implies that soil toxicity decreased with depth. The values recorded were however within the maximum acceptable limit of 300-600 mg/kg set by FEPA [12]. Similar trend was observed at 18 m from the dumpsite, around the neighbourhood. The high concentration of Zn at the surface of the dumpsite might have resulted from the corroded Zn plated materials, from car scrap dumped at the dumpsite. Förstner and Wittmann, [18] reported that Zn is an adsorbing metal, whose mobility depends strongly on the pH value and the concentration of humic substance. Also, Zn has a high affinity to clay materials. Besides, Xin, [11] reported that metal adsorption increases with the concentration of dissolved heavy metals as long as the corresponding surface sites are available. The studies reported by Fic and Schroter, [19] indicated that there were significant differences in mobility among heavy metals. They classified Zn and Cd as relatively mobile and Cu and Cr as relatively immobile. Thus, the high retention nature of Zn to the surface soil with little leached down the subsurface could be explain. This is the reason for the sharp decline seen in Figure 5.

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

Figure 8 shows that the concentration of Pb at the surface of the dumpsite was 36.85mg/kg. It decreased to 11.17mg/kg at a depth of 1.6 m. The entire Pb concentration was above FEPA maximum acceptable limit of 1.6 mg/kg [12]. This implies that there was Pb toxicity in soil in and around the dumpsite. The trend observed might be because metallic Pb is only stable in a very low redox potential condition [20]. The rate of Pb oxidation and the resulting

corrosion products are highly variable and site specific. In general, Pb is much more soluble under acidic (low pH) conditions than at neutral or alkaline (high pH) conditions [11].

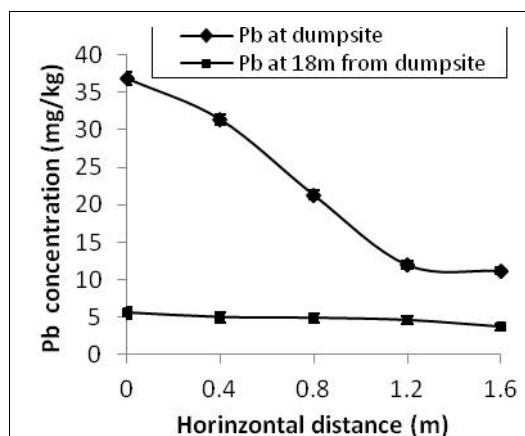


Fig. 8. Variation of Pb concentration with vertical depth at the dumpsite and at 18m from the dumpsite

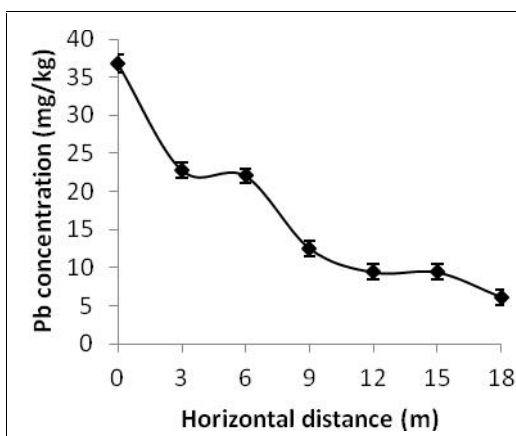


Fig. 9. Variation of Pb concentration with horizontal distance from the dumpsite

Pb sorption in clay usually increases with increasing pH, decreasing soil/solution ratio, and decreasing ionic strength [21]. It can be seen from the soil pH results in Figure 2 that as the soil depth increases, the soil becomes more acidic hence, the increasing solubility of Pb. Similar trend was observed in the variation of Pb concentration with horizontal distance from the dumpsite as shown in Figure 9.

Figure 10 shows that the concentration of Cu at the surface of the dumpsite was 78.61mg/kg and this value decreased to 2.97 mg/kg at a depth of 1.6 m. The concentration of Cu was high at the surface of the dumpsite and just about fell within the maximum acceptable limit of 70-80 mg/kg set by FEPA [12]. This could have been as a result of corrosion and leaching of Cu metal from the scrap car and vehicle parts at the dumpsite. Besides, the concentration of Cu decreased sharply within a depth of 0.4 m at the dumpsite. This concentration was within the FEPA acceptable limit. This indicates that soil toxicity decreased with depth, because Cu mobility was low. Awokunmi et al, [22] reported levels of Cu in the range of 18.00 - 133.10 mg/kg for soils taken from some dumpsites in Ekiti State of Nigeria.

The results also show that Cu concentration at the dumpsite was much lower than that of Fe and Zn. This might be due to its relatively low corrosion rate. Borg and Johansson [23] reported that copper is largely retained in the soil. They noticed that the mobility increased with decreased pH. They suggested that the mobility of Cu was associated with the transport of organic material since the Cu was highly adsorbed by them. Cu is a strongly adsorbing metal, it can bound very strongly to humus substances, Fe/Al-oxides and other variable-charge particle surfaces due to its large tendency to form complexes, so theoretically it should be well retarded in most type of soils and thus being prevented from leaching to further soil profiles. Xin, [11] and Igloria et al., [14] reported that the possibility of formation of complexes between heavy metals and organic matter colloids in solutions, as well as those attached to soil surfaces. Sposito [24], on the other hand, claimed that the effect of these colloids might retard metals transport. Ma et al. [25] suggested that the chemical speciation of the metals determined metal behaviour and mobility in the environment. These reasons explained the sharp decreased in Cu concentration. At 18 m from dumpsite, the concentration of Cu was very low and it has an approximate constant value of 1.98mg/kg

irrespective of the depth. The concentration of Cu also decreased with horizontal distance from the dumpsite as shown in Figure 11.

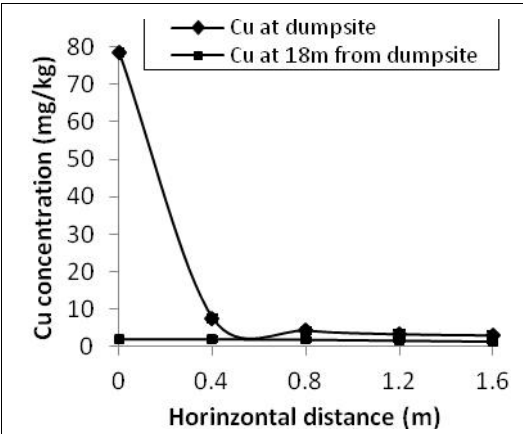


Fig. 10. Variation of Cu concentration with vertical depth at the dumpsite and at 18m from the dumpsite

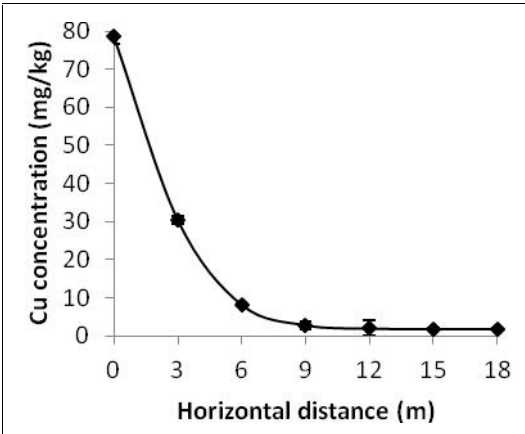


Fig. 11. Variation of Cu concentration with horizontal distance from the dumpsite

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 [12]. 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, [11] 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.

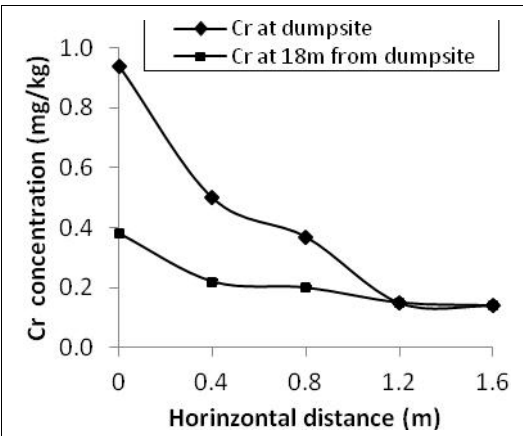


Fig. 12. Variation of Cr concentration with vertical depth at the dumpsite and at 18m from the dumpsite

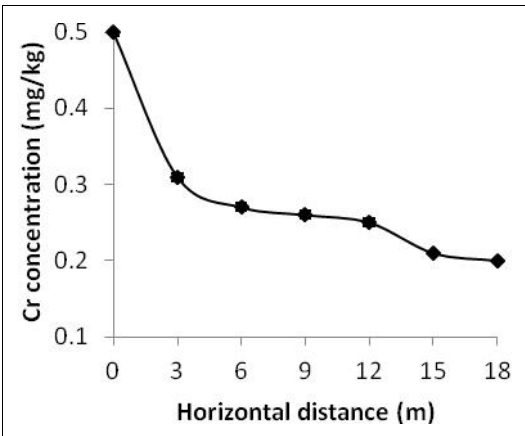


Fig. 13. Variation of Cr concentration with horizontal distance from the dumpsite

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) [26,27]. The Cr present in the dumpsite will most likely be the less toxic form (chromium (III)). Amadi and Nwankwoala [28] 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.

4. CONCLUSIONS

The conclusions made from this research study are as follows:

- 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:

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

COMPETING INTERESTS

Authors have declared that no competing interests exist.

AUTHORS' CONTRIBUTIONS

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

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