Journal of Environment Protection and Sustainable Development
Vol. 7, No. 2, 2021, pp. 30-36
http://www.aiscience.org/journal/jepsd
ISSN: 2381-7739 (Print); ISSN: 2381-7747 (Online)

Heavy Metals Distribution in Soils of Selected Dumpsite and Scrap Yard in Akure, Nigeria

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Abstract

Dumpsites and scrapyards are of great concern in the recent times, especially dumpsites containing materials made from heavy metals because they pose dangers to people in contact with the soils and plants of these sites. In Nigeria, one of the major sources of heavy metal pollution to soil is through leachates from refuse dumpsites and metal scrapyards. The Igbatoro dumpsite is in Akure township while the metal scrapyard used for this study is located at Oke-Aro Market. The metal scrapyard is in a residential area and may be a risk to the resident of such an area. Soil samples taken from these sites were analyzed for their properties, heavy metal concentration and metal speciation using standard methods. The pollution indices (index of geo-accumulation and mobility factor) of the soil samples were also examined. The result from this study showed that the total heavy metal concentration was higher in the scrap yard than in the dumpsite. The control sites had lesser heavy metal concentration in most instances indicating that these heavy metals concentrations are due to anthropogenic activities. Lead and Cadmium were found more in the Fe-Mn and carbonate fraction from the sequential extraction of the metal suggesting that these metals may be mobile given the right condition. The Cd, Cr and Pb fraction at the scrapyard have high mobility percentage because of its much occurrence in the carbonate fraction. The higher mobility of Cd and Pb in the scrapyard makes these metals very much available to leach into the ground water or become bioavailable for plant around the sites at favorable condition like acidic pH.

Keywords

Heavy Metals, Dumpsite, Scrap Yard, Sequential Extraction, Mobility Factor

Received: April 21, 2021 / Accepted: May 15, 2021 / Published online: May 31, 2021

1. Introduction

Waste generation is a result of human daily activities which has resulted to environmental pollution. This is more dominant in developing countries like Nigeria. In many developing countries, the high volume of wastes generated are more than what the capacity of the waste management sector in these countries can handle. The effect of these waste mismanagement is the practice of open dumping method of waste disposal by citizens and the ugly look of many beautiful cities [1]. Materials made from heavy metals which are disposed in open dumpsites are of concern and pose dangers to people in contact with the soils and plants of these sites in which they are disposed. In Nigeria, one of the major sources of heavy metal pollution to soil is through leachates from refuse dumpsites [2]. Idera et al. (2005) [3] reported that concentrations of heavy metals pollution in soil around waste dumpsites are influenced by different factors which include types of wastes, topography, run-off, and level of scavenging. A more concerning matter was highlighted by Oyelola et al. (2009) [4] explaining that once heavy metals are deposited in the soil, they are not degraded for a long time which eventually will lead to environmental pollution.

A metal scrap yard is a type of dumpsite that consists of

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majorly metal scraps. Scraps could be new or old, the former are from pre consumer in the form of cuttings, trimmings, and off specification materials while old scrapes are from post-consumer sources generated once a product completes its useful product life. Examples include used beverage cans, used jet engine blades. Heavy metals may, however, also be lost to waste during production, use phases and during storage for recycling in scrapyard.

Due to the non-biodegradability nature and characteristics of heavy metals, they are not quickly removed by metabolic activities nor easily detoxified, rather, the increase of their resident time within the soil environment has long-term implications for the biological, chemical, and physical properties of soil and could equally affect productivity. Metals exist in several forms which have significant effect on their mobility and bioavailability of the metals. The toxicity of metals in soil strongly related to their existing form which makes heavy metal speciation have an increasing attention [5].

This research is aimed at evaluating the level and distribution of heavy metals (Cd, Cr, Fe, Mn, Ni and Pb) in the soils of a selected dumpsites and metal scrapyards in Akure Metropolis, Ondo state, Nigeria. Pollution assessment such as contamination index, enrichment factor, index of geo-accumulation was computed to evaluate the pollution status of the study arears.

2. Materials and Method

2.1. Study Area

Ondo state is the fourth most populous state in southwest Nigeria. Akure, the state capital is situated in the tropic rainforest zone in Nigeria. Akure is bounded with a geographical coordinate of 7°15′0″N 5°11′42″E. Residential districts in Akure are of varying density. The Igbatoro dumpsite is in Akure township while the metal scrapyard used for this study is located at Oke-Aro Market. The metal scrapyard is in a residential area and may be a risk to the resident of such an area. The control samples were taken from within the campus of Federal University of Technology, Akure, Nigeria (FUTA). The maps of the dumpsite and scrapyard are shown in figure 1(A and B) respectively.

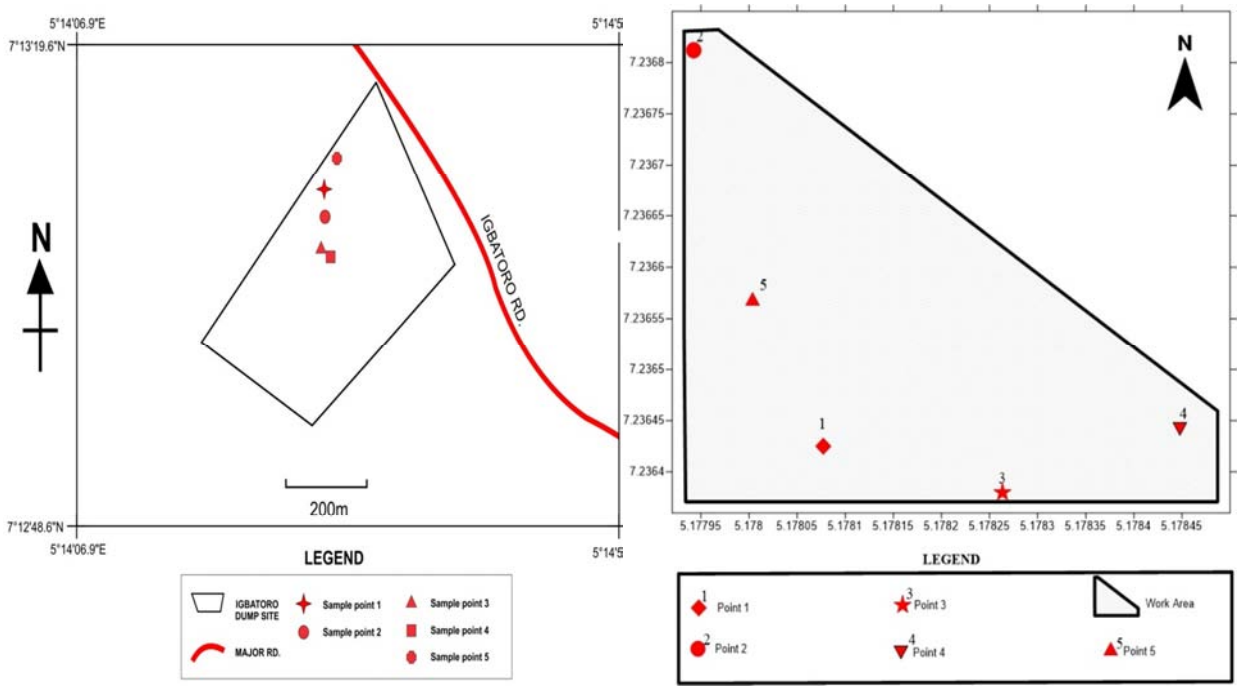

Figure 1. (A) The Map of Igbatoro dumpsite, Akure, Ondo State showing the sampled sites. (B) The Map of Oke-Aro metal scrapyard, Akure, Ondo State showing the sampled sites.

2.2. Sample Collection and Processing

A total of twelve soil samples (Five from the dumpsite), (Five from the scrapyard) and (Two control samples) were collected for this study (Figures 1 and 2). Each sampling points was sampled to a depth of 15cm (topsoil). A stainless-steel soil auger and a meter rule were used for the soil sample collection. The samples were stored in a polyethylene and labelled properly. The samples were labelled in the following pattern: D1-D5, S1-S5, DC and SC where D = dumpsite sample, S = scrapyard sample, DC = control sample for dumpsite and SC = control sample for the scrapyard.

The soil samples were air-dried for seven days and were ground into powdered form. The samples were sieved with a 2.0 mm sieve to obtain a uniform size sample. The samples

were stored in airtight containers until analysis were done. All these were carried out in the environmental chemistry laboratory of the Federal University of Technology Akure, Ondo state, Nigeria. Precautions were taken to avoid contamination during sampling, drying and storage.

2.3. Physicochemical Analysis

The standard methods described by Inengite et al. (2015) [6] was used to determine physiochemical properties of the soil samples.

2.4. Total Metal Analysis of Soil

Standard method as used by Thompson et al. (2019) [7] was used. One gram of the soil sample was weighed into a 100 ml clean Kjedahl digestion flask and 20ml of a mixture of concentrated nitric acid (HNO_3) and concentrated hydrochloric acid (HCl) in a ratio of 1:3 was added. The sample solution was then heated in a fume hood until a slightly clear color solution was obtained. The sample solution was left to cool and then filtered using Whatman filter paper (№. 42) into a 50ml standard flask and made up to mark with deionized water. Triplicate determinations were carried out. The instrumental analysis for total metal concentration for the studied metals (Cd, Cr, Mn, Ni and Pb) was carried out using Atomic Absorption Spectrophotometer (AAS) in appropriate instrumental conditions.

2.5. Chemical Speciation

1.0 gram of the soil sample was weighed and extracted into five fractions (exchangeable fraction, carbonate fraction, Iron and Manganese fraction, organic matter fraction and residual fraction) as described by Osakwe (2010) [8]. The supernatant from each extraction step was filtered using Whatman filter paper (№. 42) into a 50 ml standard flask and was made up to mark with deionized water and were analyzed using AAS in appropriate instrumental conditions.

2.6. Pollution Assessment: Index of Geo-accumulation

Index of geo-accumulation (I_{geo}) was computed using the equation below:

$$I_{geo} = \mathrm{Log}_2 Cn/1.5Bn$$

C_n is the heavy metal concentration in the study areas while B_n is the reference sample background value (Nowrouzi and Pourkhabbaz 2014). There are 7 grades in I_{geo} (0-6), $I_{geo}<0$ means the soil is practically uncontaminated; $0< I_{geo}<1$ means the soil is uncontaminated to moderately uncontaminated; $1< I_{geo}<2$ means the soil is moderately contaminated; $2< I_{geo}<3$ means the soil is moderately to heavily contaminated; $3< I_{geo}<4$ means the soil is heavily contaminated; $4< I_{geo}<5$ means the soil is heavily to extremely contaminated; $5< I_{geo}<6$ means the soil is extremely contaminated.

2.7. Pollution Assessment: Mobility Factor

The sequential extraction of the soil samples fractionates heavy metals in the soil is in order of decreasing solubility. Therefore, the exchangeable and carbonate (F1 and F2) fractions that are the early fractions, capture the most reactive and the most mobile and bioavailable fractions. Mobility factor (MF) is used to calculate the index of metal mobility and is calculated as follows [9].

$$MF = (F1 + F2) * 100)/(F1 + F2 + F3 + F4 + F5)$$

Where, F1 = Exchangeable metal content fraction; F2 = Metal content bound to carbonate fractions; F3 = Metal content bound to Fe-Mn oxide fraction; F4 = Metals content bound to organic matter fraction; F5 = Residual metal content fraction.

Table 1. Result of the physico-chemical analysis of the samples.

Samples	pH	%Organic Carbon	%Organic Matter	%Silt	%Clay	%Sand
D1	7.13± 0.57	2.41 ± 0.05	4.15 ±0.08	10.56 ± 0.05	7.75 ± 0.05	81.68 ± 0.05
D2	7.23 ± 0.10	2.00 ± 0.01	3.45 ± 0.01	8.57 ± 0.01	13.75 ± 0.01	7.67 ± 0.11
D3	7.13 ± 0.05	0.46 ± 0.02	0.83 ± 0.02	10.56 ± 0.05	13.75 ± 0.05	76.34±0.13
D4	7.20 ± 0.57	0.76 ± 0.02	1.34 ± 0.03	8.51 ± 0.04	7.79 ± 0.07	83.66 ±0.07
D5	6.36 ± 0.57	2.84 ± 0.02	4.91 ± 0.36	6.70 ± 0.24	5.73 ± 0.20	87.53 ±0.08
DC	6.90 ± 0.05	0.88 ± 0.03	1.55 ± 0.03	6.56 ± 0.05	13.76 ± 0.05	79.67 ±0.04
S1	8.06 ± 0.57	2.25 ± 0.16	3.96 ± 0.32	7.56 ± 0.05	6.76 ± 0.05	85.63 ±0.07
S2	7.26 ± 0.57	1.74 ± 0.05	3.01 ± 0.75	8.56 ± 0.05	7.76 ± 0.05	85.63 ±0.04
S3	7.30 ± 0.04	2.75 ± 0.04	4.74 ± 0.08	2.56 ± 0.05	5.76 ± 0.05	89.64 ±0.11
S4	7.50 ± 0.57	1.43 ± 0.02	2.43 ± 0.04	6.56 ± 0.05	8.76 ± 0,05	87.64 ± 0.10
S5	7.10 ± 0.05	1.48 ± 0.03	2.59 ± 0.36	10.56 ± 0.05	4.71 ± 0.07	80.64 ± 0.12
SC	7.20 ± 0.38	0.83 ± 0.06	0.83 ±0.01	4.49 ± 0.06	8.50 ± 3.26	90.78 ± 0.12

3. Result and Discussion

Heavy metals in soils which have their pH value ranging between 6.0 and 9.0 are known not to be bioavailable for plant uptake [10]. The pH results of the soil samples in this study (Table 1) are within the pH range 6.0 -9.0, i.e the range where their metals are not bioavailable to the plant, this state

will remain until when favourable conditions like acidic precipitation prevailed on the soil. It has been known that important role of pH in the soil include solute concentration and also in sorption and desorption of contaminants [10]. The percentage organic matters of soil collected from the dumpsite and metal scrapyard sites ranges from 0.83 to 4.91 and 2.59 to 4.74 respectively which similar to the percentage reported by Akinnusotu and Arawande (2016) [11] for dumpsites in Rufus Giwa, Ondo State. This shows positive indication that these sites are fertile and likely to support healthy growth of vegetable which may attract attention of farmers to the locations [12]. The soil texture class was evaluated for all both sites and their respective controls taken. The soils of all the studied sites have very low silt content and high percentage of sand content which plays a very important role in plant species establishment and development and influences physical parameters of the soil [13].

3.1. Total Heavy Metal Concentration

The result of the total concentration of the studied metals (Cd, Mn, Cr and Pb) are reported in Figure 2. Manganese (Mn) is found naturally in the most soil as it is one of the most essential minerals for life [14]. In this study, concentration of manganese in the dumpsite soils ranges from 2.08 to 4.12 mg/kg similar to Adaikpoh (2013) [15] while it ranges from 2.29 to 8.5 mg/kg in the scrapyard soils. Anthropogenic input of Cr comes from solid wastes, where approximately 30% of Chromium (Cr) originates from plastics, packaging materials and lead-chromium batteries [10]. The mean concentration of chromium in this study was 1.86 mg/kg for dumpsite and 2.71 mg/Kg in the scrapyard soils samples. Concentrations of Cadmium (Cd) in the locations ranged from 1.01 – 2.11 mg/kg at the dumpsite and 1.83 – 4.84 at the scrapyard which is considerably higher than that of the control of 1.06 and 1.21 mg/kg in dumpsite and scrapyard respectively. The results obtained in this study for the Cadmium concentration were lower than the ones reported by Awokunmi et al., (2015) [16] on the study on selected dumpsite in Osun State and higher than the concentration discovered on some scrapyards in similar studies by Adedeji et al., (2014) [17] on soil and water around urban scrapyards. The difference is based on the constituent of the dumpsites and scrapyards. The maximum concentration of Lead (Pb) was found at the scrapyard site with a mean value of 3.95 mg/Kg and the dumpsite value was found with a mean value of 1.25 mg/Kg. The result of the lead concentration on the dumpsite and scrapyard are in the same trend with the result reported by Awokunmi et al., (2015) [16] on a dumpsite in Ilesha and Victoria and Lajide (2014) [18] on a dumpsite in Akure. Short-term exposure to Pb could result in diarrhoea, vomiting, convulsion, while long term exposure could result in kidney and nervous damage, cause brain and blood disorder and could leads to death [15].

DPR standard and WHO maximum permissible level limit for the studied heavy metal in soil were given in Table 2., these standards were compared to the result of these study. All the concentrations of Manganese (Mn), Lead (Pb) and Chromium (Cr) in the dumpsites and scrapyards reported in this study were found to be lower than the World Health Organization (WHO) and Department of Petroleum Resources (DPR) maximum permissible level. This implies that the present level of the reported concentrations of Mn and Cr are at safe level. For both the dumpsite and scrapyard, the concentrations of Cadmium were above the WHO and DPR (target value) maximum permissible level limit of Cadmium in soil. For metals like cadmium which have not been known for any biological function, this calls for public concern. Under suitable migration conditions, these metals in the soil constitute a serious threat to plants, surface and ground water. Cadmium and cadmium compounds are known human carcinogens with severe damage to the lungs which may occur through breathing high levels of cadmium. A secondary critical effect is skeletal damage as a secondary response to kidney damage or direct action on the bone cells by the cadmium [15, 18].

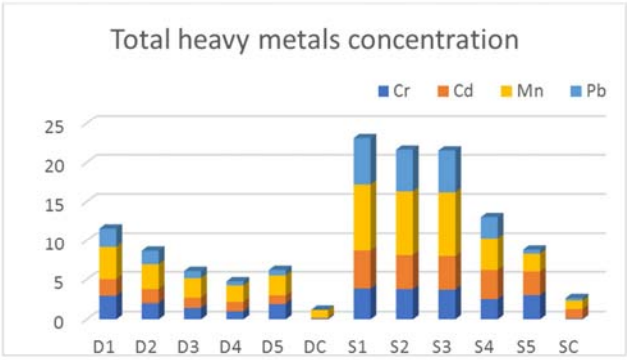

Figure 2. Result of the total heavy metal concentration.

Values are mean ± SD (n=3) Where; D = Dumpsite samples, DC = Dumpsite control sample, S = Scrapyards samples, SC = Scrapyard control sample.

Table 2. DPR standard and WHO maximum permissible level limit for selected Heavy metal in soil.

Metals	DPR Target value (mg/kg)	DPR intervention Value (mg/kg)	WHO MPL Soil (mg/kg)
Pb	85	530	100
Cd	0.8	12	3
Cr	100	380	100
Mn	-	-	2000

WHO MPL: World Health Organization maximum permissible level.
DPR: Department of Petroleum Resources.
Source: FAO/WHO, (2011) [19]; DPR, 2002 [20]

3.2. Heavy Metals Distribution into Sequential Fraction

The heavy metal distribution result for Cadmium, Lead, Chromium and Manganese metal are shown in Figures 3, 4,

5, and 6 respectively. The concentration of Cadmium and Lead metal (Figures 3 and 4) had dominant distribution in the Fe-Mn fraction and carbonate in the dumpsites. The carbonate and exchangeable fraction of the scrapyard had more dominant concentration of the cadmium metal. The carbonate fraction suggests that this percentage of cadmium in these soils can be mobilized when favorable conditions like acidic pH prevailed which indicates that the source is likely to have been from anthropogenic activities of man. The control sites of both of the dumpsite and scrapyard have very high concentration in the residual fraction. The percentage distribution of Cd showed that the highest percentage was found in the residue fraction which indicates that the concentration may have been from lithogenic (natural) act. The percentage distribution of chromium concentration in all the sites is presented in Figure 5. The percentage of chromium is ranges from 10% to 25 % at the dumpsites sample soils and while at the scrapyard it ranges from 13 % to 30 %. In the dumpsites, the chromium metal was evenly distributed into the fractions more than the residual fraction. This result is much expected because chromium is not a predominant metal in the soil of Akure, Ondo state. Chromium was lowly concentrated in the residual fractions except for the control sites. The partly low percentage of chromium detected in the residual fraction of the sample soils is not consistent with the result obtained by Iwegbue (2011) [21] on a research on polluted soils in Niger Delta. The metals found in this fraction are not bio-available and are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature [21].

The residual fraction of manganese had the highest concentration of manganese in the dumpsite and scrapyard throughout the soils samples. Manganese (Mn) is found naturally in the most soil as it is one of the most essential minerals for life [14]. The other concentration of the manganese metal was distributed almost equally in the other sequential fractions. Similar association of manganese with exchangeable fraction has been reported by Abeh et al., (2007) [22] and Iwegbue, (2011) [21]. The relative percentage present in exchangeable and carbonate fractions suggest that manganese is available on the exchange sites [8, 21]. The Mn^{2+}ion is very soluble in water at pH less than 7 [8] and given the pH range of these soils (7.6-9.7), soluble exchangeable Mn^{2+} is not likely. The association of manganese in the exchangeable and carbonate fraction may be attributed to its interference in the crystal of Fe oxide precipitate leading to its less occlusion [22]. Though, this fraction may be considered relatively stable, it becomes more soluble under acidic conditions and less so under oxidizing conditions [23, 24].

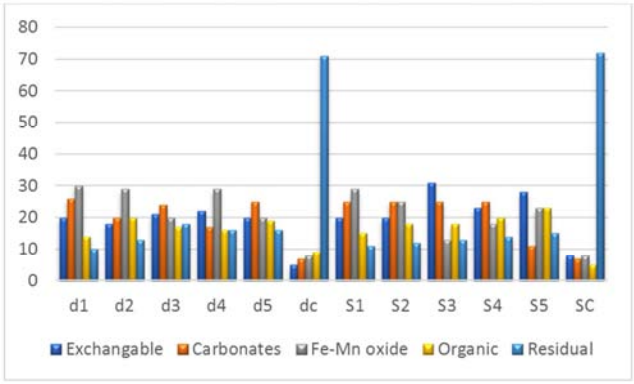

Figure 3. Percentage distribution of Cadmium metal in the soils**.**

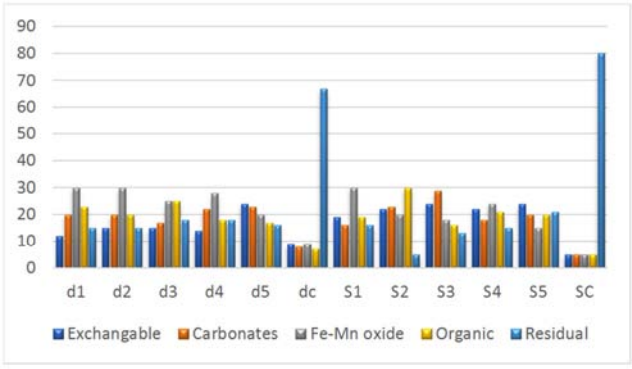

Figure 4. Percentage distribution of Lead metal in the soils.

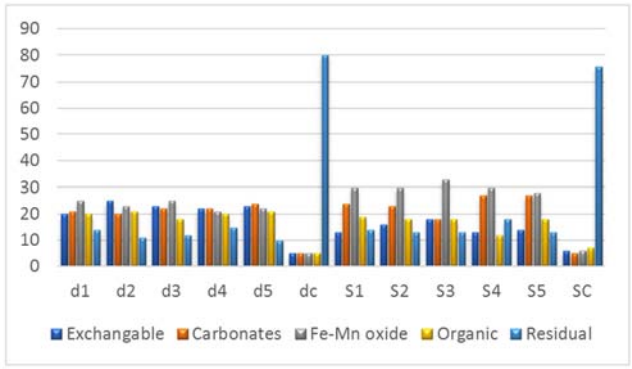

Figure 5. Percentage distribution of Chromium metal in the soil**.**

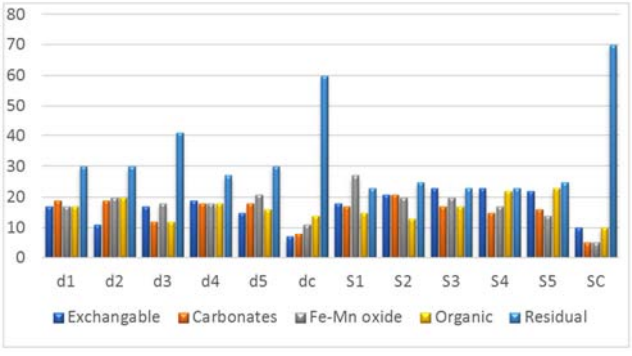

Figure 6. Percentage distribution of Manganese metal in the soil.

3.3. Geo Accumulation Index of Heavy Metals in the Soil

Igeo levels of different metals in soil sample are given in Table 3. The Igeo of Mn at the dumpsite was found to have mean value of 1.03 which is moderately contaminated and 0.8 at the scrapyard which denotes not contaminated. This study result is not similar to the result on Igeo of Mn by Adaikpoh (2013) [15] on waste dump sites within Imoru. The pollution at the dumpsite might have come from the nature of materials at the scrapyard. The Igeo of Cr ranges from 0.28 to 0.81 at the dumpsite and 0.55 to 1.68 at the scrapyard, which is interpreted as moderately uncontaminated to moderately contaminated. This Igeo Cr result is similar to the result form Adaikpoh (2013) [15]. The Igeo of Cd was found to be moderately contaminated in most of the dumpsites and moderately uncontaminated at most of the scrapyard site. The Igeo of Pb in the dumpsite and scrapyard site indicates extremely contaminated. From the result of the Igeo, the lead pollution on the sites is high and needs urgent attention.

Table 3. Geo Accumulation Index of Heavy Metals in the Soil.

Sample	Cr	Cd	Mn	Pb
D1	0.81	1.85	1.00	6.02
D2	0.56	1.53	0.77	4.31
D3	0.61	1.21	0.62	3.21
D4	0.40	1.07	0.61	2.28
D5	0.28	0.99	0.51	1.30
S1	0.20	0.20	0.20	0.20
S2	1.72	1.00	0.91	19.72
S3	1.68	0.90	0.88	17.72
S4	1.65	0.88	0.88	17.87
S5	1.12	0.56	0.44	9.14

Where D = dumpsite samples, S = Scrapyard sample,
I_{geo}<0 Practically uncontaminated
0< I_{geo}<1 Uncontaminated to moderately uncontaminated
1< I_{geo}<2 Moderately contaminated
2< I_{geo}<3 Moderately to heavily contaminated
3< I_{geo}<4 Heavily contaminated
4< I_{geo}<5 Heavily to extremely contaminated
5< I_{geo}<6 Extremely contaminated…….
Source: Muller, 1969 [25]

3.4. Mobility Factor (MF)

The mobility factors (MF) percentage of the metals for all the sites are presented on Table 4. There isn't a specific pattern of decreasing or increasing order in which the mobility of the studied metals occured. At the dumpsite, the mobility factor (MF) values of the Cr metals is the highest while Cd is has the highest mobility value in the scrapyard sites. The relatively high mobility factor observed for Chromium in the dumpsite is quite in agreement with the high percentage of carbonate and exchangeable fraction of chromium recorded from the chemical fractionation results. The mobility factor values of the metals in the Scrapyard sites differs from site dumpsite. The relatively high Cd and Pb fraction at the scrapyard have high mobility percentage because of its much occurrence in the carbonate fraction. The higher mobility of Cd and Pb in the scrapyard makes these metals very much available to leach into the ground water or become bioavailable for plant around the sites at favorable condition like acidic pH. This might eventually lead to the entry of lead and cadmium into the food chain and therefore causing harm to life.

Table 4. Mobility percentage of Heavy Metals in the Soil.

Sample	Cr	Cd	Mn	Pb
D1	41	46	36	32
D2	45	38	30	35
D3	45	45	29	32
D4	44	39	37	36
D5	47	45	33	47
S1	10	12	15	17
S2	37	45	35	35
S3	39	45	42	45
S4	36	56	40	53
S5	40	48	38	40

Where D = dumpsite samples, S = Scrapyard sample.

4. Conclusion

The result from this study showed that the total heavy metal concentration was higher in the scrap yard than in the dumpsite. The control sites had lesser heavy metal concentration in most instances which is an indication that these heavy metals concentrations are due to anthropogenic activities. Lead and Cadmium were found more in the Fe-Mn and carbonate fraction from the sequential extraction of the metal suggesting that these metals may be mobile given the right condition. Moreover, the dumpsites and scrapyards are near to farm areas, water bodies and residential areas; should this metal mobility occur, severe environmental and health issues may be inevitable.

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