DETERMINATION OF HEAVY METAL CONCENTRATIONS IN SOIL AND PLANTS OF THREE WASTE DUMPSITES IN ILORIN KWARA STATE, NIGERIA

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Abstract: **The levels of heavy metals were assessed in three randomly chosen dump sites. Nine soil samples were drawn at the depth of 0-15 cm, 15-30 cm and 30-45 cm on each of the three randomly chosen locations and plant samples from three locations from the dumpsites, one plant from each site. The result of the analysis carried out showed that Iron (Fe) has the highest total mean concentration in both the soil and plants from the three dumpsites with the mean values of 763.86 mg/kg and 148.86 mg/kg respectively. The total mean concentrations for lead (Pb) in soil and plant samples were 0.35 mg/kg and 0.23 mg/kg respectively. The total mean concentration of Manganese (Mn) in the soil and plant samples was 11.70 mg/kg and 2.37 mg/kg respectively. Zinc, in the order of concentration had total mean concentrations of 4.01 mg/kg and 2.24 mg/kg for soil and plant samples respectively. Cadmium (Cd) had the least total mean concentration from the soil samples with the value of 0.0078 mg/kg, although it was absent in the soil samples of Sites A and B, and also not detected in all of the plant samples. Assessments of some physicochemical properties of these metals were also carried out. The results show that the soils around the dumpsites were slightly alkaline with mean pH of 7.4. The soil moisture, Organic carbon and organic matter contents had mean values of 1.92%, 1.19% and 2.06%, while the plants moisture and ash contents were 14.78% and 63.29% respectively.**

Keywords: **Heavy metals, Metalloids, dumpsites, physicochemical parameters, Environmental Contamination.**

1. INTRODUCTION

Heavy metals are metals and metalloids having atomic densities greater than 5 g/cm^3 (Wild, 1993).They include Mercury, Zinc, Copper, Cadmium, Lead and Nickel among others. At some levels of exposure and absorption, they are harmful to most living things. Heavy metals are released into the environment through man's industrial, domestic and commercial activities, industrial effluents, pesticides and fungicides as well as manure from poultry farms. In Ilorin, Kwara State and in Nigeria as a whole, leachates from dumpsite constitute a major source of heavy metal pollution. Due to the rapid increase in the population of Kwara State, a high degree of generation of solid waste is taking place at a rate faster than they can be evacuated. Municipal solid waste usually contains paper, food waste, metal scraps, glass, ceramics, ashes etc. Decomposition or oxidation process releases the heavy metals contained in these wastes to the soil. According to John et.al, (1972), the bioaccumulation of these metals in plant tissue constitutes a hazard to man on consumption. The higher the concentration of these metals in soils, the higher the uptake by plant. Apart from uptake by plants, they can also be leached into underground water sources. Voogt, et.al (1980) noted that even slow movement of heavy metals in the soil profile may result in the deterioration of ground water quality. Other sources of heavy metals in the environment include: gas from automobile exhaust fumes and chemical discharges from industries into the soil. Once these metals enter the soil, they are not static but are absorbed by plants, which is a source of nutrient to man (Adefemi et. al; 2012).

Thus environmental contamination is a serious problem facing man in recent years. Since these metals constitute a hazard to man and other living things, they require a more serious attention. One of the major sources of heavy metal in Nigeria is leachate from waste dumpsite. Collection and disposal of solid waste has therefore become one of the greatest problems facing Nigeria. In Ilorin metropolis, the capital of Kwara State, waste dumpsites are still found in some streets despite government's effort to evacuate them. Abdul-Salam N. 2009 is of the opinion that poor management of dumpsites is

Page | 63

capable of creating a number of adverse environmental impacts including wind-blow litter, attraction of mice and pollutants such as leachates which is capable of polluting underground soil bed and/or aquifers. Since municipal wastes usually contain materials capable of releasing heavy metals on decomposition or oxidation process, they can be harmful to the environment and organism. These metals are non degradable in soil and gradually bio-accumulate until they reach toxic level. Plants grown on such soils pick up these metals and transfer them to man, the ultimate consumer of such plants, which sometimes leads to death of the consumers (Sherene 2010).

According to Alloway (1996), toxicity sets in when the heavy metal content in the soil exceeds natural background level. This may cause ecological destruction and deterioration of environmental quality, influence yield and quality of crops as well as atmosphere, and health of animal through food chains. In most cases, crops are cultivated on and around the waste dumpsites. As a result of this, crops accumulate heavy metals in their edible parts and consumption by man may result in severe implication on health as investigated by (Adefemi et.al 2012).

2. MATERIALS AND METHODS

2.1 Material Used

2.1.1 Apparatus/Instruments Used:

In the course of carrying out this research work, the following apparatus were used; 250 ml conical flasks, Burette and Burette stand, Pipette, measuring cylinder, wash bottle, volumetric flasks, Atomic Absorption Spectrophotometer, soil pulverizer, dessicator, crucibles, digital $_p$H meter, Muffle furnace, hot-air oven and 2-mm sieve.

2.1.2 Reagents Used:

All the reagents used were of analytical grade and were obtained from the Industrial Chemistry department of the University of Ilorin Nigeria. The following reagents and chemicals were used; concentrated Hydrochloric acid (HCl), concentrated Trioxonitrate (v) acid (HNO_3), concentrated Tetraoxosulphate (vi) acid (H_2SO_4), distilled water (H_2O), 1 N Potassium heptaoxodichromate (vi) solution ($K_2Cr_2O_7$), 0.5 N Iron (11) Sulphate and Ferroin indicator.

2.2. Study Area

This project research work was carried out in Tanke area of Ilorin, Kwara State, located at 10^0E, 24^0N in the North Central part of Nigeria. The mean annual temperature in Ilorin Urban is 29.5^o C. The relative humidity varies through the year from 70 – 80%. The city has two distinct seasons, namely; dry and rainy seasons. The mean annual rainfall is 2384 mm. The dry season usually starts in November and ends in March. The rainy season starts usually in April and end in October. During the rainy season, the temperature varies from 24^0C to 32^0C. Samples were collected from three dumpsites. The first site is located at Ademola Akanji street, besides number 12 building (Students' Hostel), off University road, Tanke Iledu, Ilorin, Kwara State. The second site is located behind K-Dom's students' hostel, Tanke Oke-Odo, while the third dumpsite is located at the outskirts of University of Ilorin premises near Department of Works.

2.3. Sample Collection and Treatment

Representative soil and plant samples were collected from three dumpsites in February 2015. Soil samples were collected at the depths of 0-15cm, 15-30cm and 30-45cm from the soil surface. The soil samples from each dumpsite were stored into three different well labeled containers corresponding to the depths of collection (i.e 0-15cm, 15-30cm, 30-45cm). Also, fresh plant sample was collected from each of the three dumpsites and were identified as *Ricinus communis* (Tanke Iledu Waste Dumpsite), *Azadiracta indica* (Tanke Oke-Odo Waste Dumpsite), *Chromonena oduranta* (University of Ilorin Waste Dumpsite) at the University of Ilorin Plant Biology Departmental Herbarium.

2.4. Sample Analysis 1: Physicochemical Properties Analysis

2.4.1 Analysis of Soil pH

Experimental Procedure

Twenty grams (20g) of air-dried soil sample passed through a 2-mm sieve was weighed into a $50cm^3$ beaker and $20cm^3$ of distilled water was added. The mixture was allowed to stand for 30 minutes with occasional stirring using a glass rod. The pH was determined using digital pH meter. The pH meter was calibrated with buffer solutions of pH 10 and 4 for the determinations. The electrode of the calibrated pH meter was inserted into the partly settled suspension and the pH recorded as shown in Table (3.1) [Bates R.G. (1954)].

2.4.2 Determination of Moisture Content of Soil/Plant Samples

Determination of Moisture Content

Principle

The method is based on removing sample moisture by oven-drying a sample until a constant weight is obtained. The moisture content (%) is calculated from the sample weight before and after drying.

Experimental Procedure

An empty crucible was weighed and the mass recorded. Thereafter, 5g of sample with crucible was also weighed and their combined mass was recorded. The crucible plus the sample was kept in a hot air oven at 155^0C for five hours, after which the hot crucible containing the sample was removed and kept in a dessicator for an hour. After cooling, the crucible plus the dried sample was weighed and the mass recorded. The crucible plus the dried sample was repeatedly kept in a dessicator, cooled and weighed until a constant mass was obtained. This same experimental procedure was used in determining the moisture content of the plant samples. Thereafter, the moisture contents of both samples were collected using the formular below and the results are as shown in table (3.1) (Miliud et. al., 2009).

$$\text{Moisture content } (\%m) = \frac{(B-F)}{(B-G)} \times \frac{100}{1}$$

Where G = mass of empty crucible

B = mass of empty crucible + wet sample

F = Mass of crucible + dried sample

2.4.3 Determination of Ash Content of Plant Samples

Experimental Procedure

The weight of empty crucibles were determined and recorded. Thereafter, 5g of each plant sample plus the crucibles was weighed a weighed and their weights recorded. This was followed by the calculation of the ash content using the formular below and the results are as shown in table (3.1) (Miliud et. al. 2009).

$$\text{Ash Content } (\%A) = \frac{(F-G)}{(B-G)} \times \frac{100}{1}$$

Where G = Mass of empty crucible

B = Mass of crucible + sample

F = Mass of crucible + Ashed sample

2.4.4 Determination of Organic Carbon/Organic Matter Contents of Soil Sample

Determination of Organic Carbon Content

Principle

The principle is based on the oxidation of organic matter by potassium dichromate ($K_2Cr_2O_7$), Sulphuric acid mixture followed by back titration of the excessive dichromate by ferrous Sulphate. The titre value is inversely related to the amount of Carbon C present in the soil sample.

Experimental Procedure

Soil organic carbon and organic matter contents were determined by titrimetric method. 2 g of air-dried samples ground and passed through a 2-mm sieve were weighed in duplicate and transferred to 250 cm^3 Erlenmeyer flasks. Exactly 10 cm^3 of 1N Potassium dichromate was pipetted into each flask and swirled gently to disperse the soil, followed by addition of 20 cm^3 of concentrated, Sulphuric acid. The flask was swirled gently until soil and reagents were thoroughly mixed. The mixture was then allowed to stand for 30 minutes on a sheet of asbestos to allow for the oxidation of potassium dichromate to chromic acid. After standing for 30 minutes, 100 cm^3 of distilled water was added followed by addition of four (4) drops of ferroin indicator, after which the mixture was titrated with 0.5 N Ferrous Sulphate solution until the solution turned greenish cast and then to dark green. At this point, Ferrous Sulphate solution was added drop by drop until the colour of the solution changed sharply from blue to red (i.e maroon colour). Two blank titrations were similarly carried out but without soil samples and the titre values (i.e volumes of ferrous Sulphate used) were read off and recorded as shown in table (3.1). The organic carbon and organic matter contents were calculated using the formula below:

$$\% \text{Organic Carbon C in soil} = \frac{(MeK_2Cr_2O_7 - MeFeSO_4) \times 0.003 \times 100 \times (f)}{\text{g of air-dry soil}}$$

Where

Correction factor, f = 1.33

Me = Normality of solution x ml of solution used

% Organic matter in soil = % Organic Carbon x 1.729

(Walkley A. and Black 1934)

2.5.0 Sample Analysis II: Determination of Heavy Metal

2.5.1 Determination of Heavy Metals in Soil Samples

Experimental procedure

The representative soil samples were air-dried and all clods and crumbs were removed. The soil samples were passed through a 2-mm sieve to remove coarse particles before chemical analysis. 1g of the air-dried ground soil sample was transferred to a 250 ml conical flask. This was preceded by the additions of 5mls of concentrated Sulphuric acid (H_2SO_4), 25 mls of concentrated Nitric acid (HNO_3) and 5 mls of concentrated Hydrochloric acid (HCl). Immediately, there was solution of brown fumes, after which the conical flask was placed on a hot plate for some minutes until there was disappearance of brown fumes and appearance of white fumes. Thereafter, 20 mls of distilled water was added and filtration was carried out to complete digestion. Finally, the filtrate was transferred to a 50 ml standard flask and made up to the mark with distilled water. The filtrate was then poured into sample bottles prior to heavy metal analysis using Atomic Absorption Spectrophotometer (AAS Buck Scientific model 210VGP). The results are as shown in tables (3.2, 3.4 and 3.6) [Adu et. al., 2012].

2.5.2 Determination of Heavy Metal in Plant Samples

Experimental Procedure

Plant samples were first washed with distilled water to remove dust particles. The plant samples were air-dried and ground into fine powder using a commercial blender, sieved and stored in polyethylene bags prior to chemical analysis.

Five grammes (5 g) of powder from plant sample were put into 250 ml conical flask. Following were the additions of 5 mls of concentrated Sulphuric acid (H_2SO_4), 25 mls of concentrated Nitric acid (HNO_3) and 5 mls of concentrated Hydrochloric acid (HCl) into the conical flask. Immediately, there was evolution of brown gas, after which the conical flask was placed on a hot plate for some minutes until brown fumes disappeared and white fumes emerged. Thereafter, 20mls of distilled water was added and the mixture was filtered to complete digestion. Finally, the mixture was transferred to a 50ml standard flask filled to the mark with distilled water. The filtrate was analyzed for heavy metal content (i.e, Zn, Fe, Cd, Mn, Pb) using Atomic Absorption Spectrophotometer (Bulk Scientific Model 210VGP). The results are as shown in tables (3.3, 3.5 and 3.7) [Adu et. al., 2012].

3. RESULTS AND DISCUSSIONS

Sites	Soil Depth (cm)	Soil pH	Soil Moisture Content (%)	Soil Organic Carbon Content (%)	Soil Organic matter (%)	Plant Moisture Content (%)	Plant Ash Content (%)
A	0 – 15	7.4	2.36				
	15 – 30	7.7	2.48	1.39	2.40	8.32	57.44
	30 – 45	7.6	2.72				
B	0 – 15	6.8	2.24				
	15 – 30	6.5	2.36	1.43	2.47	5.01	94.90
	30 – 45	6.9	2.40				
C	0 – 15	7.6	0.48				
	15 – 30	7.8	0.86	0.75	1.30	4.34	37.52
	30 – 45	7.9	1.42				
Mean		7.4	1.92	1.19	2.06	14.78	63.29

Table 3.1: Physicochemical Parameters of Soil and Plant Samples Collected from the Dumpsites

Soil Depth [cm]	Cd (mg/kg)	Pb (mg/kg)	Mn(mg/kg)	Fe (mg/kg)	Zn(mg/kg)
0 – 15	0.02	1.72	7.74	405.36	12.14
15 – 30	0.03	0.60	6.65	416.58	6.35
30 – 45	0.02	ND	6.37	400.52	2.48
Mean	0.02	0.77	6.92	407.49	6.99

Table 3.2: Heavy Metal Concentration (mg/kg) in Soil Sample from Dumpsite at Tanke Iledu [Site A]

Sample Code	Cd (mg/kg)	Pb (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	Zn (mg/kg)
A1	ND	ND	1.90	191.25	2.31
A2	ND	ND	2.32	256.32	2.56
A3	ND	2.11	2.83	432.28	2.97
Mean	0.00	0.70	2.35	293.28	2.61

Table 3.3: Heavy Metal Concentration (mg/kg) in Plant Sample from Dumpsite at Tanke Iledu [Site A]

Soil Depth [cm]	Cd (mg/kg)	Pb(mg/kg)	Mn (mg/kg)	Fe(mg/kg)	Zn(mg/kg)
0 – 15	ND	0.30	22.21	2025.01	0.78
15 – 30	ND	0.25	27.58	1615.27	1.07
30 – 45	ND	0.30	22.14	1340.28	3.02
Mean	0.00	0.28	23.98	1660.19	1.62

Table 3.4: Heavy Metal Concentration (mg/kg) in Soil Sample from Dumpsite at Tanke Oke-Odo [Site B]

Sample Code	Cd(mg/kg)	Pb(mg/kg)	Mn (mg/kg)	Fe(mg/kg)	Zn(mg/kg)
B1	ND	ND	0.61	27.26	0.68
B2	ND	ND	0.60	25.13	0.66
B3	ND	ND	0.62	27.36	0.72
Mean	0.00	0.00	0.61	26.58	0.69

Table 3.5: Heavy Metal Concentration (mg/kg) in Plant Sample from Dumpsite at Tanke Oke-Odo [i.e Site B]

Soil Depth [cm]	Cd(mg/kg)	Pb(mg/kg)	Mn(mg/kg)	Fe (mg/kg)	Zn(mg/kg)
0 – 15	ND	ND	4.01	206.57	3.84
15 – 30	ND	ND	4.43	268.58	3.45
30 – 45	ND	ND	4.16	196.53	2.96
Mean	0.00	0.00	4.20	223.89	3.42

Table 3.6: Heavy Metal Concentration (mg/kg) in Soil Sample from University of Ilorin Dumpsite [i.e Site C]

Sample Code	Cd(mg/kg)	Pb(mg/kg)	Mn (mg/kg)	Fe(mg/kg)	Zn (mg/kg)
C1	ND	ND	4.31	171.52	0.42
C2	ND	ND	4.52	123.07	0.97
C3	ND	ND	3.65	85.56	0.70
Mean	0.00	0.00	4.16	126.71	0.70

Table 3.7: Heavy Metal Concentration (mg/kg) in Plant Sample from University of Ilorin Dumpsite [i.e Site C]

Sites	Soil Depth (cm)	Cd(mg/kg)	Pb(mg/kg)	Mn(mg/kg)	Fe(mg/kg)	Zn(mg/kg)
A	0 – 15	0.02	1.72	7.74	405.36	12.14
	15 – 30	0.03	0.60	6.65	416.58	6.35
	30 – 45	0.02	0.00	6.37	400.52	2.48
B	0 – 15	ND	0.30	22.21	2025.01	0.78
	15 – 30	ND	0.25	27.58	1615.27	1.07
	30 – 45	ND	0.30	22.14	1340.28	3.02
C	0 – 15	ND	ND	4.01	206.57	3.84
	15 – 30	ND	ND	4.43	268.58	3.45
	30 – 45	ND	ND	4.16	196.53	2.96
Mean		0.0078	0.35	11.70	763.86	4.01

Table 3.8: Total Mean Concentration (mg/kg) of Heavy Metals in Soil Sample of the Dumpsites

Sites	Sample Code	Cd(mg/kg)	Pb(mg/kg)	Mn(mg/kg)	Fe(mg/kg)	Zn(mg/kg)
A	A1	ND	ND	1.90	191.25	2.31
	A2	ND	ND	2.32	256.32	2.56
	A3	ND	2.11	2.83	432.28	2.97
B	B1	ND	ND	0.61	27.26	0.68
	B2	ND	ND	0.60	25.13	0.66
	B3	ND	ND	0.62	27.36	0.72
C	C1	ND	ND	4.31	171.52	3.84
	C2	ND	ND	4.52	123.07	3.45
	C3	ND	ND	3.65	85.56	2.96
Mean		0.00	0.23	2.37	148.86	2.24

Table 3.9: Total Heavy Metal Concentration (mg/kg) in Plant Samples of the Dumpsites

3.1 Physicochemical Parameters

3.1.1 Soil pH

The results of the physicochemical parameters of the samples are presented in Table (3.9). The soil pH values of the soil samples studied in all the Dumpsites range from 6.5 – 7.9 with a mean value of 7.4. There was no regular trend in pH values with depths. This near neutrality to slight alkaline nature of the soil samples is common with reduced anaerobic soils and sediments in Ilorin, Kwara State. The soil pH values obtained in this study are in the same range with the values reported in soil along Enugu-Port Harcourt expressway in refuse dumpsites, dumpsite soils at Obafemi Awolowo University, Ile-Ife, in soil receiving Cassava Mill effluent in leachates from waste dumps in Abeokuta, soil of automobile mechanic waste dumps in Port Harcourt and in other Nigerian soils. The pH values recorded in this study are however lower than those reported for soils in municipal solid waste dumpsites in Alexandria Egypt.

The soil pH determines the availability of nutrients and the potency of toxic substances as well as the physical properties of the soil. The pH of soil, sediment and interstitial water affects metal retention by developing a pH dependent charge at a weak acidic surface. Soil pH also determines the extent of ionic exchange reactions. Previous studies have shown decreased metal availability with increasing pH. The pH values of these study sites indicate a decrease in the availability of heavy metals. Hence, this decreases the risk of heavy metals uptake. The soil pH is very important for most metals since metal availability is relatively low when pH is around 6.5 to 7.0 (Osakwe 2010).

3.1.2 Soil Organic Carbon/Organic Matter Content

The results of the organic carbon content and organic matter contents are presented in Table (3.9). The presence of organic carbon increases the cation exchange capacity of the soil which retains nutrients and heavy metals assimilated by plants (Bradly 1996). The organic carbon in the dumpsites is low to moderate, ranging from 0.75% to 1.43% as indicated in Table (3.9) with dumpsite soil of Tanke Oke-Odo (Site B) having the highest organic carbon content of 1.43%. The trend in the organic carbon content across the sites is: B > A > C. The moderately high amount of organic carbon of the dumpsites soils is suggestive of the level of degradation or presence of degradable and compostable wastes (Munoz et. al., 1994).

The organic matter enhances the usefulness of soils for agricultural purposes. It supplies essential nutrients and has unexcelled capacity to hold water and absorb cations. It also functions as a source of food for soil microbes and thereby helps to enhance and control their activities (Bradly 1996). The organic matter content of the dumpsites soil presented in Table (3.9) were low as these sites are located close to domestic areas and are richer in domestic waste than organic or agricultural waste. The organic matter content of the sites followed the same trend as the organic carbon content, with soil sample from Site B (i.e Tanke Oke-Odo Dumpsite) having the highest organic matter content of 2.47% while Site A (Tanke Iledu Dumpsite) and Site C (Unilorin Dumpsite) recording 2.40% and 1.30% respectively. The trend is B > A > C. The exposure of these dumpsites to contrasting (dry and rain) weather conditions over the years may have contributed to the loss of organic matter in the gaseous form into the atmosphere. The organic matter content depends on a number of factors which include the level of microbial activity, the proportion of organic refuse and the relative age of the dumpsite (Abdus-salam et. al 2011).

3.1.3 Moisture Content/Ash Content of Samples

The moisture content results are presented in Table (3.9). The low percent moisture content of the sites is proportional to the depths. As seen in Table (3.9), as the depth increases, the moisture content increases, the moisture content increases since there is more water below the soil surface than at the surface. The low percentage moisture content obtained is consistent with the sampling period, the dry season (January/February 2015) when the waste had lost substantial fluid through evaporation and percolation.

The moisture and ash content of plant samples from the dumpsites are presented in Table (3.9). The moisture content of plant from Site A (Ricinus communis) is highest with 8.32% when compared with the plant samples from Site B (Azadiracta indica) and C (Chromonena oduranta) with moisture contents of 5.01% and 4.34% respectively. The difference in the moisture content of the plant samples may be attributed to the water absorption and retention capacity of the plants.

The Ash content presented in table (3.9) shows the relative amount of ash contained in the plant samples from the result, the trend of ash content is; B > A > C, which follows the organic carbon content trend. The result shows that the plant sample from Site B (Azadiracta indica) has the highest ash content of 94.90% followed by plant sample from Site A (Ricinus communis) with ash content value of 57.44% and plant sample from Site C (Chromonena oduranta) with the least ash content of 37.52%. These results may be due to the nature of some plants, as some have higher fibre content than others.

3.2 Concentration of Heavy Metals in the Soil Sample of the Dumpsites

3.2.1 Cadmium (Cd)

From the results presented in tables (3.1), (3.3), (3.5), Cadmium concentration at dumpsite A is low with a mean value of 0.02 mg/kg. In dumpsites B and C, Cd was not detected. The reason for the absence of Cd in sites B and C may be as result of the fact that the refuse in these sites do not contain Cadmium enriched materials. The values of Cadmium obtained from the dumpsites are all far below the maximum tolerable levels proposed for agricultural soil. This is in agreement with the findings of Asawalam and Eke (2006) and Njoku and Ayoka (2007) who investigated the trace metal concentration and heavy metal pollutants from dump soils in Owerri, Nigeria. These values of Cd obtained also are far lower than the natural limits of 0.01 – 3.0 mg/kg in soils as given by MAFF (1992) and EC (1986).

3.2.2 Lead (Pb)

The results presented in tables (3.1), (3.3) and (3.5) show that Pb was only detected in dumpsites A and B with Pb absent in dumpsite C. Site A has higher Pd content than Site B with mean concentration of 0.77 mg/kg as against 0.28 mg/kg of site B. The concentration of Pb in sites A and B could be as a result of its sources from automobile exhaust fumes as well as dry cell batteries, sewage effluents, run off wastes and atmospheric depositions owing to the proximity of the sites to high vehicular traffic along the University road and their nearness to domestic areas. These values of Pb obtained were lower than EC (1986) upper limit of 300 mg/kg and the maximum tolerable levels proposed for agricultural soil, 90 – 400 mg/kg set by WHO (1993). The result is in agreement with the results obtained from dumpsites within Ikot-Ekpene in Akwa-Ibom State, Nigeria.

3.2.3 Manganese (Mn)

The results of manganese concentrations in dumpsite soils are presented as shown in tables (3.1), (3.3) and (3.5) and revealed that Mn is highest in site B with a mean value of 23.98 mg/kg, seconded by Site A with mean value of 6.92 mg/kg and the Site C with the lowest mean concentration of 4.20 mg/kg. The higher concentration of Manganese Mn in Site B than the other sites (A and C) could be as a result of more of batteries, discarded metal rails, machinery parts and wastes from welding works in the dumpsite than sites A and C. The levels of Mn obtained in this study are above the range of World Health Organization (WHO) standard and permissible limits for manganese (i.e 0.2 mg/kg).

3.2.4 Iron (Fe)

From the results presented in table (3.1), (3.3) and (3.5), Fe has the highest concentration in all the dumpsites with the mean value of 407.49 mg/kg, 1660.19 mg/kg and 223.89 mg/kg in sites A, B and C respectively. From these results, it can be inferred that Site B has the highest concentration of Iron, Fe when compared to Sites B and C. The higher levels of Fe obtained from these sites could be attributed to the high loads of Fe – containing wastes dumped at these sites.

In addition, the consistently high load of iron recorded in all the sites is not surprising considering the fact that natural soils contain significant concentration of Iron, Fe. Moreover, it had been earlier stated by a good number of researchers that iron occurs in high proportion in Nigerian soil implying that the concentration is contributed from both anthropogenic and coastal origin. The levels of Fe observed in this study are in the same range with those reported by Osakwe 2010.

3.2.5 Zinc (Zn)

The results of Zinc presented in tables (3.1), (3.3) and (3.5) show that the mean concentration of zinc in Site A, Site B and Site C are 6.99 mg/kg, 1.62 mg/kg and 3.42 mg/kg respectively. The trend in the mean is A > C > B. From the result, it can be inferred that Site A contains the highest load of Zinc in its soil with Site C ranking next to Site A and Site B containing the least concentration of Zinc (Zn). The difference in Zn concentration in all the sites could be linked to the zinc containing refuse dumped at these sites. The highest zinc content of Site A may be due to the proximity of this site to a building site as there is this tendency of dumping some pieces of zinc scraps in the site.

To better explain this research work, the mean concentrations of these heavy metals in the dumpsites are represented with bar charts as shown in figures (3.1), (3.2) and (3.3).
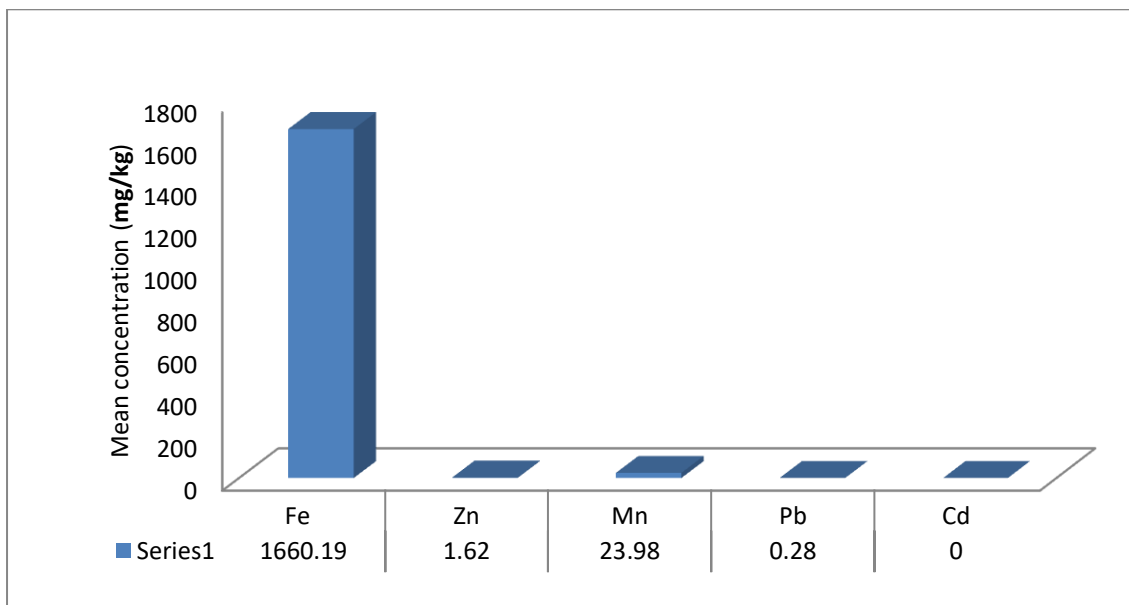

	Fe	Zn	Mn	Pb	Cd
Series1	1660.19	1.62	23.98	0.28	0

Fig 3.1: Mean Concentration (mg/kg) of heavy metals in soils of dumpsite A (Tanke Iledu Dumpsite)

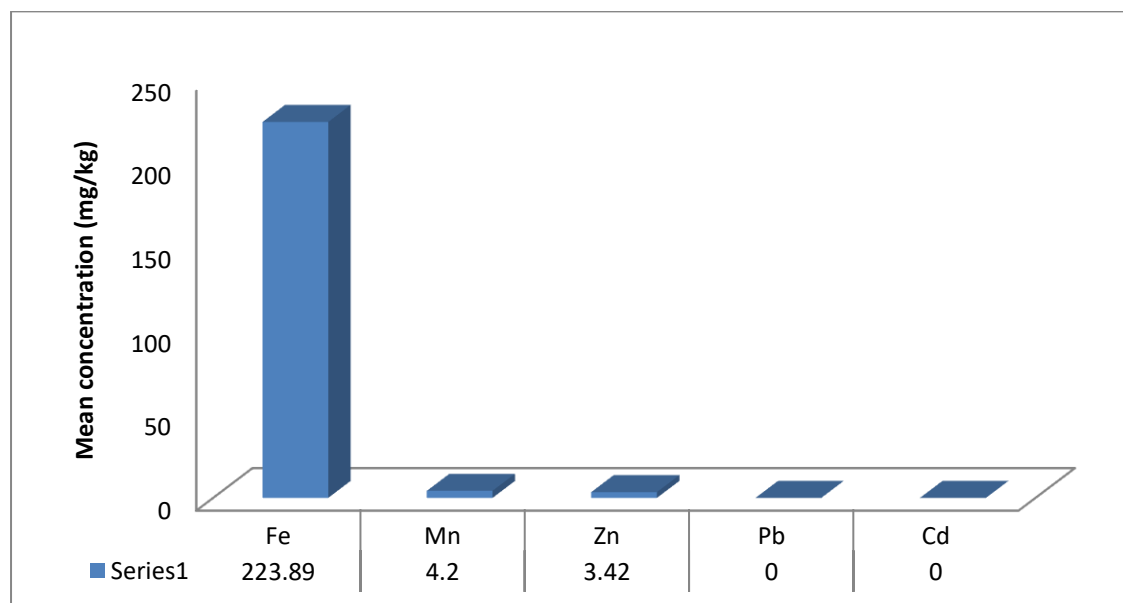|	Fe	Mn	Zn	Pb	Cd
Series1	223.89	4.2	3.42	0	0

Figure 3.2: Mean Concentration (mg/kg) of heavy metals in soil of dumpsite B (Tanke Oke-Odo dumpsite)
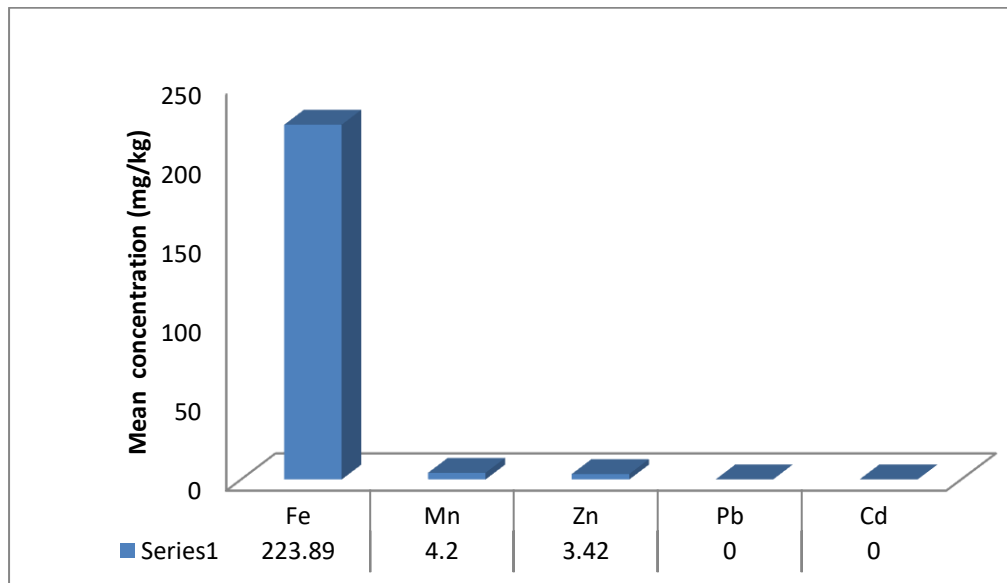
Figure 3.3: Mean Concentration (mg/kg) of heavy metals in soil of dumpsite C [University of Ilorin Dumpsite)

From the bar charts presented, the concentrations of the heavy metals in the dumpsite soil are proportional to the peak of the bar charts. From Fig 3.1, the trend in the concentration of heavy metal is Fe>Zn>Mn>Pb >Cd. This is depicted by the bar representing iron having the highest peak and the bar representing Cadmium having the lowest peak.

On the other hand, figures 3.2 and 3.3 show similar trend in mean heavy metal concentrations. The trend in the mean concentrations of the mean concentration in Sites B and C is as Fe>Mn>Zn>Pb>Cd. Iron in Site B has a mean concentration of 1660.19 mg/kg as shown in the height of its bar, while in Site C, Fe mean concentration is 223.89 mg/kg. Manganese, ranking next to Fe in the order of mean concentration has a value of 23.98 mg/kg in Site B and 4.20 mg/kg in Site C as shown by the bar representing it. Also, Zn ranking next to Mn in mean concentration showed the value of 1.62 mg/kg in Site B and 3.42 mg/kg in Site C and this represented by its bar. Lead has a mean concentration of 0.28 mg/kg in Site B and was not detected in Site C as shown in figures 3.2 and 3.3. The least in the trend is Cadmium which was not detected in both Sites B and C.

In summary, the total mean concentrations of all the heavy metals in all the sites studied is in the increasing order of Fe>Mn>Zn>Pb>Cd as presented in table 3.7 and represented in figure 3.4. From the results, Iron has the highest concentration in all the sites while Cadmium has the least concentration. The concentrations of these heavy metals show the rate at which the wastes containing them are being dumped at the sites.
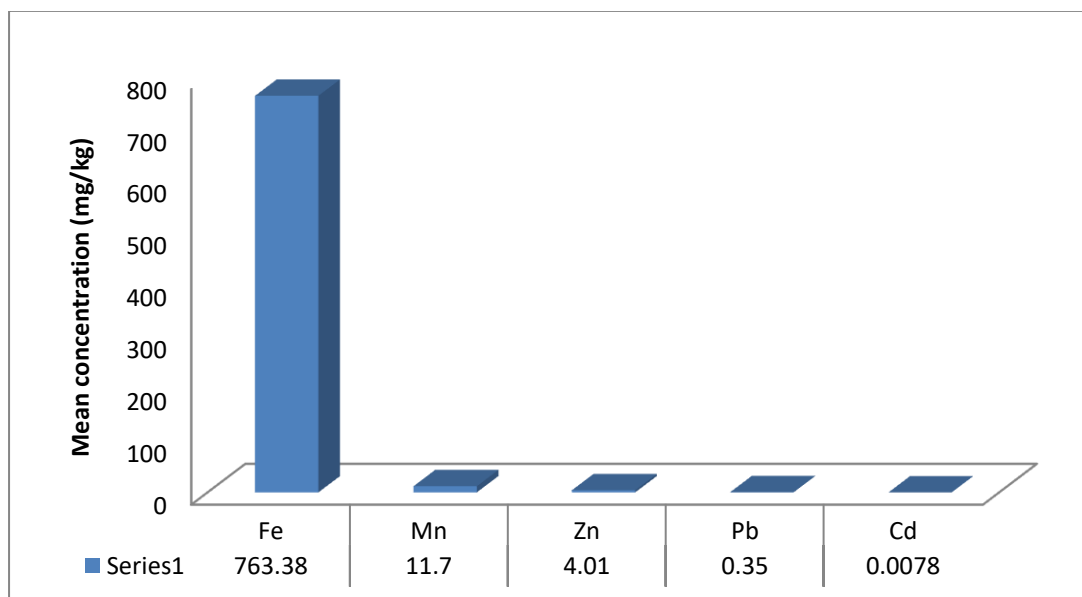

Figure 3.4: Total Mean Concentration (mg/kg) of heavy metals in all the dumpsites

3.3 Heavy Metal Concentration/Uptake by Plants from the Waste Dumpsites

The mean concentrations of the heavy metals in plant sample from the dumpsites are presented in tables (3.2), (3.4) and (3.6). From the result, the mean concentrations of the heavy metals in plant sample from Site A are as follows: Cd (ND), Pb (0.7 mg/kg), Mn (2.35 mg/kg), Fe (293.28 mg/kg), Zn (2.61mg/kg). For plant sample from Site B (*Azadiracta indica*), the heavy metal uptake was obtained as: Cd (ND), Pb(ND), Mn(0.61 mg/kg), Fe (26.58 mg/kg), Zn (0.69 mg/kg). The heavy metal uptake by plant sample from Site C (*Ricinus communis*) is also given as Cd (ND), Pb (ND), Mn (4.16 mg/kg), Fe (126.71 mg/kg), Zn (0.70 mg/kg).

3.3.1 Cadmium (Cd)

In respect of the result obtained, Cd was not detected in plant samples from all the sites even though a low mean concentration was obtained in soil sample from Site A. This result is reasonable, considering the fact that Cadmium was not detected in the soils of Sites B and C excluding in Site A where a low mean concentration of Cd was detected (0.02 mg/kg). This shows that the plant sample from Site A has no tendency to take up Cadmium and as a result not suitable to be used as a phytoextractor in remedying Cadmium contaminated soils.

3.3.2 Lead (Pb)

On the other hand, Pb was not detected in plant samples from Site A. The reason Pb was not detected in plant sample from Site C could be as a result of the fact that Pb was not present at the soil sample from the dumpsite. Pb was detected in soil of Site B, but it was not detected in the plant sample from the site. This result depicts that the plant sample (*Azadiracta indica)* collected from this site has no affinity for Pb and as result, not suitable to be used in phytoextraction of Pb contaminated soil. Also, there is about 90% uptake of Pb by plant sample from Site A and signifies that this plant is an ideal phytoextractor for remedying Pb contaminated soil.

3.3.3 Manganese (Mn)

Furthermore, the result of Mn obtained from plant samples shows that 33.6%, 2.54% and 99.05% of Mn analyzed was obtained for plant samples from Sites A, B and C respectively. It can be inferred from the result that plant sample from Site C (*Chromonena oduranta*) has more tendency to absorb Mn followed by plant sample from Site A (*Ricinus communis*) and plant sample from Site B (*Azadiracta indica*) showing the least affinity for Mn. The result concludes that *Chromonena oduranta* is best suitable for use in remedying Mn-contaminated soil, of all the plant samples analyzed.

3.3.4 Iron (Fe)

Iron being highly concentrated in all the dumpsites was also detected and found to be more in all the plant samples from the sites, except in Site B where a low concentration was detected as against the highest concentration in the dumpsite. The trend in Fe uptake by the three plants from the dumpsites is A > C > B corresponding to 71.97%, 56.59% and 1.60% of Fe extracted by plants from sites "A, C and B" respectively. The results depict that for an Iron-contamination soil, plant sample of Site A is best suited, among all the plants studied for use as phytoextractor to remedy the Fe toxicity in soil.

3.3.5 Zinc (Zn)

Among all the heavy metals studied, Zinc is the least toxic and an essential element in human diet as it is required to maintain the functioning of the immune system. From this study, Zn concentration in the plant sample was found to be highest in plant sample of Site A with mean value of 2.61 mg/kg and in plant sample of Site B with a mean value 0.69 mg/kg while the mean value of 0.70 mg/kg was detected in plant sample of Site C. However, comparing this mean value of Zn in plant to its bioavailability in the sites, it can be deduced that plant sample from Site B (*Azadiracta indica*) has more tendency to bio-accumulate Zn-metal than all other plant samples, as greater percentage (42.59%) of Zn was obtained in it, whereas plant sample of sites "A and C" bio-accumulated 37.34% and 20.47% of this metal respectively. As a result, Site B plant sample should be recommended for use in cleaning up Zn-contaminated soil when phytoremediation technique is to be used.

The bar charts showing the mean concentration of the heavy metals in plant samples of the dumpsites are shown in figures 3.5, 3.6 and 3.7. Also, the overall mean concentration of these heavy metals in the plant samples is presented in figure 3.8.
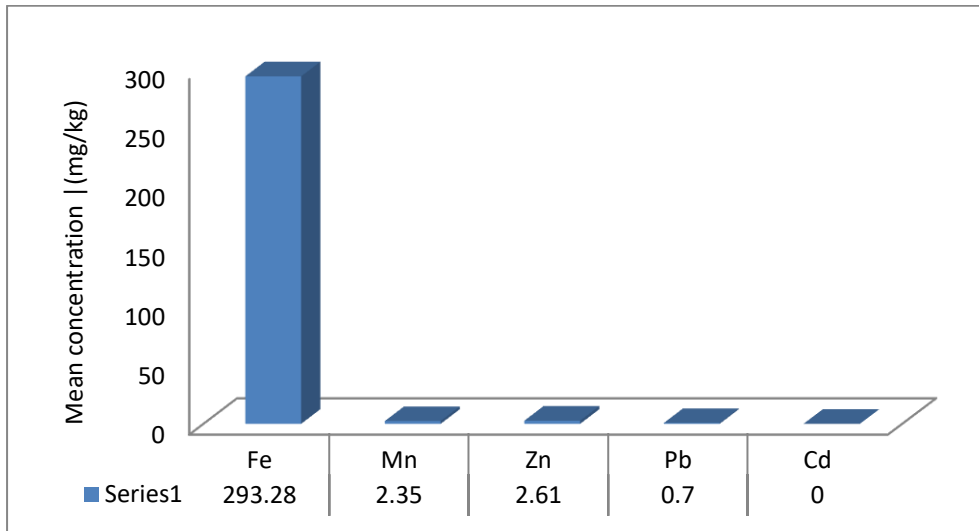
Series1	Fe	Mn	Zn	Pb	Cd
	293.28	2.35	2.61	0.7	0

Figure 3.5: Heavy metal uptake (mg/kg) by plant sample of Site A (*Ricinus communis*)

Series1	Fe	Mn	Zn	Pb	Cd
	26.58	0.61	0.69	0	0
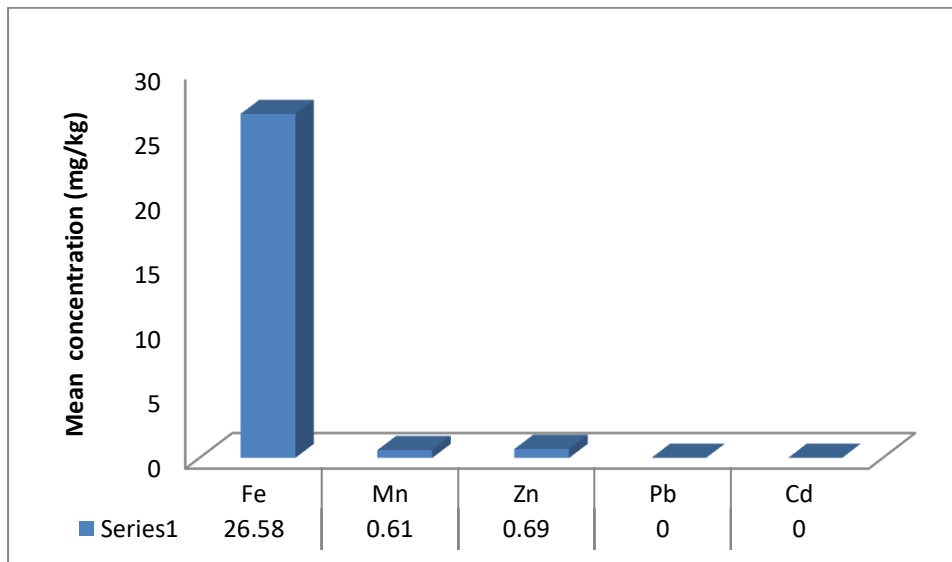
Figure 3.6: Heavy metal uptake (mg/kg) by plant sample of Site B (*Azadiracta indica)*

Series1	Fe	Mn	Zn	Pb	Cd
	126.71	4.16	0.7	0	0
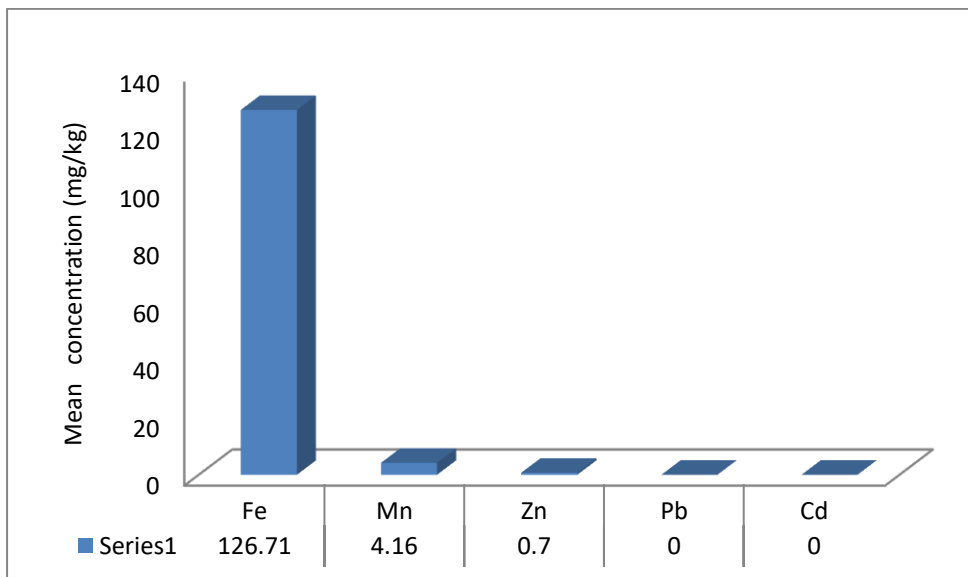
Figure 3.7: Heavy metal uptake (mg/kg) by plant sample of Site C (*Chromonena oduranta)*
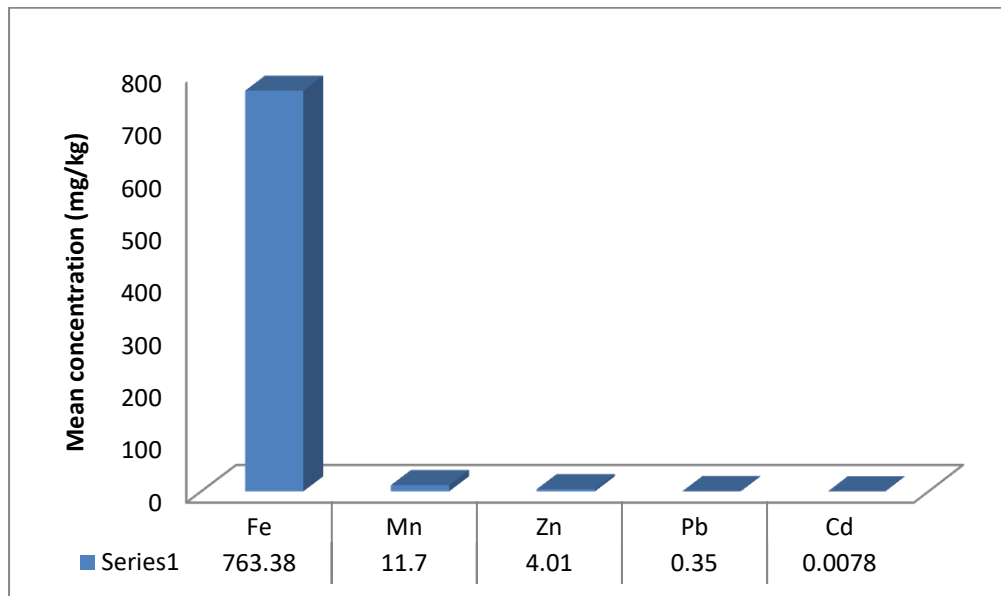
Figure 3.8: Total Heavy metal uptake (mg/kg) by all the plant samples of the dumpsites

4. CONCLUSION

Determination of soil metals (Zn, Pb, Cd, Fe, and Mn) from selected dumpsites in Ilorin city was made. The relatively high average content of the metals investigated in this study present significant exposure risks. The values obtained from contamination distribution of these metals revealed that iron showed range of high concentration while other metals showed very slight contamination. The slight contamination of some of the metals does not rule out the possibility of increase in concentration of these metals with time, since the extent of heavy metal levels in the soil suggests that these metals are of natural origin with contribution from anthropogenic influences. The mean concentration of iron in all the dumpsites showed that the soil around the dumpsites is highly polluted. Hence, the cumulative effect through bio-accumulation might be of concern in future, thus calling for urgent attention on regular monitoring of the refuse being dumped around the sites and its influence on the surrounding environment.

The results of this study have clearly demonstrated that the low levels of heavy metals in the studied soil samples are consistent with the composition of the municipal wastes generated in Ilorin and its environs. Lead was not detected in soil and plant samples collected from Site C. A smaller concentration of Pb was obtained in soil sample from Site C but was absent in plant sample from this site. A low concentration of Pb was obtained in soil and plant samples from Site C. In all the dumpsites, Fe showed the highest concentrations both in soil and plant samples. The values of the metals in this research work suggest that anthropogenic activities are a major source of these metals in the dumpsite soil. Also, with the exception of Fe and Mn, the levels of Pb, Zn, and Cd in this study were lower as compared with results found by other researchers in various countries worldwide.

The research was also carried out to determine the heavy metal uptake potential of some selected plant samples namely Ricinus communis from Site A (Tanke Iledu Waste dumpsite), Azadiracta indica from Site B (Tanke Oke – Odo Waste Dumpsite) and Chromonena oduranta from Site C (University of Ilorin Waste Dumpsite). The results obtained indicate that Ricinus communis has the highest uptake capability of heavy metal with an average of 298.94 mg/kg when compared with other plants.

REFERENCES

[1] Abdus-Salam, N; Ibrahim, M.S.; Fatoyinbo F.T. (2011) Dumpsites in Lokoja Nigeria: A Silent Pollution Zone For Underground Water. Journal of Waste Management and Bioresource Technology 1: 21-30

[2] Abdus-salam N. (2009) Assessment of Heavy Metals Pollution in Dumpsites in Ilorin Metropolis. Ethiopian Journal of Environmental Studies and Management 2(2):92 – 99.

[3] Adefemi O.S.; Ibigbami O.A.; Awokunmi E.E. (2012) Level of Heavy Metals in some Edible

[4] Plants Collected from Selected Dumpsite in Ekiti State, Nigeria. Global Advanced Research Journal of Environmental Science and Toxicology 1(5):132-136.

[5] Adu A. A.; Aderinola, O.J; Kusemiju, V (2012) Heavy Metals concentration in Garden Lettuce Grown along Badagry Expressway, Lagos, Nigeria. Transnational Journal of Science and Technology 2:115-130.

[6] Alloway, B.J. (1996). Heavy Metal in Soils John Wiley and Sons London Incorporated pp 149

[7] Asawalam D.O.; Eke C.I. (2006). Trace Metal Concentration in Soils Used for Waste Disposal around Owerri, Nigeria. In: proceedings of the 110th Conference of the Agriculture Society of Nigeria, Michael Opara University of Agriculture, Umudike, Abia State,

[8] Braddy N.C. (1996) The Nature and properties of Soils 11th Edition, Macmillan: New York p 621.

[9] E.C. (Council of the European Communities) (1986) Directive 86278 EEC on the Protection of the Environment and in Particular of the Soil when Sewage Sludge is used EEC. Brussels.

[10] Applied Environmental Microbiology 56:2268-2270

[11] John, M.K.; Vanlaehoven, C.J.; Chukwuma, C.S. (1972) Factors Affecting Plants Uptake and Phytotoxicity of Cadmium Added to Soils. Environment Science and Technology, 6:12

[12] Miliud R.O.; Julie D.; Snehal (2009) Comparative Adsorption Studies on Activated Rice Husk and Risk Hush Ash by using Methylene Blue as Dye. International Congress on

[13] Ministry of Agriculture, Fisheries and Food (MAFF) and Welch Office Agriculture Practice for the Protection of Soil, Draft Consultation Document, MAFF London

[14] Munoz, M.; Pena L.; Halloroms J.O. (1994) Use of an Industrial by-product as a Liming Source, Journal of Agriculture, University of Puerto Rilo 78(3-4): 73-86.

[15] Njoku P.C; Ayoka A.O. (2007) Evaluation of Heavy Metal Pollutants from Soils at Municipal Solid Waste Deposit in Owerri, Imo State, Nigeria, Journal of Chemical Society of Nigeria 32(1): 57-60.

[16] Osakwe S.A (2010). Chemical speciation and mobility of some heavy metals in soils around automobile waste dumpsites in Northern part of Niger Delta, South Central Nigeria. J. Applied Sci. Environ. Manage. 14: 123-130.

[17] Salam, A.K.; Helinke P.A (1998) The pH Dependence of Free Ionic Activities and Total Dissolved Concentrations of Copper and Cadmium in Soil Solution. Geoderma 83 – 281

[18] Sherene, T. (2010) Mobility and Transport of Heavy Metals in Polluted Soil Environment.

[19] Voogt, D.E.P.; Van, H.B.; Fermstra, J.P.; Copus P.J.W. (1980) Exposure and Health Effect of Cadmium Toxicological and Environmental Chemistry 3:89 – 109

[20] Walkley A.; Black (1934) An Examination of the Degtjareff Method for Determining Soil Organic Matter and Proposed Modification of the Chronic Titration Method, Soil Science

[21] Wild, A. (1993) Soil and the Environment: Great Britain Cambridge University Press,

[22] World Health Organization (WHO) (1993) Standard Maxima for Metals in Agricultural Soils