



Heavy Metal Speciation Patterns of Selected Dumpsites in Ilorin Metropolis

Solomon E. Shaibu^{2*}, Folahan A. Adekola¹, Halimat I. Adegoke¹, Nasir Abdus-salam¹

¹Department of Chemistry, University of Ilorin, P.M.B 1515, Ilorin, Nigeria

²Department of Chemistry, University of Uyo, P.M.B 1017, Uyo, Nigeria

(Received: November 01, 2014; Accepted: December 03, 2014)

Abstract

A five-step Tessier sequential extraction procedure was carried out on soil samples obtained from two different dumpsites in Ilorin: the Ilorin metropolis dumpsite and the University of Ilorin dumpsite. The study was centered on the determination of the concentration of Cr, Cu, Pb, Cd, Fe and Zn as the behaviour of heavy metals in natural system depends on the chemical forms in which they exist as well as their magnitude. Results obtained from this investigation showed that the total metal concentration at Ilorin metropolis dumpsite follow the order Fe > Zn > Cu > Cr > Pb > Cd, while the concentration of bioavailable metals follow the order Fe > Zn > Cr > Cu > Cd > Pb. The total metal concentration and the bioavailable metal concentration at the University of Ilorin dumpsite followed the same order of Fe > Cu > Cr > Zn > Pb > Cd. Higher enrichment factor was calculated for the Ilorin metropolis dumpsite compared to that of the University of Ilorin dumpsite indicating anthropogenic sources of contamination to both dumpsites.

Keywords: Heavy metals, dumpsite, speciation, pollution, bioavailability, mobility

1. Introduction

Large arable expanse of lands in Ilorin metropolis, have been transformed to dumpsites over time due to high population density and increasing urbanization rates which promote waste accumulation. Usually, the assorted waste is never screened or sorted out and consequently, heavy metals eventually find their way into the soil from metal scraps, agricultural and industrial wastes [1] deposited at such sites, thereby making it almost impossible for plants survival and healthy human habitation. Unlike many organic pollutants that can undergo degradation, heavy metals tend to accumulate in the environment especially in the soil, lake, estuarine or marine sediments and also fauna [2]. Metals can be transported from one environment compartment to another and many of these heavy metals are toxic to living organisms at low concentrations [3]. Due to their cumulative behaviour and toxicity, heavy metals are potentially hazardous not only to crop productivity, but also to human health through food consumption [4]. Heavy metals in high concentration are harmful to the environment because of their potential toxicity to biota and indirect threat to human health from groundwater contamination and accumulation in food crops [5]. The total metal concentration in soils cannot provide insight regarding their mobility and bioavailability [6]. Thus, the sequential extraction procedure (SEP) has been adopted by many researchers for diverse types of soils including the upland soils [7] and paddy soils [8, 9]. Such procedures were proven to provide information on heavy metal speciation, including their origin, mode of occurrence, bioavailability, mobilization and transport in soils. The theory

* Corresponding author:
shaibusolomon@gmail.com

Published online at www.ijcmer.org

Copyright © 2015 Int. J. Chem. Mater. Environ. Res. All Rights Reserved.

behind SEP is that the most mobile metals are removed in the first fraction and continue in order of decreasing of mobility [10, 11]. However, some heavy metals such as copper, iron and zinc are also essential elements. Whether the source of heavy metals is natural or anthropogenic, the concentration in terrestrial and aquatic organisms is determined by the size of the source, adsorption and precipitation in soils and sediments [12]. The concentration of metals in bioavailable form is not necessarily proportional to the total concentration of the metals, rather. The extent of adsorption depends on the metal, the adsorbent (soil), the physiochemical characteristics of the environment (e.g pH, water hardness and redox potential) and the concentrations of other metals and complex chemicals present in the soil, water, river or lake [11]. Heavy metals tend to bioaccumulate and become deleterious overtime.

The aim of this study was to determine the concentration of some heavy metals (Cr, Cd, Cu, Pb, Zn and Fe) in their bioavailable and non-bioavailable forms present in the major dumpsite in Ilorin metropolis along Eiyenkorin and that of University of Ilorin dumpsite in order to ascertain their level of contamination and origin of pollution.

2. Materials and Methods

All glasswares used were well washed with hot, soapy water and rinsed several times with distilled water. Thoroughly washed and dried polythene bags were used for collection of samples from the different dumpsites using a clean stainless steel spoon to avoid contamination. Deionised water was used for the preparation of all solutions. The soil sample was weighed with Mettler Toledo 20 weighing balance, and all pH measurements were carried out with Crison 2000 pH meter. HY Orbital shaker was used for agitation, while Garmin GPS 76 was used to obtain the geo-positions (longitude and latitude) of the different sample sites. The concentration of the heavy metals was recorded using atomic absorption spectrophotometer (AAS) Perkin Elmer model 214.

2.1. Sample collection

Samples were collected from Ilorin metropolis major dumpsite at Eiyenkorin located at N08°24'15.2" and E004°28'47.8" at an elevation of 344 m which is a government designated dumpsite which has been in existence for the past 15 years and is a mixed site that consist of heterogeneous municipal wastes such as plastics, leathers, papers, textiles, rubbers, broken glasses, industrial waste, tyres, wood, saw dust, lead batteries etc. It is always characterised with scavengers sorting out for materials with perceived residual values. The University of Ilorin dumpsite located at N08°29'7.2" and E004°40'707" at an elevation of 378.2 m above sea level is a relatively recent site approved by the University for dumping of waste within the University community about 8 years and by implication it is comparatively smaller and littered with predominantly domestic waste. The selected dumpsites were divided into quadrants and the four cardinal points were further subdivided into northwest, northeast, southwest and southeast (Figure 1).

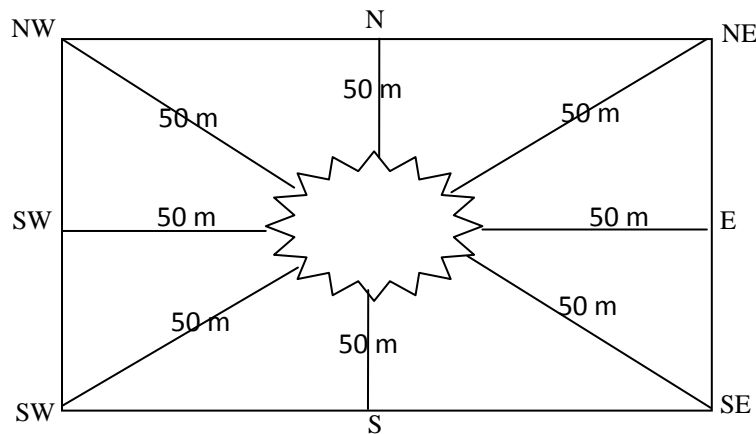


Figure 1. An illustration of sample collection from the major dumpsite in Ilorin metropolis at Eiyenkorin

In both dumpsites, two spots were pinpointed along each of the cardinal points, starting from the periphery of the dumpsite and then 50 m away from the starting point except in the North and South points of the University of Ilorin dumpsites where 100 m distance apart was used. These points were dug 30 cm into the soil and some quantity of the soil samples were taken using a stainless steel spoon to avoid external metal contamination. A total of 16 samples were taken from Ilorin metropolis dumpsite while a total of 10 samples were taken from University of Ilorin dumpsite. The samples were then homogenised and finally stored in polythene bags prior to further analysis.



Figure 2. A Pictorial View of University of Ilorin Dumpsite



Figure 3. A Pictorial View of Ilorin Metropolis Dumpsite at Eiyenkorin

2.2. Sampling Points and Description of the Dumpsites

Samples A, B, C, D, E, F, G and H were taken at the periphery of the dumpsite at the north, northeast, east, southeast, south, southwest, west, and northwest positions, respectively. Whereas samples I, J, K, L, M, N, O and P were taken 50 m from the comparable positions mentioned for the peripheral and in that order while samples A*, B*, C*, D*, E*, F*, G* and H* were collected from the periphery of the dumpsite of the University of Ilorin dumpsite shown in Figure 2 at the north, northeast, east, southeast, south, southwest, west, and northwest positions, respectively while samples I* and J* were taken 100 m from the north and south positions, respectively.

2.3. Analytical Methods

The treatment of the soil samples into different fractions was to systematically leach the metals that are exchangeable (loosely bound), followed by those bound to carbonates, to Fe-Mn oxides, organic and finally the residual metals as elaborated below by Tessier et al. [10].

- i. Fraction 1 (F1): Exchangeable metals - The sediment sample is extracted for 10 min with 1 M $MgCl_2$, at pH 7.0.
- ii. Fraction 2 (F2): Metals bound to carbonates - The residue from (i) is leached for 5 h with 1 M sodium acetate (NaOAc) adjusted to pH 5.0 with acetic acid (HOAc).
- iii. Fraction 3 (F3): Metals bound to Fe-Mn oxides - The residue from (ii) is extracted for 6 h at $96^\circ C$ with 0.04 M $NH_2OH - HCl$ in 25% (v/v) HOAc.

iv. Fraction 4 (F4): Metals bound to organic matter - The residue from (iii) is extracted at 85°C for 5 h with 30% H₂O₂ adjust to pH 2 with HNO₃, and then at room temperature with 3.2 M NH₂OAc in 20% (v/v) HNO₃.

v. Fraction 5 (F5): Residual metals - The residue from (iv) is dried and fused with lithium metaborate; the fused material is dissolved in a minimum amount of 12 N HCl and then is diluted to a final acid concentration of 1.2 N.

The method adopted for this study was a modified sequential extraction procedure by Tessier *et al.* [10] in which 2 g of the sample was weighed into 50 mL centrifuge tube. This was followed by the addition of 8 mL of 1 M MgCl₂ solution at pH 7, then agitated at room temperature for 1 hr. It was centrifuged, decanted, and 4 mL of aqua regia was added and the analytical fraction diluted to 1 L with distilled water prior to analysis.

The residue from the above stage was washed with deionised water. 8 mL of 1 M sodium acetate solution adjusted to pH 5 with acetic acid was carefully added, it was agitated periodically at room temperature for 5 h. The resulting solution was centrifuged, decanted, and 4 mL of aqua regia was added. The analytical fraction was diluted to 1L with distilled water.

The resulting residue obtained was again washed with deionised water and 20 mL of 0.04 M NH₂OH-HCl in 25% (v/v) acetic acid was added. It was subsequently agitated periodically in boiling water bath for 5 h and then centrifuged, decanted, followed by the addition of 4 mL aqua regia and the analytical fraction was diluted to 1L with distilled water prior to analysis. The residue was then washed with deionised water.

To the residue obtained above, 3 mL of 0.02 M HNO₃ and 5 mL of 30% H₂O₂ which had been adjusted to pH 2 with HNO₃ were added. The resulting solution was agitated periodically at 85°C for 2 h then 3 mL of H₂O₂ at pH 2 was added and agitated periodically at 85°C for 3 h. Then the resulting solution was later cooled at room temperature. Furthermore, 5 mL of 3.2 M ammonium acetate in 20% (v/v) HNO₃ was added and agitated periodically at room temperature for another 30 min. The solution was centrifuged, decanted and 4 mL aqua regia was added. The dilute analytical fraction was made up to 1 L with distilled water prior to analysis. The residue was washed with deionised water.

10 mL of HClO₄ and 16 mL of aqua regia was added to the resulting residue, heated in hot water bath for 2 h, then diluted to 1 L with distilled water. Finally, 400 mg sample was digested with 8 mL aqua regia then diluted to 500 mL with distilled water. The decanted filtrates from each of the five stages above were used for metal content analysis using AAS. The purpose of treating the soil samples differently at each stage was to sequentially leach the metals of interest that are exchangeable (loosely bound), followed by those bound to carbonates, to Fe-Mn oxides, organic and finally the residual metals for eventual analysis.

3. Results and Discussion

The soil samples selected for analysis have been formed from weathering and complete decomposition of the waste deposited at both dumpsites. Soil properties generally indicate the ability of soils to bind heavy metals as well as to transform them from easily soluble to hardly available forms. It also plays a decisive role in the reverse process. The total amount of each metal in all the soil sample was calculated by adding the extracted fractions together i.e F1 + F2 + F3 + F4 + F5 where F1, F2, F3, F4 and F5 represent the Fraction 1 (exchangeable), Fraction 2 (metals bound to carbonates), Fraction 3 (metals bound to Fe-Mn bound), Fraction 4 (metals bound to organic) and Fraction 5 (residual metals), respectively.

The average abundance of the metals present at the Eiyekorin dumpsite is of the order Fe>Zn>Cr>Cu>Pb>Cd as shown in Table 1. The concentration of chromium found in the samples that were obtained from points just at the periphery of the dumpsites was higher than those of spots 50 m away which is considered to be largely anthropogenic.

Table 1. Concentrations of Heavy Metals at University of Ilorin Dumpsite

| Sample Location | Fraction | Cr (mg/kg) | Cu (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Fe (mg/kg) | Zn (mg/kg) |
|-----------------|-------------------------|------------|------------|------------|------------|------------|------------|
| A | Exchangeable | <0.01 | 4.5 | 1.23 | 1.31 | 31 | 22.31 |
| | Bound to carbonate | 1.8 | 0.9 | <0.01 | <0.01 | 49 | 3.26 |
| | Bound to Fe & Mn oxides | 1.75 | 1.25 | <0.01 | <0.01 | 579 | 1.32 |
| | Bound to organic matter | <0.01 | 5.6 | <0.01 | <0.01 | 30 | <0.01 |
| | Residual | 8.4 | 15.75 | 3.82 | 2.87 | 7655 | 26.2 |
| B | Exchangeable | <0.01 | <0.01 | <0.01 | <0.01 | 231 | <0.01 |
| | Bound to carbonate | <0.01 | <0.01 | <0.01 | <0.01 | 847 | 321.65 |
| | Bound to Fe & Mn oxides | 19.85 | 19.1 | 1.75 | 3.85 | 17528 | 297.1 |
| | Bound to organic matter | <0.01 | 1.25 | <0.01 | <0.01 | 1110 | <0.01 |
| | Residual | <0.01 | 1.6 | <0.01 | <0.01 | 526 | <0.01 |

| | | | | | | | |
|---|-------------------------|-------|-------|-------|-------|---------|--------|
| C | Exchangeable | 20.5 | 17.2 | <0.01 | <0.01 | 16874 | 284.45 |
| | Bound to carbonate | 5.05 | 10.95 | 2.05 | 3.65 | 13582 | 261.1 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | <0.01 | 3.45 | 425.5 | <0.01 |
| | Bound to organic matter | <0.01 | <0.01 | <0.01 | <0.01 | 307 | <0.01 |
| | Residual | <0.01 | <0.01 | <0.01 | <0.01 | 645.5 | <0.01 |
| D | Exchangeable | 27 | 27 | <0.01 | <0.01 | 16621.5 | <0.01 |
| | Bound to carbonate | 15.2 | 15.2 | <0.01 | 4.45 | 13845.5 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | <0.01 | 4.75 | <0.01 | <0.01 |
| | Bound to organic matter | <0.01 | <0.01 | <0.01 | <0.01 | 799 | <0.01 |
| | Residual | <0.01 | <0.01 | <0.01 | <0.01 | 539.5 | <0.01 |
| E | Exchangeable | 35.8 | 21.2 | <0.01 | <0.01 | 15334 | <0.01 |
| | Bound to carbonate | 15 | 9.55 | <0.01 | 4.3 | 10973 | 248.3 |
| | Bound to Fe & Mn oxides | 3.4 | 10.1 | <0.01 | <0.01 | 963 | <0.01 |
| | Bound to organic matter | 3.5 | 57.75 | <0.01 | <0.01 | 135.5 | 225.25 |
| | Residual | 3.55 | 63.1 | <0.01 | <0.01 | 2879.5 | 19.05 |
| F | Exchangeable | <0.01 | <0.01 | <0.01 | <0.01 | 600 | 0.65 |
| | Bound to carbonate | 12.9 | 9.95 | 1.15 | 4.25 | 7988 | 232.45 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | <0.01 | <0.01 | 786 | 12.3 |
| | Bound to organic matter | <0.01 | 5.7 | <0.01 | <0.01 | 252.5 | 0.95 |
| | Residual | 2.95 | <0.01 | <0.01 | <0.01 | 750.5 | <0.01 |
| G | Exchangeable | 20.1 | 7.75 | 38 | 3.75 | 15081 | <0.01 |
| | Bound to carbonate | <0.01 | <0.01 | <0.01 | 3.75 | 3118.5 | 24.15 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | <0.01 | <0.01 | 118.5 | 0.5 |
| | Bound to organic matter | 1.6 | <0.01 | <0.01 | <0.01 | 305 | <0.01 |
| | Residual | 90.8 | 9.55 | <0.01 | <0.01 | 16969 | 48.4 |
| H | Exchangeable | 1.45 | <0.01 | <0.01 | <0.01 | 2201 | 48.4 |
| | Bound to carbonate | <0.01 | 4 | <0.01 | <0.01 | 307 | 293.35 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | <0.01 | <0.01 | 1058.5 | 317.55 |
| | Bound to organic matter | 2.75 | <0.01 | <0.01 | <0.01 | 500.5 | <0.01 |
| | Residual | 18 | 6.95 | <0.01 | <0.01 | 15505 | <0.01 |
| I | Exchangeable | <0.01 | <0.01 | <0.01 | <0.01 | 3309 | <0.01 |
| | Bound to carbonate | <0.01 | <0.01 | <0.01 | <0.01 | 1121 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | <0.01 | <0.01 | 616.5 | <0.01 |
| | Bound to organic matter | 1.5 | <0.01 | <0.01 | <0.01 | 47 | <0.01 |
| | Residual | 9.7 | <0.01 | <0.01 | <0.01 | 3587.5 | <0.01 |
| J | Exchangeable | <0.01 | <0.01 | <0.01 | <0.01 | 557.5 | <0.01 |
| | Bound to carbonate | <0.01 | <0.01 | <0.01 | <0.01 | 359 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | Bound to organic matter | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | Residual | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| K | Exchangeable | <0.01 | <0.01 | <0.01 | <0.01 | 498.5 | <0.01 |
| | Bound to carbonate | <0.01 | <0.01 | <0.01 | <0.01 | 408.5 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | <0.01 | <0.01 | 579 | <0.01 |
| | Bound to organic matter | <0.01 | <0.01 | <0.01 | <0.01 | 325.5 | <0.01 |
| | Residual | 2.85 | <0.01 | <0.01 | <0.01 | 687.5 | <0.01 |

| | | | | | | | |
|---|-------------------------|-------|-------|-------|-------|---------|-------|
| L | Exchangeable | <0.01 | <0.01 | <0.01 | <0.01 | 1613.5 | <0.01 |
| | Bound to carbonate | <0.01 | <0.01 | <0.01 | <0.01 | 157.5 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | <0.01 | <0.01 | 419 | <0.01 |
| | Bound to organic matter | <0.01 | <0.01 | <0.01 | <0.01 | 58 | <0.01 |
| | Residual | <0.01 | <0.01 | <0.01 | <0.01 | 222.5 | <0.01 |
| M | Exchangeable | <0.01 | <0.01 | <0.01 | <0.01 | 133 | <0.01 |
| | Bound to carbonate | 12.5 | 8.05 | 33.5 | 3.45 | 14152.5 | <0.01 |
| | Bound to Fe & Mn oxides | 5.95 | 16.95 | 13 | 3.6 | 4733.5 | <0.01 |
| | Bound to organic matter | 1.6 | <0.01 | 1.05 | 0.6 | 2180.5 | <0.01 |
| | Residual | <0.01 | 21.55 | 0.65 | <0.01 | 1716.5 | <0.01 |
| N | Exchangeable | 9.6 | 6.15 | <0.01 | <0.01 | 5478 | <0.01 |
| | Bound to carbonate | 11.05 | <0.01 | <0.01 | <0.01 | 2733.5 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | <0.01 | <0.01 | 4733 | <0.01 |
| | Bound to organic matter | 31.5 | <0.01 | <0.01 | <0.01 | 1978 | <0.01 |
| | Residual | 10.5 | <0.01 | <0.01 | <0.01 | 2322 | <0.01 |
| O | Exchangeable | 10.6 | <0.01 | <0.01 | <0.01 | 1733.5 | <0.01 |
| | Bound to carbonate | 1.7 | <0.01 | <0.01 | <0.01 | 1172.5 | <0.01 |
| | Bound to Fe & Mn oxides | 11.55 | 2.7 | <0.01 | <0.01 | 2472.5 | <0.01 |
| | Bound to organic matter | <0.01 | 10.85 | <0.01 | <0.01 | 2650.5 | <0.01 |
| | Residual | <0.01 | <0.01 | <0.01 | <0.01 | 2461 | <0.01 |
| P | Exchangeable | 15.55 | <0.01 | <0.01 | <0.01 | 6787.7 | 1.45 |
| | Bound to carbonate | <0.01 | <0.01 | <0.01 | 2.1 | 1722 | 5.75 |
| | Bound to Fe & Mn oxides | 5.55 | <0.01 | 2.01 | <0.01 | 1227.5 | 76.6 |
| | Bound to organic matter | 12.55 | <0.01 | 0.91 | <0.01 | 2221 | 49.15 |
| | Residual | <0.01 | 7 | 4.61 | <0.01 | 1988 | 243.1 |

It was observed that the concentration of Fe is high in all the fractions which can be attributed to the geogenic nature of the metal in this part of the world and partly due to high content of Fe based waste materials been generated through domestic and industrial wastes and its high presence accounts for the rich red colour of the soil sample.

Table 2. Concentrations of Heavy Metals at University of Ilorin Dumpsite

| Sample Location | Fraction | Cr (mg/kg) | Cu (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Fe (mg/kg) | Zn (mg/kg) |
|-----------------|-------------------------|------------|------------|------------|------------|------------|------------|
| A* | Exchangeable | <0.01 | <0.01 | <0.01 | <0.01 | 327.5 | 1.4 |
| | Bound to carbonate | <0.01 | <0.01 | 3.8 | <0.01 | 259 | 0.8 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | 1.05 | <0.01 | 130.5 | 1.1 |
| | Bound to organic matter | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | Residual | <0.01 | 11 | <0.01 | 3.2 | 447 | <0.01 |
| B* | Exchangeable | <0.01 | 9 | <0.01 | <0.01 | 275 | <0.01 |
| | Bound to carbonate | 4.6 | 7.5 | <0.01 | <0.01 | 200 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | 7 | <0.01 | <0.01 | 764 | <0.01 |
| | Bound to organic matter | <0.01 | 7 | <0.01 | <0.01 | 455.5 | <0.01 |
| | Residual | 13.6 | 13 | 5.4 | 5.05 | 10167 | <0.01 |
| C* | Exchangeable | <0.01 | 7.5 | <0.01 | <0.01 | 259 | <0.01 |
| | Bound to carbonate | <0.01 | 7 | <0.01 | <0.01 | 251.5 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | 6 | <0.01 | <0.01 | 249 | <0.01 |
| | Bound to organic matter | <0.01 | 6 | <0.01 | <0.01 | 685.5 | <0.01 |

| | | | | | | | |
|----|-------------------------|-------|-------|-------|-------|---------|-------|
| D* | Residual | 13.35 | 22.5 | 31.5 | 3.75 | 9192 | <0.01 |
| | Exchangeable | <0.01 | 5 | 21 | <0.01 | 89 | <0.01 |
| | Bound to carbonate | <0.01 | 5 | <0.01 | <0.01 | 308 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | 5 | <0.01 | <0.01 | 232 | <0.01 |
| | Bound to organic matter | <0.01 | 4 | <0.01 | <0.01 | 351 | <0.01 |
| E* | Residual | 13.85 | 16.5 | 54 | <0.01 | 3636.5 | <0.01 |
| | Exchangeable | <0.01 | 6 | <0.01 | <0.01 | 613 | <0.01 |
| | Bound to carbonate | <0.01 | 6.5 | <0.01 | <0.01 | 50.5 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | 6 | <0.01 | <0.01 | 273.5 | <0.01 |
| | Bound to organic matter | <0.01 | 5 | <0.01 | <0.01 | 355 | <0.01 |
| F* | Residual | 18.55 | 16 | <0.01 | <0.01 | 6716 | <0.01 |
| | Exchangeable | <0.01 | 5.5 | <0.01 | <0.01 | 463 | <0.01 |
| | Bound to carbonate | <0.01 | 5.5 | <0.01 | <0.01 | 115 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | 6 | <0.01 | <0.01 | 622.5 | 16.05 |
| | Bound to organic matter | <0.01 | 6.5 | <0.01 | <0.01 | 462.5 | 6.2 |
| G* | Residual | 13.35 | 22.5 | <0.01 | 5.05 | 10185.5 | <0.01 |
| | Exchangeable | <0.01 | 6 | <0.01 | <0.01 | 253 | <0.01 |
| | Bound to carbonate | <0.01 | 4.5 | <0.01 | <0.01 | 364.5 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | 4.5 | <0.01 | <0.01 | 106.5 | <0.01 |
| | Bound to organic matter | <0.01 | 6.5 | <0.01 | <0.01 | 4046 | <0.01 |
| H* | Residual | 2.2 | 12.5 | <0.01 | <0.01 | 10228.5 | <0.01 |
| | Exchangeable | <0.01 | 6 | <0.01 | <0.01 | 405.5 | <0.01 |
| | Bound to carbonate | <0.01 | 7 | <0.01 | <0.01 | 620 | 0.4 |
| | Bound to Fe & Mn oxides | <0.01 | 7 | <0.01 | <0.01 | 174 | 0.6 |
| | Bound to organic matter | <0.01 | 5.5 | <0.01 | <0.01 | 5428.5 | <0.01 |
| I* | Residual | 6.4 | 9 | <0.01 | <0.01 | 7217.5 | <0.01 |
| | Exchangeable | <0.01 | 4.5 | <0.01 | <0.01 | 767.5 | <0.01 |
| | Bound to carbonate | <0.01 | 6.5 | <0.01 | <0.01 | 1014 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | 5 | <0.01 | <0.01 | 341.5 | <0.01 |
| | Bound to organic matter | 14.55 | 17.5 | <0.01 | <0.01 | 12698 | <0.01 |
| J* | Residual | <0.01 | 6.5 | <0.01 | <0.01 | 75.5 | <0.01 |
| | Exchangeable | <0.01 | 5.5 | <0.01 | <0.01 | <0.01 | 2.93 |
| | Bound to carbonate | <0.01 | <0.01 | <0.01 | <0.01 | 29 | <0.01 |
| | Bound to Fe & Mn oxides | <0.01 | <0.01 | <0.01 | <0.01 | 68 | <0.01 |
| | Bound to organic matter | 9 | 6.5 | <0.01 | <0.01 | 1372 | <0.01 |
| | Residual | 6.5 | 14.5 | 0.95 | 3.9 | 19 | 30.25 |

Tables 1 and 2 show the concentration of each metal found in the five different fractions, that is, the exchangeable, bound to carbonate, bound to Fe and Mn oxide, bound to organic matter and residual. The concentration of Fe is similarly high in the soil samples of University Ilorin dumpsite and the same reason attributed to that of the major dumpsite at Eiyenkorin could be responsible.

The total metal concentration of Cr, Cu, Pb, Cd and Zn in the samples from Ilorin metropolis dumpsite has more elevated values compared to those of the University of Ilorin dumpsite as shown in Table 3 and Table 4, respectively. This could be as a result of the types and volume of refuse dumped and the duration of which the dumpsite has been in use.

Table 3. Total Metal Concentration (mg/kg) of Metals in Ilorin Metropolis Dumpsite at Eiyenkorin

| Sample | Cr (mg/kg) | Cu (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Fe X 10 ³ (mg/kg) | Zn (mg/kg) | Total Metal Conc. X 10 ³ (mg/kg) |
|--------|------------|------------|------------|------------|------------------------------|------------|---------------------------------------------|
| A | 11.95 | 28 | 5.05 | 4.18 | 8.34 | 52.79 | 8.44 |
| B | 19.85 | 21.95 | 1.75 | 3.85 | 20.24 | 618.75 | 20.91 |
| C | 25.55 | 28.15 | 2.05 | 7.1 | 31.83 | 545.6 | 32.44 |
| D | 42.5 | 42.2 | <0.01 | 9.2 | 31.81 | <0.01 | 31.9 |
| E | 61.25 | 161.7 | <0.01 | 4.3 | 30.29 | 492.6 | 31.01 |
| F | 15.85 | 15.65 | 1.15 | 4.25 | 10.38 | 246.35 | 10.66 |
| G | 112.5 | 17.3 | 38 | 7.51 | 35.59 | 73.05 | 35.84 |
| H | 22.2 | 10.95 | <0.01 | <0.01 | 19.57 | 659.3 | 20.26 |
| I | 11.2 | <0.01 | <0.01 | <0.01 | 8.68 | <0.01 | 8.69 |
| J | <0.01 | <0.01 | <0.01 | <0.01 | 0.92 | <0.01 | 0.92 |
| K | 2.85 | <0.01 | <0.01 | <0.01 | 2.5 | <0.01 | 2.5 |
| L | <0.01 | <0.01 | <0.01 | <0.01 | 2.47 | <0.01 | 2.47 |
| M | 20.05 | 46.55 | 48.2 | 48.25 | 22.92 | <0.01 | 23.08 |
| N | 62.65 | 6.15 | <0.01 | <0.01 | 17.24 | <0.01 | 17.31 |
| O | 23.85 | 13.55 | <0.01 | <0.01 | 10.49 | <0.01 | 10.53 |
| P | 33.65 | 7 | 7.53 | 2.1 | 13.95 | 376.5 | 14.38 |

Table 4. Total Metal Concentrations (mg/kg) at University of Ilorin Dumpsite

| Sample | Cr (mg/kg) | Cu (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Fe x 10 ³ (mg/kg) | Zn (mg/kg) | Total Metals Conc. X 10 ³ (mg/kg) |
|--------|------------|------------|------------|------------|------------------------------|------------|----------------------------------------------|
| A* | <0.01 | 11 | 4.35 | 3.2 | 1.16 | 3.3 | 1.18 |
| B* | 18.2 | 43.5 | 5.4 | 5.05 | 11.86 | <0.01 | 11.93 |
| C* | 13.35 | 49 | 3.15 | 3.75 | 10.64 | <0.01 | 10.71 |
| D* | 13.85 | 35.5 | 7.6 | <0.01 | 46.17 | <0.01 | 46.23 |
| E* | 18.55 | 39.5 | <0.01 | <0.01 | 8.01 | <0.01 | 8.07 |
| F* | 13.35 | 46 | <0.01 | 5.05 | 11.85 | 22.25 | 11.94 |
| G* | 2.2 | 34 | <0.01 | <0.01 | 15 | <0.01 | 15.04 |
| H* | 6.4 | 34.5 | <0.01 | <0.01 | 13.85 | 1 | 13.89 |
| I* | 14.55 | 40 | <0.01 | <0.01 | 14.9 | <0.01 | 14.95 |
| J* | 15.55 | 26.5 | 0.95 | 3.9 | 1.48 | 33.36 | 1.56 |

Table 5. Bioavailable and Non-bioavailable Fractions (mg/kg) of Ilorin Metropolis Dumpsite at Eiyenkorin

| Sample | Fraction | Cr (mg/kg) | Cu (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Fe x 10 ³ (mg/kg) | Zn (mg/kg) | % Bioavailable |
|--------|------------------|------------|------------|------------|------------|------------------------------|------------|----------------|
| A | Bioavailable | 3.55 | 6.65 | 1.23 | 1.31 | 0.66 | 26.59 | 8.29 |
| | Non-bioavailable | 8.4 | 21.35 | 3.82 | 2.87 | 7.69 | 26.2 | |
| B | Bioavailable | 19.85 | 19.1 | 1.75 | 3.85 | 18.61 | 618.75 | 92.17 |
| | Non-bioavailable | <0.01 | 2.85 | <0.01 | <0.01 | 1.64 | <0.01 | |
| C | Bioavailable | 25.55 | 28.15 | 2.05 | 7.1 | 30.89 | 545.55 | 97.1 |
| | Non-bioavailable | <0.01 | <0.01 | <0.01 | <0.01 | 0.95 | <0.01 | |
| D | Bioavailable | 42.2 | 42.2 | <0.01 | 9.2 | 30.47 | <0.01 | 95.81 |
| | Non-bioavailable | <0.01 | <0.01 | <0.01 | <0.01 | 1.34 | <0.01 | |
| E | Bioavailable | 54.2 | 40.85 | <0.01 | 4.3 | 27.27 | 248.3 | 89.06 |
| | Non-bioavailable | 7.05 | 120.85 | <0.01 | <0.01 | 3.02 | 244.3 | |

| | | | | | | | | |
|---|------------------|-------|-------|-------|-------|-------|--------|-------|
| F | Bioavailable | 12.9 | 9.95 | 1.15 | 4.25 | 9.37 | 245.4 | 90.47 |
| | Non-bioavailable | 2.95 | 5.71 | <0.01 | <0.01 | 1 | 0.95 | |
| G | Bioavailable | 20.1 | 7.75 | 38 | 7.5 | 18.32 | 24.65 | 51.38 |
| | Non-bioavailable | 92.4 | 9.55 | <0.01 | <0.01 | 17.27 | 48.4 | |
| H | Bioavailable | 1.45 | 4.02 | <0.01 | <0.01 | 3.57 | 659.33 | 20.9 |
| | Non-bioavailable | 20.75 | 6.95 | <0.01 | <0.01 | 16.01 | <0.01 | |
| I | Bioavailable | <0.01 | <0.01 | <0.01 | <0.01 | 5.05 | <0.01 | 58.11 |
| | Non-bioavailable | 11.2 | <0.01 | <0.01 | <0.01 | 3.63 | <0.01 | |
| J | Bioavailable | <0.01 | <0.01 | <0.01 | <0.01 | 0.92 | <0.01 | 100 |
| | Non-bioavailable | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | |
| K | Bioavailable | <0.01 | <0.01 | <0.01 | <0.01 | 1.49 | <0.01 | 59.6 |
| | Non-bioavailable | 2.85 | <0.01 | <0.01 | <0.01 | 1.01 | <0.01 | |
| L | Bioavailable | <0.01 | <0.01 | <0.01 | <0.01 | 2.19 | <0.01 | 88.66 |
| | Non-bioavailable | <0.01 | <0.01 | <0.01 | <0.01 | 0.28 | <0.01 | |
| M | Bioavailable | 18.45 | 25 | <0.01 | 46.5 | 19 | <0.01 | 82.71 |
| | Non-bioavailable | 1.6 | 21.55 | <0.01 | 1.7 | 3.9 | <0.01 | |
| N | Bioavailable | 20.65 | 6.15 | <0.01 | <0.01 | 12.94 | <0.01 | 74.91 |
| | Non-bioavailable | 42 | <0.01 | <0.01 | <0.01 | 4.3 | <0.01 | |
| O | Bioavailable | 23.85 | 2.7 | <0.01 | <0.01 | 5.38 | <0.01 | 51.34 |
| | Non-bioavailable | <0.01 | 13.55 | <0.01 | <0.01 | 5.11 | <0.01 | |
| P | Bioavailable | 21.1 | <0.01 | 2.01 | 2.1 | 9.74 | 83.8 | 68.49 |
| | Non-bioavailable | 12.55 | 7 | 5.52 | <0.01 | 4.2 | 292.2 | |

The percentage of bioavailable metals (Fe, Zn, Cu, Cd, Cr, and Pb) in the dumpsite at Eiyenkorin is quite elevated probably due to the nature and size of the waste and also regular burning of the waste at the dumpsite that imparts on the metal concentration at the dumpsite. The elevated percentage bioavailability of these metals could be a threat to both flora and fauna around the location of the dumpsite due to bioaccumulation of these metals, the amount of metal available for absorption by plants and those that can be washed into underground water body is higher than that which is locked up in the soil as shown in Tables 5 and 6. The concentration of bioavailable metals is $F1 + F2 + F3$ while that of the non-bioavailable is $F4 + F5$.

Table 6. Bioavailable and Non-bioavailable Fractions (mg/kg) at University of Ilorin Dumpsite

| Sample | Fraction | Cr (mg/kg) | Cu (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Fe x 10 ² (mg/kg) | Zn (mg/kg) | % Bioavailable |
|--------|------------------|------------|------------|------------|------------|------------------------------|------------|----------------|
| A* | Bioavailable | <0.01 | <0.01 | 4.85 | <0.01 | 7.17 | 3.3 | 61.45 |
| | Non-bioavailable | <0.01 | 11 | <0.01 | 3.2 | 4.47 | <0.01 | |
| B* | Bioavailable | 4.6 | 23.5 | <0.01 | <0.01 | 12.39 | <0.01 | 10.62 |
| | Non-bioavailable | 13.6 | 20 | 5.4 | 5.05 | 106.23 | <0.01 | |
| C* | Bioavailable | <0.01 | 20.5 | <0.01 | <0.01 | 7.6 | <0.01 | 7.29 |
| | Non-bioavailable | 13.35 | 28.5 | 3.15 | 3.75 | 98.78 | <0.01 | |
| D* | Bioavailable | <0.01 | 15 | 2.1 | <0.01 | 6.29 | <0.01 | 1.4 |
| | Non-bioavailable | 13.8 | 19.5 | 5.4 | <0.01 | 39.88 | <0.01 | |
| E* | Bioavailable | <0.01 | 18.5 | <0.01 | <0.01 | 9.37 | <0.01 | 11.84 |
| | Non-bioavailable | 18.55 | 21 | <0.01 | <0.01 | 70.71 | <0.01 | |
| F* | Bioavailable | <0.01 | 17 | <0.01 | <0.01 | 12.01 | 16.05 | 10.34 |
| | Non-bioavailable | 13.5 | 29 | <0.01 | 5.05 | 106.48 | 6.2 | |
| G* | Bioavailable | <0.01 | 15 | <0.01 | <0.01 | 7.24 | <0.01 | 48.24 |
| | Non-bioavailable | 2.2 | 19 | <0.01 | <0.01 | 142.75 | <0.01 | |

| | | | | | | | | |
|----|------------------|-------|------|-------|-------|--------|-------|-------|
| H* | Bioavailable | <0.01 | 20 | <0.01 | <0.01 | 12 | 1 | 86.54 |
| | Non-bioavailable | 6.4 | 14.5 | <0.01 | <0.01 | 126.46 | <0.01 | |
| I* | Bioavailable | <0.01 | 16 | <0.01 | <0.01 | 21.23 | <0.01 | 14.31 |
| | Non-bioavailable | 14.55 | 24 | <0.01 | <0.01 | 127.74 | <0.01 | |
| J* | Bioavailable | <0.01 | 5.5 | <0.01 | <0.01 | 0.97 | 2.94 | 6.76 |
| | Non-bioavailable | 15.5 | 2.1 | 0.95 | 3.9 | 13.91 | 30.25 | |

In Table 6, the percentage of bioavailable metals (Fe, Zn, Cu, Cd, Cr and Pb) at the University of Ilorin dumpsite is lower than that of the major dumpsite at Eiyenkorin in Table 5. The nature of the refuse and the shorter duration of use of the dumpsite as compared to that of the major dumpsite at Eiyenkorin are factors that could be responsible for the disparity in the percentage of bioavailable metals at these dumpsites.

Element enrichment factors (EFc) are widely used in environmental sciences to speculate on the origin of elements in air, atmospheric dust or precipitation [13] which subsequently informed the calculation of EFc as shown in Tables 7 and 8.

Table 7. Enrichment Factor of Metals in the Major Dumpsite in Ilorin Metropolis at Eiyenkorin

| Sample | Cr (mg/kg) | Cu (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Fe (mg/kg) | Zn (mg/kg) |
|--------|---------------|---------------|---------------|---------------|---------------|---------------|
| A | 0.36 | 4.0 | 0.67 | 1.99 | 0.6 | 0.14 |
| B | 0.59 | 3.14 | 0.23 | 1.83 | 1.45 | 1.64 |
| C | 0.76 | 4.02 | 0.27 | 3.38 | 2.28 | 1.45 |
| D | 1.26 | 6.03 | <0.01 | 4.38 | 2.28 | <0.01 |
| E | 1.82 | 23.1 | <0.01 | 2.05 | 2.17 | 1.31 |
| F | 0.47 | 2.24 | 0.15 | 2.02 | 0.74 | 0.65 |
| G | 3.34 | 2.47 | 5.05 | 3.57 | 2.55 | 0.19 |
| H | 0.66 | 1.56 | <0.01 | <0.01 | 1.4 | 1.75 |
| I | 0.33 | <0.01 | <0.01 | <0.01 | 0.62 | <0.01 |
| J | <0.01 | <0.01 | <0.01 | <0.01 | 0.07 | <0.01 |
| K | 0.08 | <0.01 | <0.01 | <0.01 | 0.18 | <0.01 |
| L | <0.01 | <0.01 | <0.01 | <0.01 | 0.18 | <0.01 |
| M | 0.6 | 6.65 | 6.4 | 22.98 | 0.16 | <0.01 |
| N | 1.86 | 0.88 | <0.01 | <0.01 | 1.24 | <0.01 |
| O | 0.71 | 1.94 | <0.01 | <0.01 | 0.75 | <0.01 |
| P | 1 | 1 | 1 | 1 | 1 | 1 |

Table 8. Enrichment Factor of Metals at University of Ilorin Dumpsite

| Sample | Cr (mg/kg) | Cu (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Fe (mg/kg) | Zn (mg/kg) |
|--------|---------------|---------------|---------------|---------------|---------------|---------------|
| A* | <0.01 | 0.42 | 0.42 | 0.82 | 0.78 | 0.1 |
| B* | 1.17 | 1.64 | 1.64 | 1.29 | 7.97 | <0.01 |
| C* | 0.86 | 1.85 | 1.85 | 0.96 | 7.15 | <0.01 |
| D* | 0.89 | 1.34 | 1.34 | <0.01 | 3.1 | <0.01 |
| E* | 1.19 | 1.49 | 1.49 | <0.01 | 5.38 | <0.01 |
| F* | 0.86 | 1.74 | 1.74 | 1.29 | 7.96 | 0.69 |
| G* | 0.14 | 1.28 | 1.28 | <0.01 | 10.07 | <0.01 |
| H* | 0.41 | 1.3 | 1.3 | <0.01 | 9.3 | 0.03 |
| I* | 0.94 | 1.51 | 1.51 | <0.01 | 10.01 | <0.01 |
| J* | 1 | 1 | 1 | 1 | 1 | 1 |

The samples P and J* from the Ilorin metropolis dumpsite at Eiyenkorin and the University of Ilorin dumpsite, respectively were collected upstream strategically away from any contaminant source around the vicinity of the dumpsites. The

enrichment factor was calculated by dividing the measured concentration of metal in the sample investigated (contaminated) by the concentration of the uncontaminated sample of the same element as shown in above Tables 7 and 8 [13]. An enrichment factor (EF_c) greater than unity, is an indication that the investigated metal is more abundant in the dumpsite relative to that found in the uncontaminated sample. However, enrichment factor of samples from Ilorin metropolis dumpsite at Eiyenkorin is quite high for Cu, Cd and Pb which is as a result of anthropogenic activities at the dumpsites in comparison to the concentration in the uncontaminated sample. The University of Ilorin dumpsite had an enrichment factor that is relatively small except for Fe, Cu, and Fe which signifies anthropogenic input, as shown in Tables 7 and 8, respectively.

4. Conclusion

The present study shows that dumpsites are conducive avenues for heavy metals to enter and accumulate in the soil and then eventually contribute significantly to the level of these metals in that environment that could be detrimental to both flora and fauna over time. Generally, concentrations of most of the metals decreased with increase in distance from the dumpsites. The concentrations of the bioavailable metals in the Ilorin metropolis dumpsite is higher than that of the University of Ilorin dumpsite which could be attributed to the types of waste, size, and duration of usage of the dumpsite and this in the long run is being transferred into food chain by the process of leaching. Therefore these elevated concentration levels of these metals pose environmental concerns to those who grow crops or consume aquatic animals in such areas.

REFERENCES

- [1] Quek S.Y., Wase D.A.J., Forster C.F., 1998. The use of sago waste for the sorption of lead and copper. *Water SA*, 24 (3), 251-256.
- [2] Nelson A., Donkin P., 1985. Processes of bioaccumulation: the importance of chemical speciation. *Mar. Pollut. Bullet.*, 16 (4), 164-169.
- [3] Ryan P.C., Hillier S., Wall A.J., 2008. Stepwise effects of the BCR sequential chemical extraction procedure on dissolution and metal release from common ferromagnesian clay minerals: a combined solution chemistry and X-ray powder diffraction study. *Sci. Total Environ.*, 407(1), 603-614.
- [4] Das P., Samantaray S., Rout G.R., 1997. Studies on cadmium toxicity in plants; A review. *Environ. Pollut.*, 98 (1), 29-36.
- [5] Martínez C.E., Motto H.L., 2000. Solubility of lead, zinc and copper added to minerals soils. *Environ. Pollut.*, 107, 153-158.
- [6] Powel K.J., Brown P.L., Bryne R.H., Gajda T., Hefter G., Sjoberg S., Warner H., 2005. Chemical speciation of environmentally significant heavy metals with inorganic ligands. Part 1 The Hg⁺, Cl⁻, OH⁻, CO₃²⁻, SO₄²⁻ and PO₄³⁻ aqueous systems. *Pure Appl. Chem.*, 77, 739-800.
- [7] Khairiah J., Lim K.H., Ahmad-Mahir R., Ismail B.S., 2006. Heavy metals from agricultural soils from Cameron Highland, Pahang, and Cheras, Kuala Lumpur, Malaysian. *Bull. Environ. Contamin. Toxicol.*, 77, 608-615.
- [8] Manceau A., Tommaseo C., Rihs S., Geoffroy N., Chateigner D., Schleges M., Tisserand D., Marcus M.A., Tamura N., Chen Z.S., 2005. Natural speciation of Mn, Ni and Zn at the micrometer scale in a clayey paddy soil using X-ray fluorescence, absorption and diffraction. *Geochimica et Cosmochimica Acta*, 16, 4007-4034.
- [9] Khairiah J., Habibah H.J., Anizan I., Maimon A., Aminah A., Ismail B.S., 2009. Content of heavy metals in soil collected from selected paddy cultivation areas in Kedah and Perlis, Malaysia. *J. Appl. Sci. Res.*, 5(12), 2179-2188.
- [10] Tessier A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, 51 (7), 844 – 851.
- [11] Tack F.M.G., Verloo M.G., 1995. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *Inter. J. Environ. Anal. Chem.*, 59, 225-238.
- [12] Tokalioglu S., Kartal S., Birol G., 2003. Application of a three-stage sequential extraction Procedure for the determination of extractable metal contents in highway soil. *Turk. Chem.*, 27,333-346.
- [13] Reimann C., De Caritat P., 2000. Intrinsic Flaws of Element Enrichment Factors (EFs) in Environmental Geochemistry. *Environ. Sci. Technol.*, 34, 5084-5091.