



Discharge of Cr, Mn, Ni, Cu and Zn from E-waste Components into Dumpsites Soil at Westminster Market, Lagos Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author EAO designed the study and wrote the first draft of the manuscript. Author OKA performed the statistical analysis. Author GOO wrote the protocol. Authors AEA and LOA managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The generation of electronic waste (e-waste) has increased due to the advancement in electrical and electronic industries. E-waste is term used to describe unwanted electronic products. E-waste contained toxic heavy metals such as barium, cadmium, chromium, copper, arsenic, zinc, nickel and lead. This study evaluated the discharge of heavy metals from e-waste in dumpsites soil located at

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Westminster Market, Lagos, Nigeria using Atomic Absorption Spectrometer. Four dumpsites from where e-waste are regularly being dumped were taken along side with control samples at a distance of 20 and 50 m away from each site for the analysis of Cr, Mn, Ni, Cu and Zn contents. The concentrations of the metals were found to range from 23.0 ± 0.1 to 46.0 ± 3.2 $\mu\text{g/g}$ for Cr, 124.8 ± 1.2 to 406.0 ± 6.2 $\mu\text{g/g}$ for Mn, 62.8 ± 2.4 to 78.0 ± 1.0 $\mu\text{g/g}$ for Ni, 23.6 ± 0.8 to 190.2 ± 4.0 $\mu\text{g/g}$ for Cu and 236.2 ± 5.6 to 746.0 ± 1.2 $\mu\text{g/g}$ for Zn. Statistical analyses of the data obtained via Pearson correlation indicated that some of the metals showed positive correlations, while others displayed negative correlations with each other. When compared with standard values, some of these metals exceeded the tolerable limit recommended which indicates the contribution of e-waste to the concentrations of heavy metals in the soil.

Keywords: E-waste; dumpsites; heavy metals; pollution; toxic effects.

1. INTRODUCTION

Vast technological advancement and aggressive market strategies in recent years have resulted in sharply shorten of the lifespan of most electrical and electronic equipment (EEE). As a result of the rapid turnover rate of these devices, large amount of electronic waste (e-waste) are generated once they are disposed. The Solving the E-waste Problem (StEP) Initiative, defined e-waste as "almost any household or business item with circuitry or electrical components with power or battery supply" that has or could enter the waste stream" [1]. As defined in the waste electrical and electronic equipment (WEEE) directive of the European Union (2002/96/EC), e-waste include equipment that are dependent on electric currents or electromagnetic field in order to work properly, and include equipment for generation, transfer and measurement of such currents and fields [2]. The concept of e-waste covers a broad spectrum of wastes from all electronic and electrical appliances and comprises of items such as computers, records

players, copying machines, refrigerators, washing machines, mobile phones, televisions (TVs), kitchen utensil, iron, diskette, compact disc, screw drivers, saws, toys, video games, therapeutic, bulbs, fluorescent lamps [3-6]. Electronic waste or e-waste is one of the fast growing problems of environmental pollution in the world with an estimated amount of about 20-50 million tons of electric and electronic waste being generated per year of which 75-80% is shipped to countries in Asia and Africa for recycling and disposal [7]. Nigeria is emerging as one of the top dumping grounds for electronic waste. According to a Seattle-based environmental group known as 'Basel Action Network (BAN)', about 500 shipping containers which contained up to 400,000 computer monitors or 175,000 large TV sets enter Lagos, Nigeria, every month and about 75 percent of such shipments are classified as e-waste [8].

Fig. 1 shows the dismantled components of cathode ray tubes as collected by scavengers.



Fig. 1. Focusing and deflecting coils of dismantled CRTs
(Source: Manhart et al. 2011 [9])

The results from the Nigerian e-Waste Country Assessment, revealed that about 70% of all the imported used equipment is functional which is sold to consumers after testing, while the non-functional part takes about 70% of share which can be repaired and latter sold to consumers. Of the total imports of used electrical and electronic equipment, 9% was reported to be non-repairable which is directly passed on to collectors and recyclers [10]. The composition of e-waste contains more than 1000 different substances, which can be categorized as hazardous and non-hazardous substances [7]. E-wastes containing elements such as cadmium, lead, arsenic, mercury, selenium, hexavalent chromium, zinc, copper, manganese and flame

retardants beyond permissible level in e-waste can be classified as hazardous waste [7,11]. E-waste collectors who are commonly referred to as 'scavengers', carried out these activities by informal methods such as hand dismantling, open fires, acid baths, and broilers to extract precious substances [12]. All these activities at these sites pose harmful threats to water, animals, plants, and can as well enter the food chain which may lead to human contamination. Fig. 2 shows the indiscriminate dumping of mostly television components after the removal of the valuable parts by scavengers, while figure 3 shows the dump site of e-waste generated mostly by refrigerator which is dangerous to the eco-system.



Fig. 2. Components of e-waste at different dumpsites locations [13]



Fig. 3. Dumping of e-waste mostly waste from fridges

(Source: [13])

Health risks are associated with the scavenging of e-waste such as cables to recover copper and the burning of plastic parts to reduce waste volumes, which also leads to the emissions of persistent organic pollutants (POPs) such as furans and dioxins which could lead to hormone disruptor [8-10]. While exposure to lead fumes or dust is known to cause several disorders such as anaemia, muscle pain, malaise, brain damage, headache, cardiovascular and gastrointestinal diseases [9,10,14], cadmium exposure can cause damage to kidneys, the respiratory system, high blood pressure, and can also be carcinogenic [10,15]. Reports have it that in Europe, workers in electronics recycling facilities have higher blood levels than other workers [16-18]. Since electrical and electronic equipment contain different hazardous materials which are harmful to human health and the environment if not disposed of carefully. The need for the evaluation of the discharge of heavy metals from e-waste on the chemical composition of the soil becomes necessary. This work focused on determination of heavy metals concentrations in top soil of WEEE dumpsites which were collected from four different e-waste dumpsites at Westminster Market, Lagos, Nigeria for the analysis of Cr, Mn, Ni, Cu and Zn which we hope that will assist relevant authorities and environmentalists in designing recycling facility and provide better means of dumping e-wastes.

2. EXPERIMENTAL

2.1 Sample Location

The Westminster Market is small, but occupies a strategic location as it is very close to Tincan Island Port in Apapa, a major route for the importation of goods in Lagos, Nigeria. There are over 300 shops in Westminster Market selling all kinds of used electrical and electronic devices such as computers, mobile phones, printers, TVs, tape recorders, CD players, kettles, irons, video-CDs and computer games [8,10]. Although off-loading and selling are the major business activities, testing and repair are also carried out. Lagos state is one of the smallest states in Nigeria with an area of 3,496 hectares of which 75,755 hectares are wetlands and has one of the highest populations of 17.5 million as reported by the Lagos state government [19]. It lies at latitude 6°27' north and longitude 3°23'45" east. Lagos has been home to a number of different ethnic groups over the years playing home to significant international populations including Lebanese, Indian and British communities and all and sundry. Fig. 4 shows the schematic diagram of Lagos State, Nigeria with an inscription indicating the area where the soil samples were taken.

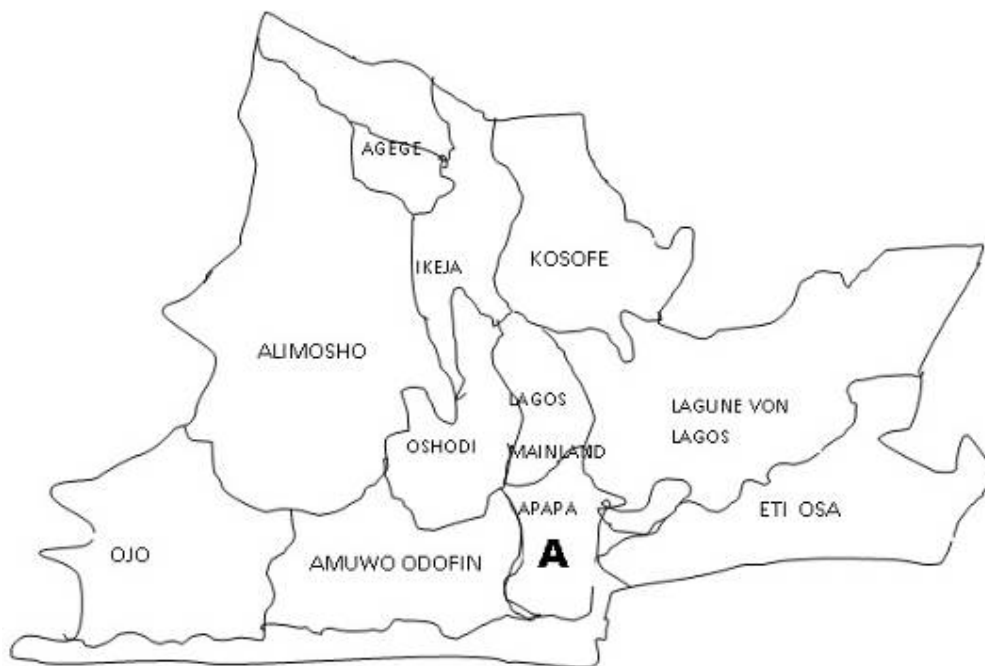


Fig. 4. Schematic diagram of Lagos State with an inscription of a showing the location site

2.2 Sample Collection and Preparations

Top soil samples (0-10 cm depth) were collected from two dumpsites where e-waste are constantly being dumped and transported into the laboratory. Control samples were also taken at a distance of 20 m and 50 m away from each site. The samples were air dried for 21 days and sorted to remove unwanted materials. The samples were then crushed using mechanical grinder and sieved for fine particle require. The method described by Adaramodu et al. [7] was adopted and modified. Briefly, a homogeneous solution of nitric acid and perchloric acid in the ratio 2:1 strength was prepared. 1 g of the dried powdered samples of each soil was added to this solution in a Kjeldahl flask. The contents of the flask were heated on a hot plate at 130°C until the volume was reduced to 3 ml. The solution was cooled and filtered with Whitman no. 1 filter paper. The filtrate was there after diluted up to the mark in a volumetric flask. All the sample solutions were analyzed for the presence of Cr, Mn, Ni, Cu and Zn using Buck Scientific model 210VGP Atomic Absorption Spectrophotometer. The results were analyzed in triplicate and the mean together with their respective standard deviations were recorded.

3. RESULTS AND DISCUSSIONS

Table 1 presents the concentrations of heavy metals at dumpsites 1 to 4 and standard values by USEPA [20] and EU [21]. It can be seen from the Table that the concentrations of Mn, Ni, Cu and Zn exceeded the Standard values, while only Cr is lower than the reference concentration in all the samples. The concentration of Cr was found to range from 23.0±0.1 to 46.0±3.2 µg/g for the dumpsites and from 6.2±0.1 to 22.0±0.1 µg/g for the control samples. Although, the concentration of chromium was lower than the recommended values by standard organizations, the gradual decrease in chromium concentrations at 20 and 50 m away from each dumpsites inferred that chromium may had been leached from chromium containing e-wastes substances such as data tapes, floppy disks etc. Chromium is widely used as a hardener in plastics, dyes in pigment and coatings of some metal parts in electrical and electronic equipment [8,10]. Although, the concentration of Cr is within tolerance limit, prolong activities such as continuous dumping of e-waste will cause an increase in chromium concentrations. Chromium is one of the toxic contaminants which could be carcinogenic and damage DNA [10,22,23]. The results were found

to be in agreement with 10.24±0.11 to 21.88±1.21 recorded in e-waste dumpsites by Ofudje et al. [24], 13.9±2.6 to 15.8±0.25 mg/kg reported in dumpsites by Ogbemudia and Mbong [25] but lower than 0.10 and 0.35 mg/kg observed in soil at Westminster market by Adaramodu et al. [7],

Mn concentration ranged from 124.8±1.2 to 406.0±6.2 µg/g in the dumpsites, while that of the control dumpsite ranged from 50.2±1.5 to 396.0±7.4 µg/g. The highest concentration of Mn was found in site 3, while the least value was recorded in site 4. A gradual decrease in Mn concentration was notice as the distance increased. Manganese is one out of three toxic essential trace elements, which means that it is not only necessary for humans survive, but also toxic when too high concentrations are present in a human body and can damage the respiratory tract and the brains [26]. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson, lung embolism and bronchitis, dullness, weak muscles, headaches and insomnia. Report has it that when men are exposed to manganese for a longer period of time they may become impotent [26]. Except for dumpsite 3, the concentration of Mn fell within the recommended value of 100-300 mg/kg by USEPA [20]. The results however fell within the values of 52.9±0.1 to 54.3±1.4 mg/kg as reported in soil at Westminster market by Adaramodu et al. [7] and from 20 to 100 mg/kg as recorded by Ademoroti [27]. The concentration of Ni was found to range from 62.8±2.4 to 78.0±1.0 µg/g for the dumpsites, while that of its control ranged from 22.8±0.8 to 64.0±3.0 µg/g. There was decrease in the concentration of Ni at the two control sites which cold be an indication that Ni is being leached from some e-waste containing substances such as rechargeable NiCd-batteries or NiMH-batteries, gun electron in cathode ray tube or Light Emitting Diodes (LEDs). The result is in agreement with our previous findings of 34.13±2.03 to 43.24±5.21 mg/kg [24], 82.70±0.06 mg/kg observed in soil around electronic waste dumpsite by Oladunni et al. [28] but lower than 0.31 to 0.42 reported in the soil around dumpsite by Opaoluwa et al. [29]. An allergic skin reaction in those who are sensitive to nickel is the most common harmful health effect of nickel in human and can cause immediate and delayed hypersensitivity noticed in occupationally exposure [30]. The metal is not only an allergen but also a potential immunomodulatory and immunotoxic agent in

humans [31]. Death due to nickel-induced adult respiratory distress syndrome (ARDS) was reported for a worker spraying nickel using a thermal arc process [32]. Some of the health disorders noticed in people contaminated with nickel are nausea, vomiting, abdominal pain, diarrhea, headache, cough, shortness of breath, and giddiness [33].

The concentration of copper in the soil samples from e-waste dumping sites was found to range from 23.6 ± 0.8 to 190.2 ± 4.0 $\mu\text{g/g}$, while that of the control sample ranged from 28.8 ± 0.3 to 138.0 ± 5.0 $\mu\text{g/g}$. The highest concentration of Cu in the dumpsites was observed at site 3, while the least value was observed in site 4. Copper was not detected in site 1 as well in the control samples. This may indicate that there are no copper containing substances at this site. The high concentration of copper at sites 1 and 2 as well as the gradual decrease in copper concentrations at 20 and 50 m away from each dumpsite may be as a result of the discharge of copper containing substances such as copper wires into the soil. Copper is an essential element which is required in the growth of animals can help in the production of blood and disease resistance. However, at high concentrations, copper can cause several disorders such as damage to liver, kidney, stomach and intestinal irritation, irritations of eyes, nose and skin, headache, dizziness, vomiting, diarrhea, anaemia [22,23,34]. Zn concentration ranged from 236.2 ± 5.6 to 746.0 ± 1.2 $\mu\text{g/g}$ from the dumpsites, while that of its control was found to range from 155.8 ± 4.2 to 629.2 ± 1.7 $\mu\text{g/g}$. In all the samples, the concentrations of the control sites were lower than the various dumpsites analyzed. The high concentration of Zn at various dumpsites compared with the control sites could be as a result of the release of Zn from Zn containing e-waste substances like cables, CRT, small motors and reading or writing devices of drives into the soil of the dumpsites. Water-soluble zinc which has been leached into the soils can contaminate ground water, while that which is discharged can as well retard the degradation of organic matter in the soil. Excess of Zn can also lead to electrolyte imbalance, vomiting, abdominal pains and dehydration [23,34,35]. Except for site 4, the values of Zn in all dumpsites exceeded the recommended value by USEPA [20] and EC [21]. The results were higher than literature report of 57.61 ± 4.25 to 111.48 ± 9.71 mg/kg by Ofudje et

al. [24] agrees well with 213.00 to 295.50 mg/kg observed in indoor dust and outdoor dust from Westminster electronic market in Lagos State as reported by Adarmodu et al. [7].

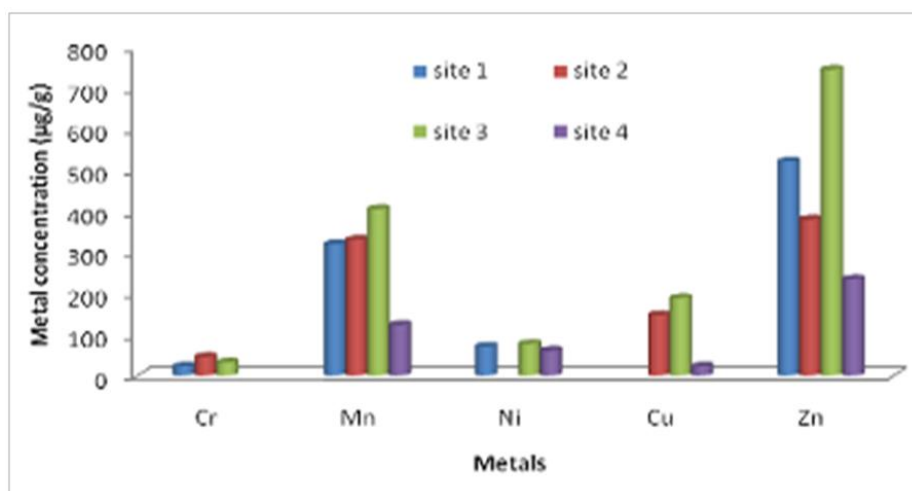
Comparison of the soil samples from the sites with the USEPA [20] and EU, [21], shows that the activities of dumping of WEEE had affected the soil composition in these areas with most of these heavy metals exceeding the permissible limits stipulated by these standard bodies. This implies that the high concentration of heavy metals observed at the dumpsites may be associated with the continuous dumping of e-waste such as printed circuit board, TV sets, batteries, cathode ray tubes, refrigerators, screen coating, light emitting diode and mobile phones etc. Heavy metal can be discharged into the environment through various anthropogenic activities, industrial effluent and leaching from some substances such as e-waste which then sinks into the soil and unlike organic contaminants which may be degraded by microbial action, most metals do not undergo microbial or chemical degradation and their presence in soil persist for a long time [22,24].

Fig. 5 shows the comparative mean concentration of metals from different soil locations. As revealed from Fig. 5, Cr was not detected in dumpsite 1, Ni was not found in site 2 and Cu was not detected in site 4 including some of the control samples. This could be an indication that substances containing these elements were not present at these sites. In all, zinc had the highest concentration which was noticed in dumpsite 3, while Cr from site 1 had the least value. It was also observed that zinc was present in abundance at all the dumpsites studied. Fig. 6 showed the comparative metal concentrations of all the control samples. The result showed that the concentration of all the metals at each dumpsite decreased gradually from 20 and 50 m away except for Cr in site 4 and Ni in site 2. This further confirmed the leaching of these metals from e-waste component from EEE at the dumpsites. In the case of Cr from site 4 and Ni in site 2 where the respective metal was not detected in the soil sample of the dumpsites but was found at 50 and 20 m away respectively, suggest the likely contamination from other sources or due to the natural metal background. Similar observations had been reported in our previous report [24].

Table 1. Elemental composition of soil from WEEE dumpsites at westminster market, Lagos state

| Sample | Cr ($\mu\text{g/g}$) | Mn ($\mu\text{g/g}$) | Ni ($\mu\text{g/g}$) | Cu ($\mu\text{g/g}$) | Zn ($\mu\text{g/g}$) |
|------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Site 1 | 23.0 \pm 0.1 | 321.0 \pm 3.0 | 71.0 \pm 1.0 | ND | 522.0 \pm 4.0 |
| 20 m away | 14.7 \pm 0.4 | 234.2 \pm 5.2 | 53.1 \pm 0.2 | ND | 326.0 \pm 3.8 |
| 50 m away | 8.3 \pm 1.4 | 186.0 \pm 1.0 | 52.1 \pm 1.8 | ND | 223.1 \pm 4.0 |
| Site 2 | 46.0 \pm 3.2 | 331.0 \pm 4.0 | ND | 148.0 \pm 2.0 | 381.0 \pm 4.0 |
| 20 m away | 22.0 \pm 0.1 | 225.0 \pm 6.1 | 97.2 \pm 3.0 | 125.8 \pm 3.1 | 205.2 \pm 2.0 |
| 50 m away | 14.1 \pm 0.6 | 185.0 \pm 3.0 | ND | 103.5 \pm 7.0 | 185.3 \pm 3.8 |
| Site 3 | 33.5 \pm 1.2 | 406.0 \pm 6.2 | 78.0 \pm 1.0 | 190.2 \pm 4.0 | 746.0 \pm 1.2 |
| 20 m away | 18.0 \pm 0.4 | 396.0 \pm 7.3 | 64.0 \pm 3.0 | 138.0 \pm 5.0 | 629.2 \pm 1.7 |
| 50 m away | 10.4 \pm 0.3 | 143.3 \pm 2.0 | 40.3 \pm 1.4 | 128.5 \pm 2.9 | 436.3 \pm 8.2 |
| Site 4 | ND | 124.8 \pm 1.2 | 62.8 \pm 2.4 | 23.6 \pm 0.8 | 236.2 \pm 5.6 |
| 20 m away | ND | 80.1 \pm 2.3 | 44.2 \pm 1.5 | 40.5 \pm 1.4 | 182.5 \pm 2.8 |
| 50 m away | 6.2 \pm 0.1 | 50.2 \pm 1.5 | 27.8 \pm 0.8 | 28.8 \pm 0.3 | 155.8 \pm 4.2 |
| USEPA [20] | 100 | 100-300 | - | 250 | 300 |
| EU[21] | 150 | - | 75 | 140 | 300 |

ND means not detected

**Fig. 5. Comparative mean concentration of metals ($\mu\text{g/kg}$) from different dumpsites locations**

3.1 Analysis of Correlation Coefficient

In order to determine the correlation among the metals, correlation coefficient was performed using Statistical Package for Social Scientist (SPSS) and correlation was considered significant at the 0.05 level (2-tailed with $n = 7$).

From Table 2, Mn showed a positive correlation value ($r = 0.80$) with Cr, while Ni displayed very strong positive correlation value ($r = 0.96$) with Cr and ($r = 0.98$) with Mn. It was also observed that Cu showed positive correlations ($r = 0.68$) with Mn, ($r = 0.86$) with Ni but negative correlation values ($r = -0.62$) with Cr. Zn showed a positive correlation values ($r = 0.23$, $r = 0.84$, $r = 0.79$, $r = 0.89$) with Cr, Mn, Ni and Cu. From Table 3, Cr-dumpsite displayed positive correlation ($r = 0.96$,

0.52 , 0.67 and 0.35) with Cr, Mn, Ni and Cu-control samples respectively but displayed negative correlation with Zn-control ($r = -0.89$). Mn in dumpsite showed a positive correlation ($r = 0.75$, 0.88 , 0.73) with Mn, Ni and Zn-control respectively but displayed negative correlation ($r = -0.48$ and -0.29) with Cr and Cu-control. The correlation coefficient of Ni-dumpsite displayed a positive correlation ($r = 0.94$, 0.68 , 0.48 and 0.75) with Cr, Mn and Cu-control, but negative correlation ($r = -0.25$ and -0.75) with Ni and Zn-control. Cu-dumpsite showed positive correlation ($r = 0.48$, 0.97 , and 0.82) with Mn, Ni and Zn, but negative correlation ($r = -0.86$, and -0.69) with Cr and Cu-control. Zn-dumpsite showed a positive correlation with Cr, Mn, Cu and Zn-control ($r = 0.73$, 0.85 , 0.94 and 0.23) but negative correlation with Ni-control ($r = -0.59$).

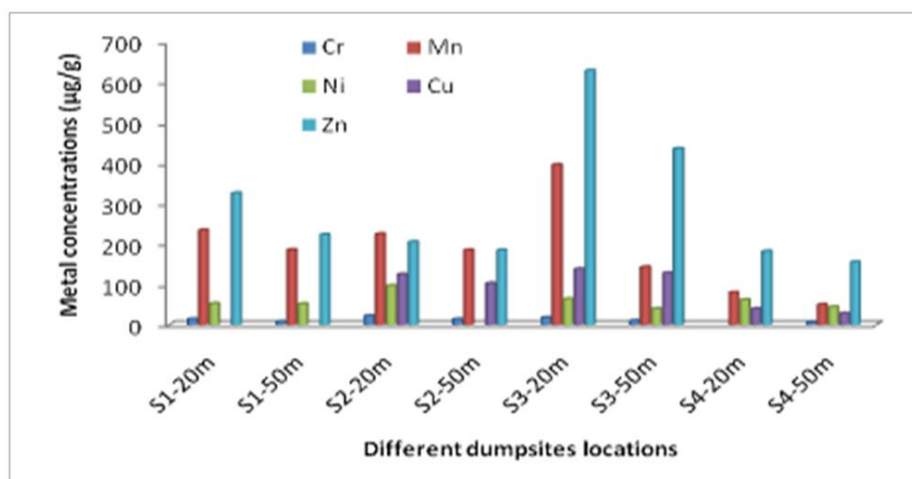


Fig. 6. Comparative mean concentration of metals (µg/kg) of control samples from different dumpsites locations

S1-20m = control sample from site 1 at 20 m away; S1-50m = control sample from site 1 at 50 m away; S2-20m = control sample from site 2 at 20 m away; S2-50m = control sample from site 2 at 50 m away; S3-20m = control sample from site 3 at 20 m away; S3-50m = control sample from site 3 at 50 m away; S4-20m = control sample from site 4 at 20 m away and S4-50m = control sample from site 4 at 50 m away

Table 2. Correlation of element at e-waste dumpsites

| | Cr | Mn | Ni | Cu | Zn |
|----|-------|------|------|------|------|
| Cr | 1.00 | | | | |
| Mn | 0.80 | 1.00 | | | |
| Ni | 0.96 | 0.98 | 1.00 | | |
| Cu | -0.62 | 0.68 | 0.86 | 1.00 | |
| Zn | 0.23 | 0.84 | 0.79 | 0.89 | 1.00 |

Table 3. Correlation between the levels of metals in dumpsites against control samples

| | Cr-control | Mn-control | Ni-control | Cu-control | Zn-control |
|-------------|------------|------------|------------|------------|------------|
| Cr-dumpsite | 0.96 | 0.52 | 0.67 | 0.35 | -0.89 |
| Mn-dumpsite | -0.48 | 0.75 | 0.88 | -0.29 | 0.73 |
| Ni-dumpsite | 0.94 | 0.68 | -0.25 | 0.48 | 0.75 |
| Cu-dumpsite | -0.86 | 0.48 | 0.97 | -0.69 | 0.82 |
| Zn-dumpsite | 0.73 | 0.85 | -0.59 | 0.94 | 0.23 |

The positive correlation indicate possible common sources of contamination such as the dumping of e-waste in the affected area, while the negative correlation indicates uncommon source origins which could be other contamination sources such as industrial emissions from vehicles and other solid wastes or as a result of the natural background contribution of individual metals in the soil and not necessarily from the e-waste.

4. CONCLUSION

This study was design to evaluate the discharge of heavy metals from e-waste components at four different dumpsites in Westminster Market,

Lagos, Nigeria. The following elements Cr, Mn, Ni, Cu and Zn were detected in the samples at varied concentrations with their respective control sites taken at distance of 20 and 50 m away from each dumpsite. Comparison with standard reference materials shows that the dumpsites where e-wastes are been regularly dumped contained high concentration of Cr, Mn, Zn, Ni, and Cu when compared with standard values and their respective control samples. Pearson correlation showed positive and negative correlations among the metals with each others. The positive correlation could imply common source of contamination from e-waste containing substances at these dumpsites. Thus, continues dumping of e-wastes will lead to

increase in the concentrations of heavy metals, thus, relevant authorities should ensure proper disposal of e-waste components, while e-waste recyclers should improved on their scavenging techniques.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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