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# **An Evaluation of the As, Cd, Mn and Hg Contamination in Soils and Plants (***Amaranthus spinusis)* **of Kaduna Metropolis Dumpsites**

**Omoniyi Kehinde Israel1\*, Ekwumemgbo Patricia Adamma<sup>1</sup> and Sanni Habibu Adinoyi<sup>1</sup>**

*<sup>1</sup>Department of Chemistry, Ahmadu Bello University, Zaria, P.M.B. 1044, Kaduna, Nigeria.*

*Authors' contributions*

*This work was carried out in collaboration between all authors. Author OKS co-supervised the M.Sc. research thesis and edited the first draft of the manuscript. Author EPA chaired the supervisory team for the research and edited the first draft of the manuscript. Author SHA conceptualized the research and managed the literature searches. All authors read and approved the final manuscript.*

*Research Article*

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# **ABSTRACT**

**Aim:** The study assesses the qualities of contaminated soils of ten municipal waste dumpsites in Kaduna metropolis, Nigeria.

**Study Design:** Physico-chemical parameters and heavy metals were analyzed in soils and plants of ten dumpsites across wet and dry season in Kaduna metropolis.

**Place and Duration of Study:** Department of chemistry of Ahmadu Bello University, Zaria and National Fertilizer Development Centre, Goningora, Nigeria. Within August 2011 to June 2012.

**Methodology:** Wet acid digestion and atomic absorption spectrophotometry were used for the determination of heavy metals in both soil and the plant (*Amaranthus spinusis*) while standard procedures were employed for determination of the physicochemical parameters**.**

**Results:** The pH of the dumpsite soils ranged from 7.90 ± 0.02 to 9.30 ± 0.02. The organic matter contents of the dumpsite soils during the wet season were lower for most of the sites when compared to the dry season values; the control sites had organic matter contents  $(2.60 \pm 0.01 \text{ mq/kg})$  which was 10% of the mean dumpsites value. Using atomic absorption

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*<sup>\*</sup>Corresponding author: Email: israelflourish@yahoo.com;*

spectrophotometry The range of the total metal contents of the dumpsite soils for the wet season were: As 0.013-0.054; Cd 0.22-0.29; Hg 0.133-0.624 and Mn 2.615-22.89 mg/kg. The ranges were As 0.001-0.51; Cd 0.22-0.46; Hg 0.253-0.881 and Mn 1.005-30.206 for the dry season. *Amaranthus spinusis* had the ranges for the wet season being: As 0.001-0.030; Cd 0.019-0.250; Hg 0.144-0.590 and Mn 0.167-0.690 mg/kg. During the dry season *A. spinusis* had the ranges As 0.004-0.056; Cd 0.051-0.483; Hg 0.156-0.598 and Mn 0.228- 0.700 mg/kg. Metal contamination at the dumpsites follows the ranking:  $Mn > Hq > Cd > As$ . Levels of these metals in *Amaranthus spinusis* and the soils did not vary significantly across the season  $(P < 0.05)$ . High level of contamination of these metals was recorded at Tudun Wada (TW), Rafin Guza (RG), Angwan Dosa (AD) and Angwan Shanu (AS). The transfer ratio indicates that As and Hg were more accumulated in the plant (*Amaranthus spinusis*) grown on TW. Cd in the control soil  $(0.020 \pm 0.0018 \text{ mg/kg})$  was 10 fold the dumpsite mean, mean As at dumpsites soil was  $0.034 \pm 0.0031$  mg/kg but not detectable in the contro. Level of Hg in the control soil was within that obtained for the dumpsite soils(  $0.502 \pm 1$ 0.003mg/kg), being higher than the threshold limit. Mn in the dumpsite soils was higher than the UNEPA limit of 10.0 mg/kg; the control value was  $0.690 \pm 0.003$  mg/kg.

**Conclusion:** The study indicates pollution of the dumpsite soils by Hg and Mn, and this could pose health risk to man.

*Keywords: Heavy metals; dumpsite; soils; Amaranthus spinusis; contamination.*

## **1. INTRODUCTION**

Refuse generation, dumping and management have become a serious environmental problem in many urban areas in Nigeria. The volume of waste generated in many of these urban areas has been on the increase in recent times. Many human factors such as: technology, industrialization, agricultural practices, transportation, education, construction trade, commerce, nutrition and most importantly population increase are directly responsible for increase in refuse generation in any human society [1].

Although solid waste can be an asset when properly managed, it poses the greatest threat to life amongst all the classes of waste since, it has the potential of polluting the terrestrial, aquatic and aerial environments [2]. Several fluxes of waste and cover materials from different sources end up at dumpsites and due to the heterogeneity and complexity of wastes, these dumpsites contain a variety of contaminants which can pollute the soil of the area [3].

The physico-chemical properties of the degraded soils at these sites are one of the important factor playing roles in vegetation development. For instance, soil structure and acidity affects the absorption and accumulation of mineral elements by plants and thus play a very important role in vegetation establishment and development at such sites [4].

One of the predominant occupations in Northern Nigeria is farming. However, due to the unaffordable cost of modern fertilizer, low income earning farmers use waste soils from dumpsites as manure in many towns and villages of Northern Nigeria. This however, lead to accumulation of heavy metals in plants grown on dumpsite soils or fertilized from such manure which on subsequent transfer through food chain end up in man, posing potential health risk [5].

It is based on these facts that this study is aimed at determining the total concentration of arsenic, cadmium, manganese and mercury in soils and plants of Kaduna metropolitan dumpsites including the variation of the physico-chemical properties across the seasons in the selected dumpsites. This work would provide recent and additional information relevant for soil quality monitoring and assessment of human health implications associated with dumpsites.

## **2. MATERIALS AND METHOD**

## **2.1 Study Area**

The present study was performed on ten municipal waste dumpsites and a control site which is 10 m away from one of the dumpsites (Badarawa) in Kaduna state. Kaduna State lies between longitude  $30^\circ$  east and latitude 0900 and  $1130^\circ$  North of the equator. The State occupies an area of approximately 48,473.2 square kilometres and has a population of more than six million (2006 census). It falls into Guinea Savannah climate, which has distinct wet and dry seasons. The wet season in Kaduna State is usually from April through October with great variations as one moves North-ward. The studied areas recorded an average rainfall of about 1016 mm during the research periods. The ten study sites are Kawo (KW), Rafin Guza (RG), Malali (ML), Angwan Dosa (AD), Badarawa (BD), Angwan Shanu (AS), Kurmum Mashi (KM), Tudun Wada(TW), Trikania (TK) and Kakuri (KK) waste dumping sites (Fig. 1), ranging from about two to twenty- two years of existence. Fig. 1 below shows the map of the ten dumpsites studied.



**Fig. 1. Map showing the ten study sites**

## **2.2 Sample Collection / Pre-treatment**

The ten dumpsites sampled in each location were divided into four quadrant; five plant samples were collected from each quadrant in a diagonal basis following the methods of [6]. The plants *(Amaranthus spinusis*) were collected in the quadrants from the dumpsites and also from the control sites. The plants were carefully uprooted and bagged in a labelled polythene bag and taken to the laboratory. The dumpsite soils were also collected from each site with the aid of a clean stainless steel spoon at 10 cm below the top soil. The soil samples were placed in labelled polythene bags and were then taken to the laboratory for treatment. The sample collection was done from August 2011 to June 2012 at three months interval, spanning rainy and dry seasons. All the samples were collected in triplicate. Soil samples from each site were homogenized in an agate mortar and air dried in a circulating air in the oven at 30ºC overnight and then passed through a 2 mm sieve. The sieved soils were placed in polythene bags and ready for analysis. Plant samples were properly rinsed with tap water and then with distilled water to remove any attached soil particles, cut into smaller portions and then placed in large clean crucible where they were oven dried at  $100^{\circ}$ C for 48 hrs in order to remove moisture. The dried plant samples were grounded into fine particles using a clean acid washed agate mortar and pestle*. Amaranthus spinusis* commonly called "Turgunuwa" was selected because it grows massively in dumpsites and ruminants mostly feed on them.

#### **2.3 Physico-chemical Analysis**

Physico-chemical properties such as pH, electrical conductivity, moisture content, organic matter, cation exchange capacity (CEC) were analyzed. The pH and electrical conductivity were measured in a soil suspension (1:10 w/v dilution) by digital pH meter and conductivity meter respectively according to [7] and [8]. Moisture content and cation exchange capacity were determined by the procedures outlined by [7]. Organic matter was determined by the wet oxidation method of [9]

## **2.4 Heavy Metal Analysis**

Total concentrations of Mn, Cd, Hg, As were analyzed in the soil samples by wet digestion according to [10]. A 1.00 g of the soil sample was digested in Teflon cup with 30.00 ml aqua - regia (HCl: HNO<sub>3</sub> 3:1) on a thermostatted hot plate at 150°C. After about 2 hrs of digestion, the Teflon cup with its content was brought down from the hot plate to simmer. Then, 5.00 ml HF was added and the mixture was heated further for 30 mins. The Teflon cup with the content was allowed to cool down to room temperature after which the content was quantitatively transferred into a 50.00 ml volumetric flask and made to the mark with distilled water. Triplicate digestion of each sample was carried out together with the blank.

The *A. spinusis* samples was digested according to [11], 0.50 g of dried *A. spinusis* was weighed into 100.00 ml beaker, a mixture of 5.00 ml concentrated HNO<sub>3</sub> and 2.00 ml HClO<sub>4</sub> was added and this was digested at low heat using hot plate until the content was about 2.00 ml. The digest was then allowed to cool and was filtered into a 50.00 ml standard flask. The beaker was rinsed with small portions of double distil water and then filtered into the flask. Triplicate digestion of each sample was carried out together with the blank.

## **3. RESULTS AND DISCUSSION**

#### **3.1 Physico-chemical Properties of the Soil**

Table 1 shows that the dumpsites coded BD and AD are the oldest while RG is the least aged. The dimensions and the soil texture of the ten dumpsites.





The physico-chemical properties used as indicator of the soil quality are presented in Tables 2 and 3 for wet and dry seasons respectively. Pearson correlation coefficient and analysis of variance ( $p < 0.05$ ) were used to analyse the data obtained. Generally  $pH$  differed significantly among dumpsites and the seasons. In the wet season RG had the highest pH of 9.30 and TK had the least (7.90) while in the dry season RG and AD had the highest (9.20) and TK the least (7.55).

These indicate that most of the dumpsites soils are alkaline which enhances soil fertility and plant growth. These values are in line with other studies by [12]. However, compared to the control, these values on the average were significantly higher. This may be linked to the buffering effect of soil organic matter against pH change in addition to the release of basic cations during the organic matter decomposition [13]. At low pH, metals are more soluble in the soil solution, thus more bioavailable to plants, and hence pose severe toxicity problems in acidic than in alkaline soil [14]. Electrical conductivity (EC) ranged from 0.010 mho/m (KM)  $-0.280$  mho/m (TW) in the wet season and 0.0015 mho/m (AS)  $-0.093$  mho/m in the dry

season at AD. The electrical conductivity values were found to vary significantly across the seasons, with majority of the dumpsites recording lower values in the dry season. The relatively high EC values may be attributed to the presence of metal scraps which is one of the constituents of the refuse dumpsites [15].

The ages of the dumpsites presented in Table 1 could proffer explanations for the soil texture being loamy sand in both BD and AD and sandy loam in RG. Partly, this account for the relatively high values obtained for the physicochemical properties of the soils. The control is sandy-sand by texture as expected, since it is not a dumpsite and is free of humus or organic matter. The radius of BD (45.0670m), AD (51.567m), TK (55.467m) and TW (35.0330m) shows they occupy large land area spreading into major roads and nearby houses, thereby constituting nuisance to the environment where they are located.





The lowest organic matter content in the wet season was recorded at AS (20.30 gkg<sup>-1</sup>) and the highest at TK (36.30 gkg<sup>-1</sup>) while in the dry season organic matter ranged from 20.20  $gkg^{-1}$  at AS - 37.20  $gkg^{-1}$  at TK. The significantly higher organic matter contents of the dumpsites soil in the dry season compared to wet season could be due to the lower soil moisture contents during the dry season which retards the activities of the micro - organisms involved in the organic matter decomposition, thereby accumulating more organic matter in the dry season.

The organic matter contents of the soil plays an important role in absorption reaction in the soil, hence prevents pollutants from reaching ground water sources [16]. Cation exchange capacity in the wet season ranged from 7.10 at both AD and ML to 10.40 Cmolkg $^{-1}$  at TW and in the dry season recorded a range of 6.90 at TK to 9.80 Cmolkg<sup>-1</sup> at RG. Clay along with organic matter accounts for a great percentage of the total cation exchange sites. The soil concentrations of exchangeable bases significantly differ across the seasons and among the dumpsites as seen in this study. This may also be connected to the heterogeneous nature of wastes deposited in the dumpsites which is expected to impact differently on soil properties. In addition, the slightly higher mean values in the dry season can be attributed to leaching of cations down the profile by rainfall [17].

Moisture content which is directly proportional to the water holding capacity of the soil ranged in the wet season from 46% at RG to 91.24% at TW while in the dry season the recorded range was 40.20 at RG to 81.24 at TW. These mean values as seen vary significantly between dumpsites depending on their location. The higher moisture contents in wet season explain why plants grow healthily compared to dry season. As expected most of the parameters recorded the lowest mean values at Control which is not a dumpsite. More so, highest mean values were recorded in wet season for pH, electrical conductivity cation exchange capacity and moisture while in the dry season. organic matter recorded highest values. Also there was no remarkable difference in the mean values of most parameters across the seasons with exception of electrical conductivity and moisture content. Correlation analysis shows that pH, electrical conductivity, cation exchange capacity and moisture content were positively correlated.





## **3.2 Heavy Metal Concentrations in Dumpsite Soil (mgkg-1 )**

The soil distribution of heavy metals is shown in the Figs. 2a-2d. The Figs showed that the soil heavy metal content was significantly lower on the control site with no waste compared to the dumpsites studied. As seen in Fig. 2a, arsenic content is generally low though it is higher in the dry season than the wet season. It recorded highest value (0.054) at ML and lowest (0.013) at both KM and TW in the wet season while in the dry season highest value (0.51) at KK and lowest (0.001) at TK, this could be connected to the fact that residential area dumps compose less toxic waste than the industrial sites. Arsenic contents was thus extremely high at KK in the dry season, probably this is due to the nature of industrial wastes deposited.



**Fig. 2a. Mean concentrations of As in the soil**



**Fig. 2b. Mean concentrations of Mn in the soil**

In Fig. 2b, manganese concentration is generally higher than all the other metals recorded. During the wet season it was lowest at AD (2.605) and highest at RG (22.88), while in the dry season, lowest value was also recorded at AD (1.005) and highest at RG (30.206). This shows that the observed concentration of Mn might have been largely due to background concentration. [18] reported that manganese may be found in most soil since it is one of the elements in the earth crust.



**Fig. 2c. Mean concentrations of Cd in the soil**

Cadmium contents shown in Fig. 2c are relatively low compared to Mn and Zn, though higher than As. There was no significant difference in cadmium contents during dry and wet season in most of the dumpsites except KW, RG, TK and TW. In wet season, TW had the lowest value (0.223) and AD had the highest (0.291), while in dry season (0.218) was the lowest value recorded at KK and 0.459 at TW. In both KM and KK it was observed that Cd contents were higher in wet than in dry season, this could be linked to the location of the dumpsites and also the nature of wastes been dumped. From the results, Cd contents may pose little or no environmental hazard on man.

Mercury (Fig. 2d) shows least concentration in TW (0.133) and highest in AS (0.624) in the wet season, while in the dry season lowest value was recorded for BD (0.029) and the highest (0.881) for AD. In RG, AD, KM and TW there was a sharp increase in the Hg contents during the dry season, this could be probably due to the nature of the solid wastes deposited during the dry season. The trend of metal contents in the dumpsite soils studied across the season follows the order. Mn > Hg > Cd > As



**Fig. 2d. Mean concentrations of Hg in the soil**

## **3.3 Heavy Metal Concentrations in** *Amaranthus spinusis* **(mgkg-1 )**

Heavy metal concentrations in *Amaranthus spinusis* were found to be mostly lower than that of the soil, though in few cases *A*. *spinusis* recorded higher metal contents than in the soil as shown in Figs. 3a-3d. Also, as expected the metal contents were mostly higher during dry season than wet season and control site metal contents were mostly below detection limit across the seasons.



**Fig. 3a. Mean concentrations of As in** *A. spinusis*

Arsenic (Fig. 3a) recorded lowest value at AD and KM in both wet and dry season being below detection limit, this could be due to the low arsenic content in the soil where the plants grow. Higher values were recorded for arsenic (0.037) in the wet and 0.056 for dry season both at AS. The values were found to be significantly different for wet and dry seasons,



though they are within the tolerance limit and hence may pose little or no health hazard on man.





**Fig. 3c. Mean concentrations of Cd in** *A***.** *spinusis*

Manganese contents (Fig. 3b) were the highest levels recorded among all the metals studied, the lowest value in the wet season was recorded for TW (0.167) and the highest was recorded for ML (0.690), while in the dry season, 0.288 was lowest for KM and 0.599 the highest recorded for AD. From the graph it indicates that the control site had very low values in both the wet and dry seasons, which is as expected. In addition, there was no significant difference in the values obtained for both the wet and dry seasons.

Concentrations of cadmium (Fig. 3c) during the wet season was found to be lowest (0.019) in TW and highest (0.054) in BD while in dry season, lowest value was 0.051 (ML) and highest value was 0.483 (AS). These values recorded, were however seen not to be distinct across the seasons though in AS, there was a large difference, which could be due to the non-leaching of cadmium in soil and nature of solid wastes deposited in the dry season.

As seen from Fig. 3d mercury contents in *A. spinusis* during the wet season ranged from 0.114 (KM) to 0.592 (RG), while in the dry season it ranged from 0.156 (KM) to 0.598 (RG). Unlike other dumpsites, ML recorded highest Hg concentration in the wet season compared to dry season; this could be attributed to dumping of higher Hg containing wastes. Mercury contents in the control were also below detection limit, indicating non-pollution of the control sites. Trend of *A*. *spinusis* metal contents in the dumpsites across the seasons is also given as: Mn > Hg > Cd > As.



**Fig. 3d. Mean concentrations of Hg in** *A***.** *spinusis*

#### **3.4 Transfer Factor of Heavy Metals**

To be able to determine the contents of heavy metals contamination of the soil, an enrichment factor was computed. This was expresses as the ratio of the concentration of the metals in the plants to that of the soil [19] as shown in Table 4 (wet season) and Table 5 (dry season). The transfer factor (TF) varied significantly among the dumpsites species of the heavy metals. Transfer factor obtained in the wet season were found to be highest for heavy metals in the following dumpsites; As, 1.54 (AS); Mn, 0.303 (ML); Cd, 1.06 (AS) and Hg, 3.38 (TW). While transfer factors during the dry season were also highest for; As, 21 (TW); Zn, Mn, 0.59 (AD); Cd, 2.1 (AS) and Hg, 0.99 (RG). These results indicated *A*.*spinusis* had the potential of accumulating more of Hg at TW and less of Mn at ML in the wet season while more of As is accumulated at TW and less of Mn at AD in the dry season. The transfer factor values recorded in TW for As and Hg at both wet and dry season respectively in this study is an indication of the potential of these heavy metals in the dumpsite to be transferred into the food chain through the consumption of edible plants on the site by either animals or man. Hence consumptions of these plants may cause some health implications as reported by [15]. According to [20] some environmental factors such as pH, exchange binding capacities and climate change might have contributed to some of the low transfer factor values in dumpsites.

<b>Dumpsites</b>	As	Mn	Cd	Hg
<b>KW</b>	$0.441 \pm 0.0041$	$0.066 \pm 0.0022$	$0.191 \pm 0.0032$	0.778±0.0057
<b>RG</b>	$0.047 \pm 0.0071$	$0.011 \pm 0.0091$	$0.215 \pm 0.0043$	$2.667 \pm 0.0001$
<b>BD</b>	$0.095 \pm 0.0002$	$0.115 \pm 0.0041$	$0.235 \pm 0.0033$	$0.729 \pm 0.0082$
<b>AD</b>		$0.231 \pm 0.0061$	$0.099 \pm 0.0003$	$0.492\pm0.0061$
KM	0	$0.067 \pm 0.0021$	$0.123 \pm 0.0042$	$0.460 \pm 0.0043$
AS	$1.541\pm0.0022$	$0.046 \pm 0.0022$	1.106±0.0055	$0.379 \pm 0.0011$
ML	$0.296 \pm 0.0012$	$0.302\pm0.0005$	$0.131 \pm 0.0007$	1.050±0.0084
<b>KK</b>	$0.382 \pm 0.0034$	$0.066 \pm 0.0006$	$0.076 \pm 0.0001$	0.778±0.0051
TK	$0.044 \pm 0.0023$	$0.017 \pm 0.0004$	$0.125 \pm 0.0003$	$0.619 \pm 0.0065$
TW	$0.076 \pm 0.0013$	$0.060 \pm 0.0002$	$0.073 \pm 0.0005$	$3.383\pm0.0009$
Control		$0.002 \pm 0.0001$	$0.001 \pm 0.0031$	0

**Table 4. Transfer Factor of Heavy Metals from Dumpsite Soil (Wet Season)**





## **4. CONCLUSION**

The colour of soils of the control sites is light brown compared to the blackish to grayish colours in the dumpsite counterparts. The control sites had organic matter contents (2.60  $\pm$ 0.01) which was 10% of the mean dumpsites value. The heavy metal concentration in the dumpsite soils of Kaduna metropolis varied to a great extent by sampling site and metal type. Among the metals analysed, Hg (0.881 mg/kg) and Mn (30.206 mg/kg) had the highest concentration while As (0.054 mg/kg) was the least.

Cd concentration in the control soil  $(0.020 \pm 0.0018 \text{ mg/kg})$  was 10 fold in the dumpsites; mean As level was  $0.034 \pm 0.0031$  mg/kg in the dumpsites, though As was not detectable in the control samples. The mean level of Hg in the control soils was within that obtained for the dumpsite soils  $0.502 \pm 0.003$  mg/kg, being higher than the threshold limit Hg in soil. Likewise mean Mn in the dumpsite soils (11.320  $\pm$  0.093 mg/kg) indicated pollution as this

was higher than the UNEPA limit of 10.0 mg/kg; the control soils recorded  $0.690 \pm 0.003$ mg/kg. This implies that the dumpsite soils are contaminated by Hg and Mn.

Based on the findings, relatively low transfer factor were obtained especially at AD and KM, which account for the low metal contents found in the plant (*Amaranthus spinusis*) compared to metal content in soil. However, an exception was recorded in TW where transfer ratio was high for Hg (3.38, 0.99) and As (1.54, 21.00) in wet and dry seasons respectively. Thus, indicating possible Hg and As contamination on consumption of such plants by ruminants, which subsequently through food chain could pose health risk to man. Metal contents in *Amaranthus spinusis* and soil did not vary significantly in the dumpsites across the season  $(P < 0.05)$ . The physico-chemical properties of the dumpsite soils indicate that these soils have the potential to be used as compost. However, the high levels of toxic metals in the soils is of environmental concern.

## **COMPETING INTERESTS**

Authors have declared that no competing interests exist.

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