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Assessment of Heavy Metals' Contamination of Soils and Vegetable from Farmlands on Selected Floodplains in Akure and Environs, Nigeria

Ademola Aiyesanmi¹ , Precious Chukwunenye1,2 and Johnson Odukoya1,3*

1 Department of Chemistry, The Federal University of Technology, P.M.B. 704, Akure, Ondo State, Nigeria. ² Department of Chemistry, University of North Texas, Texas, USA. ³ Department of Chemical Sciences, University of Johannesburg, P.O. Box 17011, Doornfontein, Johannesburg, South Africa.

Authors' contributions

This work was carried out in collaboration among all authors. Authors AA and JO provided the concept. All authors contributed to the literature searches, methodology, analyses and writing of the manuscript first draft. Authors PC and JO wrote the protocol as well as performed the statistical analyses. All authors read and approved the final manuscript.

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ABSTRACT

Aim: Among other absorption pathways, heavy metals affect human health via their introduction into the diet through the soil-food chain. This study was carried out to determine the concentration of heavy metals in soils and plant's part of *Amaranthus hybridus* from five farmlands on floodplains in Akure and environs.

Study Design: Soil and *A. hybridus* samples were obtained from five farmlands for the assessment of their heavy metals' content and pollution levels.

Place and Duration of Study: The study (six months' duration) was conducted at the Department of Chemistry, The Federal University of Technology, Akure, Ondo State, Nigeria.

Methodology: The assessment involved the use of standard methods of analyses and an atomic absorption spectrophotometer. Mathematical expressions were employed for estimating the

**Corresponding author's email address: joodukoya@futa.edu.ng;*

bioconcentration factor, geoaccumulation index, contamination factor and pollution load index. Statistical difference of the results was evaluated using One-Way Analysis of Variance.

Results: The experimental results revealed that the farmlands' soils belong to four textural classes in which their heavy metals' contents are all below the maximum allowable concentrations provided in the considered regulatory guidelines for soil. Evaluation of the geoaccumulation index showed that concentration of all heavy metals in the soils are not enriched above the baseline concentration as most of the soils belong to Class 0 (uncontaminated category). Pollution load index estimated from the contamination factors also indicated no overall pollution of the farmlands. Uptake of the studied heavy metals by *A. hybridus* was at varied levels while vegetable samples from Ogbese farmland had the highest bioconcentration factor for copper, nickel and chromium.

Conclusion: Although most of the farmland soils have satisfactory physicochemical properties and present safe level of the studied heavy metals, the research revealed the need for cultivation of vegetables which are extremely poor bioaccumulators of heavy metals in these farmlands.

Keywords: Amaranthus hybridus; floodplain; geoaccumulation index; heavy metals; pollution load index.

1. INTRODUCTION

Heavy metals pollution has become a serious environmental challenge [1] and this group of environmental pollutants belongs to a class of illdefined subset of elements with metallic properties which include the transition metals, some metalloids, lanthanides, and actinides [2]. According to Ali et al. [1], heavy metals can be classified as essential (such as iron, manganese, copper, zinc, and nickel) and non-essential (like cadmium, lead, arsenic, mercury, and chromium) with respect to their role in biological systems. The essential heavy metals are those needed by living organisms in minute quantities for important physiological and biochemical functions while the non-essentials are those not required.

Although a large number of elements may be referred to as heavy metals (i.e. with densities exceeding 5 g per cubic centimetre), those with environmental relevance include arsenic, chromium, copper, nickel, zinc, cadmium, lead and mercury with the latter three identified as the most toxic elements to human existence [3,4].

These heavy metals enter the environment through natural and anthropogenic sources such as via human activities involving the use of pesticides, animal manures, land application of fertilizers, among others [1,5,6]. They are not biodegradable and persist for a long time in contaminated soils [7], toxic to plants, animals as well as human beings [6].

Soil is a major sink of heavy metals from the atmosphere, hydrosphere and biota; the presence of heavy metals in soil pose potential threats to the environment and can also affect human health through absorption pathways like direct ingestion, dermal contact, diet through the soil-food chain, inhalation and oral intake [6]. As noted in Song et al. [8], most individuals become exposed to toxic elements mainly via dietary sources. High concentrations of heavy metals in the food chain may accumulate in the human body and can lead to serious health disorders when ingested beyond the permissible limit [3]. Children are, however, more prone to heavy metals accumulation from the food chain than adults since they consume more foods for their body development [3]. Generally, these heavy metals can give rise to impaired growth, damage to brain, organ and nervous system as well as death [3].

On the other hand, dry season farming along floodplains of rivers under the World Bank sponsored "FADAMA" Agricultural project is a common practice in Nigeria and Ondo State in particular [9]. The floodplains are constantly subjected to inundation from nearby river with subsequent fluvial deposition during the rainy season, thus acting as sinks for suspended matter via sedimentation. In the dry season, farmers usually leverage on the high moisture content of the floodplain soil due to proximity to the river bank, rich nutrients and organic matter contents [10] occasioned by the over-bank deposition for subsistent and semi-commercial farming, mostly for leafy vegetables. Notwithstanding, studies have shown that these floodplains could also have been contaminated with chemical pollutants such as heavy metals [11-13] and persistent organic pollutants [14] resulting from the deposition, especially when the rivers constitute the sinks for municipal runoff.

Vegetables, which are economic crops [6] and highly recommended foods for human consumption [15], take up heavy metals by absorbing them from contaminated soils and aerial deposits of polluted environments on parts of the vegetables [6,16]. The factors influencing the concentration of heavy metals on and within plants include the: climatic condition, atmospheric deposition, nature of the soil on which the plant is grown, and extent of maturity of the plant at the time of harvest [17].

As heavy metal contamination of food items is one of the key aspects of food quality assurance [18,19], this study was aimed at assessing the heavy metals' distribution in soils and vegetable (*Amaranthus hybridus*) obtained from five farmlands on selected floodplains in Akure metropolis and environs. This becomes necessary as Nagajyoti et al. [20] noted that toxicity of heavy metals has ecological, evolutionary, nutritional and environmental effects. The vegetable used for this research, *A. hydridus* (African spinach), is a nutritious and leafy vegetable which belongs to the Amaranthaceae family [21,22]. Focus was on five selected heavy metals (copper, nickel, chromium, cadmium and lead) with environmental relevance.

2. MATERIALS AND METHODS

2.1 Study Area

The study area falls within three Local Government Areas (LGA) in the Central Senatorial District of Ondo State, Nigeria. These are: Akure South LGA, Akure North LGA and Ifedore LGA, all within and proximity to Akure metropolis and located between latitude 07° 12'N and 07° 26'N, and longitude 004° 59'E and 005° 24'E. The sampling locations were farmlands on floodplains of River Ala at Aule, Army Barracks (Owena Cantonement) and Isikan in Akure South LGA, River Ogbese at Ogbese (Akure North LGA), and Ilara in Ifedore LGA.

The study area experiences copious rainfall between April and July with a short break in August and continues from September to early November, with the heaviest rainfall in July and average annual rainfall of 100 \pm 40cm, while the average daily temperatures range from 22° C to 35°C [23-25].

2.2 Collection and Preparation of Samples

Soil samples were collected from five locations along the floodplains each of Owena river, Ogbese river and Ala river with the aid of soil auger to a depth 0-20 cm. The locations were geo-referenced with Geographical Position System (GPS) Germin 12 model for ease of reference. Collected samples were kept in cleaned and well-labeled polythene bags and transferred to the laboratory. In the laboratory, samples were air-dried for two weeks. They were then ground into fine particles in a mortar, sieved through a 2 mm mesh and about 200 g of the sieved samples were sub-sampled by quartering for analysis.

The vegetable (*A. hybridus*) samples were collected from five farmlands close to these rivers. Immediately after harvesting, the roots of the vegetable were cut-off. The obtained vegetable leaves were thereafter washed, airdried, oven-dried at 105° C and grounded to powder. All powdered samples of the vegetable leaves and soil were then kept in well-labelled air-tight containers prior to analysis.

2.3 Chemical Analysis

2.3.1 Determination of physicochemical parameters

pH of the soil samples was determined by mixing 5 g of soil with 10 ml of distilled water (1:2). The mixture was analysed using Jenway 3015 digital pH meter pre-standardized with buffers 4 and 9 to obtain the pH of the various soil samples [26].

Particle size of the soil samples was determined using the Bouyoucos hydrometer method. Fifty grams of soil sample was measured into a beaker and 100 ml of the dispersing solution was added to prevent aggregation and rapid settling of the soil particles. Water (300 ml) was also added and the sample solution was allowed to stand overnight so as to equilibrate. It was transferred into a 1000 ml-measuring cylinder and made up with water to about 700 ml. The hydrometer was dipped gently into the cylinder and water was still added to the 1000 ml-mark. The solution was stirred vigorously with a stirrer and the hydrometer and temperature readings were taken after 40s. The solution was allowed to stand for 2 h without agitation and the hydrometer as well as temperature readings were taken again [26].

Total organic matter (TOC) was determined using Walkey-Black method. Soil sample (0.5 g) was weighed into a conical flask, 10 ml of potassium dichromate and 20 ml of concentrated sulphuric acid was added. The mixture was left for 30 min and 100 ml of distilled water was introduced. The solution was left to cool and 3 drops of ferroin indicator was added. The mixture was eventually titrated against ammonium ferrous sulphate [27].

2.3.2 Determination of mineral content

Two grams of the dried soil sample was weighed and digested with 10 ml of aqua regia concentrated $HNO₃$ and HCl (1:3) [28] - over a hot plate to almost dryness. The digests were treated with 20 ml of 10% $HNO₃$ and filtered into a 25 ml-volumetric flask. It was made up to mark with distilled water and stored in capped plastic bottles before analysis.

For the determination of heavy metals content of the harvested vegetable samples, one gram of the dried vegetable samples was weighed, soaked in 20 ml of concentrated $HNO₃$ and HClO4 mixture in ratio 3:1 and left overnight for complete contact. The samples were digested until the solution became transparent and digestion was stopped when the sample solution reduced to about 5 ml. This was cooled and diluted with 0.1 M HNO₃. The sample solution was stored in a covered plastic bottle prior to analysis by atomic absorption spectrophotometer (Buck Scientific 210 VGP Model) [29,30]. The Limit of Detection (LOD) is taken as three times the signal/noise ratio [31,32].

2.3.3 Bio Concentration Factor (BCF)

The expression of Ghosh and Singh [33] was used for the evaluation of bioconcentration factor which is an indicator of the ability of the vegetables to accumulate the heavy metals considered in this study. In line with Abdu *et al.* [34] and Odukoya [35], this is also referred to as the metal transfer factor with the following expression:

$$
= \frac{\text{Concentration of metal in plant tissue} \left(\frac{\text{mg}}{\text{kg}}\right)}{1 - \frac{\text{mg}}{\text{kg}}}
$$

Concentration of metal in soil $(\frac{mg}{kg})$

2.3.4 Determination of geoaccumulation index (Igeo)

The expression of Muller in 1969 [*Igeo* = $log_2(C_n/1.5B_n)$] as used by several authors such as Mohiuddin et al. [36], Nowrouzi and Pourhabbaz [37] as well as Odat [38] with the descriptive classes for increasing *Igeo* values (see Table 1) was used for the determination of geoaccumulation index. This is to assess the enrichment of metal concentration in the soil samples above baseline concentrations [39] where C_n is the measured total concentration of the metal n in the soil and B_n is the background value for the metal *n* as provided by Turekian and Wedepohl [40]. The correction factor (1.5) was used for possible variations of the background data arising from lithogenic effects [37].

2.3.5 Determination of Contamination Factor (CF) and Pollution Load Index (PLI)

The procedure of Tomlinson et al. [41] was followed for the determination of Pollution Load Index (PLI). For this, contamination factor (CF) of each metal from the ratio of concentration of the metal to that of the background concentration of the same metal (CF = C_{Meta} concentration/ $C_{\text{Background}}$ concentration of same metal) was assessed. In line with Mmolawa et al. [39], the extent of contamination of soil samples by the heavy metals considered can be evaluated using the contamination factor where CF < 1, $1 \leq$ CF \leq 3, $3 \leq$ CF \leq 6 and CF $>$ 6 depict low contamination, moderate contamination, considerable contamination and very high contamination, respectively. The site

Adapted from: Nowrouzi and Pourhabbaz [37]

PLI was estimated by taking the fifth root of the product of the five highest contamination factors [41], i.e.

Pollution Load Index(PLI) $=\sqrt[n]{CF1 \times CF2 \dots \times CFn}$

Where n = number of contamination factors

2.4 Statistical Analyses

Experimental data represent means of triplicate determinations. The IBM Statistical Package for Social Scientists (Version 21) was used to carry out the One-Way Analysis of Variance (ANOVA) with statistical difference evaluated via the Duncan multiple tests.

3. RESULTS

3.1 Soil Physicochemical Analysis

As pointed out in Ekmekyapar et al. [42], some of the factors that determine the level of heavy metal accumulation and distribution in soil and plants include soil physicochemical properties like: pH, organic matter, clay content, among others. These authors, i.e. Ekmekyapar et al. [42], added that heavy metal is adsorbed by organic matter and silt/clay fraction.

Statistical analysis of the physicochemical properties of soil samples obtained from the different farmlands as shown in Table 2 revealed that there was a statistical significant difference $(p < 0.05)$ for all the parameters tested. The highest level of pH, organic matter, clay, silt and sand were found in soil samples from Isikan, Ogbese, Aule, Aule and Ogbese farmlands, respectively.

3.2 Soil Heavy Metals' Content

Result of the heavy metals' concentration in soil samples obtained from the different farmlands is shown in Table 3. Highest level of copper was

found in soil samples from Aule while Isikan farmland had significantly ($p < 0.05$) highest concentration of chromium. Soil samples from these two farmlands (Aule and Isikan) also had the highest nickel and lead contents. Cadmium was only detected in soil samples from Isikan farmland.

3.3 Geoaccumulation Index (Igeo), Contamination Factor (CF) and Pollution Load Index (PLI)

Results of the Igeo, CF and PLI values of soil samples from the five farmlands are shown in Tables 4 and 5, respectively. In line with Mmolawa et al. [39], CF indicates the extent of contamination of the soil samples by the heavy metals considered while PLI gives a simple but comparative assessment of site quality.

3.4 Vegetable

Heavy metals' contents of the harvested *A. hybridus* from the different farmlands and their bioconcentration factor (BCF) are shown in Table 6 and 7. The statistical analysis revealed that vegetables from Army Barracks, Isikan and Ogbese farmlands had significantly highest concentration of copper, nickel and chromium, respectively. Meanwhile, the cadmium and lead contents of all the vegetable samples were below the LOD.

4. DISCUSSION

According to Olorunfemi et al. [44], soil pH determines soil life and availability of essential soil nutrients for plant growth. These authors added that soil pH is governed principally by parent material, rainfall and type of vegetation. The pH of top soil under cultivation becomes reduced as a result of organic acids from plant roots, continuous use of acid-forming fertilizers, plant removal as well as replacement of calcium and magnesium by hydrogen.

Table 2. Physicochemical properties of soil samples from the different farmlands

Values are the means of three replicates± standard error.

Means followed by different letters are significantly different (p < 0 .05) according to Duncan post-hoc test

Table 3. Concentration of heavy metals (mg/kg) in soil samples

Values are the means of three replicates ± standard error.

Means followed by different letters are significantly different (p <0.05) according to Duncan post-hoc test.

LOD = Limit of Detection

**Adapted from: Kamunda et al. [43]*

Site	Сu	Ni	Сr	Cd	Pb	
Aule	-1.76	-2.38	-3.74		-0.39	
Army Barrack	-3.23	-6.62	-3.98		-1.02	
Ogbese	-5.25	-8.64	-5.55	$\overline{}$	-3.51	
Isikan	-2.31	-2.03	-2.80	-1.79	-0.12	
Ilara	-3.10	-4.67	-3.88	$\overline{}$	-0.95	
Mean	-3.13	-4.87	-3.99	-0.36	-1.19	

Table 4. Geoaccumulation index for heavy metals in the soil samples

Values are the means of three replicates ±standard error.

Means followed by different letters are significantly different (p < 0.05) according to Duncan post-hoc test. LOD = Limit of Detection

Values are the means of three replicates±standard error.

Means followed by different letters are significantly different (p < 0.05) according to

Duncan post-hoc test

As noted in Osakwe [45], pH values between pH 2 - 6 greatly favour the availability and mobility of trace heavy metals. In the current study, only pH of soils samples from Army Barracks farmland (the most acidic) fall within this range which will, thus, favour the availability and mobility of trace heavy metals. In line with Soil Survey Staff [46], the challenge of nutrient deficiencies may arise when soil pH is > 7.8. With the exception of soil samples from Isikan farmland, the pH of soil samples from the different farmlands fall within the range required for full utilization of soil nutrients.

On the other hand, organic matter is important to plant life for the maintenance of soil fertility [45]. Soil organic matter is made up of accumulation of partially disintegrated and decomposed plant material as well as animal residues with other organic compounds produced by soil microbes in the decay process [44]. The experimental results as shown in Table 2 with soil samples from Ogbese farmland having the significantly highest percentage of organic matter suggest that soil samples from this farmland have the greatest ample litter cover, organic inputs, root growth and decay as well as abundant fauna [44].

Following the USDA textural classes of soils as provided in FAO [47], the textural classes of soil samples from the different farmlands are: clay, clay loam, loamy sand, sandy loam, sandy loam for Aule, Army Barracks, Ogbese, Isikan and Ilara farmlands, respectively. In line with Jaja [48], fine-textured soil samples (clayey soils) from Aule farmland have the tendency to hold more water and drain slowly. Generally, the loamy soil samples from Army Barracks, Isikan and Ilara farmlands are able to hold water well, drain easily, and are easy to work with in agricultural practices. Meanwhile, the sand (coarse-textured) soils from Ogbese farmland will drain fast after rainfall or irrigation which make them liable to nutrient losses via leaching [48].

Result of the heavy metals analyses as shown in Table 3 revealed that the levels of copper, nickel, chromium, cadmium and lead in all the farmland soil samples are below the maximum allowable concentration for heavy metals in soil set by EU and FAO/WHO Guidelines provided in Kamunda et al. [43]. Hence, the farmland soils are safe for agricultural activities.

Outcome of the Igeo assessment revealed that concentrations of all heavy metals in the soil samples are not enriched above the baseline concentration. Following the descriptive class of I_{geo} values provided in Table 4, only the soil samples from Isikan farmland was found to be in Class 1 (within the uncontaminated to moderately contaminated class), all other farmland soil samples belong to Class 0 which is the uncontaminated category. Also, based on the classification of Mmolawa et al*.* [39] with respect to CF, all the farmland soil samples have low level of contamination by the heavy metals except Aule and Isikan farmlands which are moderately contaminated by lead. Results of the PLI as calculated from the contamination factors shown in Table 5 indicate perfect quality of the farmlands i.e. no overall pollution.

Experimental results of heavy metals contents in the harvested *A. hybridus* from the different farmlands (Table 6) showed that their uptake were at different capacities. Copper is an essential micro-element to plant growth [49,50] but its concentration becomes toxic when above 20 µg/g [49]. According to the WHO standard given in Ogundele et al. [50], the permissible limit of copper is 10 mg/kg. This suggests that only the consumption of *A. hybridus* from Ogbese and Ilara farmlands meet up with the acceptable level of copper for human consumption and as stated

in Kayastha [51], consumption of vegetables from other farmlands with copper concentration > 10 mg/kg, may give rise to health challenges like anaemia, kidney damage, stomach and intestinal irritation.

Only the vegetable samples from Ogbese and Ilara farmlands had their nickel and chromium concentration below the permissible limit of 10 mg/kg and 1.30 mg/kg, respectively, as given by WHO in Ogundele *et al.* [50]. To a large extent, the overall low level of chromium recorded in the harvested vegetable samples from the different farmlands is in line with Ogundele et al*.* [50] that the uptake of chromium by plant shoot is usually low.

Although concentrations between 5 - 700 mg/kg and 30 - 300 mg/kg have been indicated as phytotoxic levels for cadmium and lead respectively in plants [42], as earlier mentioned, the concentration of these two heavy metals in the harvested *A. hybridus* were found below the detection limit (Table 6). This showed that consumption of these vegetable samples would not lead to cadmium and lead poisoning as the concentrations of these heavy metals were far below the FAO/WHO Codex maximum level of 0.20 mg/kg and 0.30 mg/kg for cadmium and lead, respectively, in leafy vegetables [35,52].

The statistical analysis of the BCF (Table 7) showed that *A. hybridus* from Ogbese farmland with significantly highest BCF, had the greatest ability to accumulate three of the heavy metals considered in this study (copper, nickel and chromium). Meanwhile, the BCF of cadmium and lead could not be evaluated as their concentrations in the harvested vegetable samples were found below the limit of detection (see Table 6). This indicates that *A. hybridus* used for this investigation is a poor bioaccumulator of cadmium and lead.

5. CONCLUSION

The research outcome revealed that most of the farmland soils have acceptable physicochemical properties with safe levels of heavy metals for agricultural activities. Notwithstanding, some of the harvested *A. hybridus* still had harmful concentration of the studied heavy metals. Overall, the possibility of heavy metals' contamination in vegetables grown in the studied area shows the need for the cultivation of vegetables which are extremely poor bioaccumulators of heavy metals in these

farmlands. To ensure human health safety, future work is required to investigate the level of heavy metals in other farmlands within Akure which are yet to be studied.

COMPETING INTERESTS

The authors declare that no competing interests.

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