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Journal of Pure and Applied Science

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An official Publication of
College of Science
Joseph Sarwuan Tarka University,
Makurdi.



Estimation of Target Hazard Quotients and Potential Health Risks for Metals by Consumption of African Spinach (*Amaranthus hybridus* L.) Grown along the Bank of River Kaduna

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Received: 21/05/2023 Accepted: 26/06/2023 Published online: 03/07/2023

Abstract

Heavy metals have been mostly evaluated in terms of their concentration in crops but have not been always related to the menace of ill-health they pose to the populace. There is inadequate information on human health risk index associated with the consumption of heavy metal contaminated African Spinach (*Amaranthus hybridus*) in relation to location of massive production in Nigeria. This study was conducted to evaluate the heavy metals; Cd, Ni, Pb, Zn, Cu, Fe and health risk associated with the consumption of *Amaranthus hybridus* grown along the bank of River Kaduna. Samples were collected from five (5) sampling stations within the period of January to March, 2020 and were analyzed using Atomic absorption spectrometry. About 22km was covered along the bank of the river and the average distance between the stations is about 4.4km. Data collected were analysed using descriptive statistics. The order of the heavy metal concentrations were Ni>Pb>Cd>Cu>Fe>Zn, whereby the metal concentrations in Cd (1.20–2.06mg/kg) and Pb (3.10–3.80mg/kg) in most samples exceeded the limits set by World Health Organization and the guidelines set by the Food and Agriculture Organization. A health risk analysis based on the target hazard quotient (THQ) yielded values <1 for all metals except Cadmium, while for the hazard index, all the metals exceeded the limit of 1 which indicated that the samples are likely to be of health concern. For permissible maximum tolerable daily intake in the metals studied, Cd and Pb exceeded WHO/FAO PMTDI of 0.064 and 0.210 respectively. The activities around the bank of the river and irrigation of the vegetable with water contaminated with industrial effluents may have contributed significantly in raising the concentration of Cd and Pb above the WHO/FAO set standard of 0.2mg/kg and 0.3mg/kg respectively. Actions to reduce the concentration of heavy metals in African Spinach from these stations should be carried out to avoid their health hazard on consumers.

Keywords: Hazard quotient; health risk assessment; heavy metals; African Spinach; River Kaduna

Introduction

Amaranthus is a cosmopolitan genus that has between 60 to 70 species. They are cultivated for their leaves, seeds and are used as ornamental plants [1]. The species common in Nigeria is *Amaranthus hybridus* L. occasionally referred to as African spinach [2]. *A. hybridus* have considerable quantity of proteins, fat, fibre, carbohydrate and calorific value, mineral elements, vitamins, amino acids and commonly low level of toxicants [3]. Consuming vegetables frequently in diets can have numerous health advantages by decreasing many health related diseases and also helps in converting the fats and carbohydrates into energy [4]. Vegetables, particularly leafy vegetables, cultivated in heavy metal polluted soils, accumulate greater amounts of metals than those grown in unpolluted soils [5]. Heavy metals are important pollutants and are found in the surface and tissues of vegetables in environments with such pollutants [6]. Plant species have a range of abilities in extracting and accumulating heavy metals. There are discoveries indicating that some species may accumulate certain heavy metals, causing grave health risk to human health when plant based food stuff are

consumed [7]. In Nigeria, the use of contaminated water in the immediate environments of big cities for growing vegetables is a common practice. Although this water is believed to be rich source of organic matter and plant nutrients, however, it also contains considerable amount of soluble salts and heavy metals like Fe, Mn, Cu, Zn, Pb, Ni, Cd, Cr, and Co [8]. When such water is used for cultivation of crops for a long time, these heavy metals may accumulate in soil and maybe poisonous to the plants and also cause deterioration of soil [9]. Kaduna River collects over 500, 000 m³/day of untreated waste from many industries in Kaduna through 53 tributaries. Some of the industries comprises of United Nigeria Textiles Plc and Nigerian Brewery Ltd (NBL) [10]. These industries are channeled into the Makera rivulet that drains northwards and discharges into Kaduna River which flows across Kaduna town. It is a major source of water supply to the human population and various aquatic plants and animals. The drain is surrounded by the Nasarawa, Makera, Down quarters and Kinkinau communities. The prevailing activities nearby this

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communities include, farming, fishing, cattle-rearing and minor quarrying among others [11]. [11] carried out analysis of heavy metals concentration in soil and *Amaranthus retroflexus* grown on irrigated farmlands in the Makera area in Kaduna, Nigeria and recorded mean concentration of Cd (0.013-2.120, Cr (0.58-2.80) and Fe (331.6-1252) in vegetable samples which were higher than the WHO/FAO maximum permissible limits (Cd – 0.2, Cr – 1.3, Fe – 425mg/kg). Some heavy metals such as zinc, copper and iron are necessary for the proper functioning of the human body when their levels are low, intake of too much quantities of these metals is harmful. Some other metals such as cadmium, nickel and lead are not required by human body and can produce grave hazard to human health [12]. The major aim of this research is to identify and examine the level of the following heavy metals: Cadmium (Cd), Lead (Pb), Nickel (Ni), Zinc (Zn), Copper (Cu) and Iron (Fe) in *A. hybridus* irrigated with water from River Kaduna. The objectives of this research are to determine the concentrations of the above named six heavy metal pollutants in *A. hybridus* irrigated with water from River Kaduna, to compare the level of concentration of the heavy metals in *A. hybridus* with FAO/ W.H.O recommended permissible limits in vegetables, to estimate daily intake of heavy metals from consuming *Amaranthus hybridus* grown along the bank of River Kaduna, to estimate the target hazard quotients and hazard index for metals by consumption of *Amaranthus hybridus* grown along the bank of River Kaduna.

Materials and methods

Study area

The study area was the bank of River Kaduna in Kaduna State. Kaduna state shares common boundaries with Niger, Zamfara, Katsina, Kano, Plateau and Nasarawa states (Fig. 1). To the south-west, the state shares common boundary with Federal Capital Territory (FCT), Abuja. Kaduna lies on longitude 7°25' east of the Greenwich meridian and latitude 10°30' north of the equator [13]. The entire land structure of the state is mostly undulating plateau with parts of the state like Zaria town, Kagoro and Kwoi areas having protruding hard resistant granite rocks as a result of weathering of formerly existing Precambrian rocks through the ages [14].

Sampling stations

The experimental site was the bank of River Kaduna. About 22km was covered along the bank of the river with five sampling stations. The average distance between stations is about 4.4km. *Amaranthus hybridus* grown in all study stations were irrigated by water from River Kaduna. Station 1 was located within the Gamji Park. Little discharge of sewage and refuse from the scanty residential areas and the park

was observed. Station 2 was located about 500m from the railway bridge behind Ahmadu Bello Stadium. The river at this point receives discharges from residential areas, hospitals, police station and barracks. Station 3 was located by the Western by-pass bridge to Zaria (Nasarawa bridge). River receives drainage from the Kakuri, Nasarawa, Rafindadi and Makera rivulets that receives drainage from the various heavily polluted industrial establishment located in Kaduna South. Station 4 and 5 were located downstream at an average distance of 4km.

Sample collection

Heavy metals (Cd, Ni, Pb, Zn and Fe) were analysed from *A. hybridus* samples collected from five (5) sampling stations within the period January to March, 2020. This is the peak period of dry season in Kaduna where the vegetable grown along the bank of the river can only be irrigated by water from River Kaduna and during this period the river water is most likely to contain the highest amount of contaminants [16]. About 22km was covered along the bank of the river and the average distance between the stations is about 4.4km. A total of 45 vegetable samples were collected. Samples were collected three times in a month from each sampling station for three months. The sampling time was between 9am to 11am. *Amaranthus* was harvested by cutting above the second leave from the ground using a knife.

Sample preparation

Sample preparation was carried out according to [17]. The vegetable samples were washed with 20% (v/v) nitric acid and later washed with ordinary water then further rinsed using distilled water. The sample were cut into pieces with knife and were air dried in the laboratory for 5 days before oven dried at 105°C for about 24h. The samples were pounded into powder in a mortar with a pestle. The samples were then filtered through a 2mm colander and were kept in polyethylene leather for further analysis.

Sample digestion

Sample digestion was done according to [18]. 0.5g of sieved sample was weighted into 100cm³ beaker. A mixture of 5cm³ concentrated HNO₃ and 2cm³ HClO₄ were added to dissolve the sample. The beaker was heated at moderate temperature of 110°C on a hot plate for 1h in a fume hood until the content was about 2cm³. The digest was cooled, filtered into 50cm³ standard volumetric flask and made up to the mark with distilled water.

Sample analysis

The filtrates were taken and analyzed for cadmium, nickel, lead, zinc, copper and iron using Atomic Absorption Spectrometer (AAS) (Pye Unicam SP 9). Atomic Absorption Spectrometry (AAS) is a sensitive method for the qualitative and quantitative measurement of more than 60 metals/elements [11].

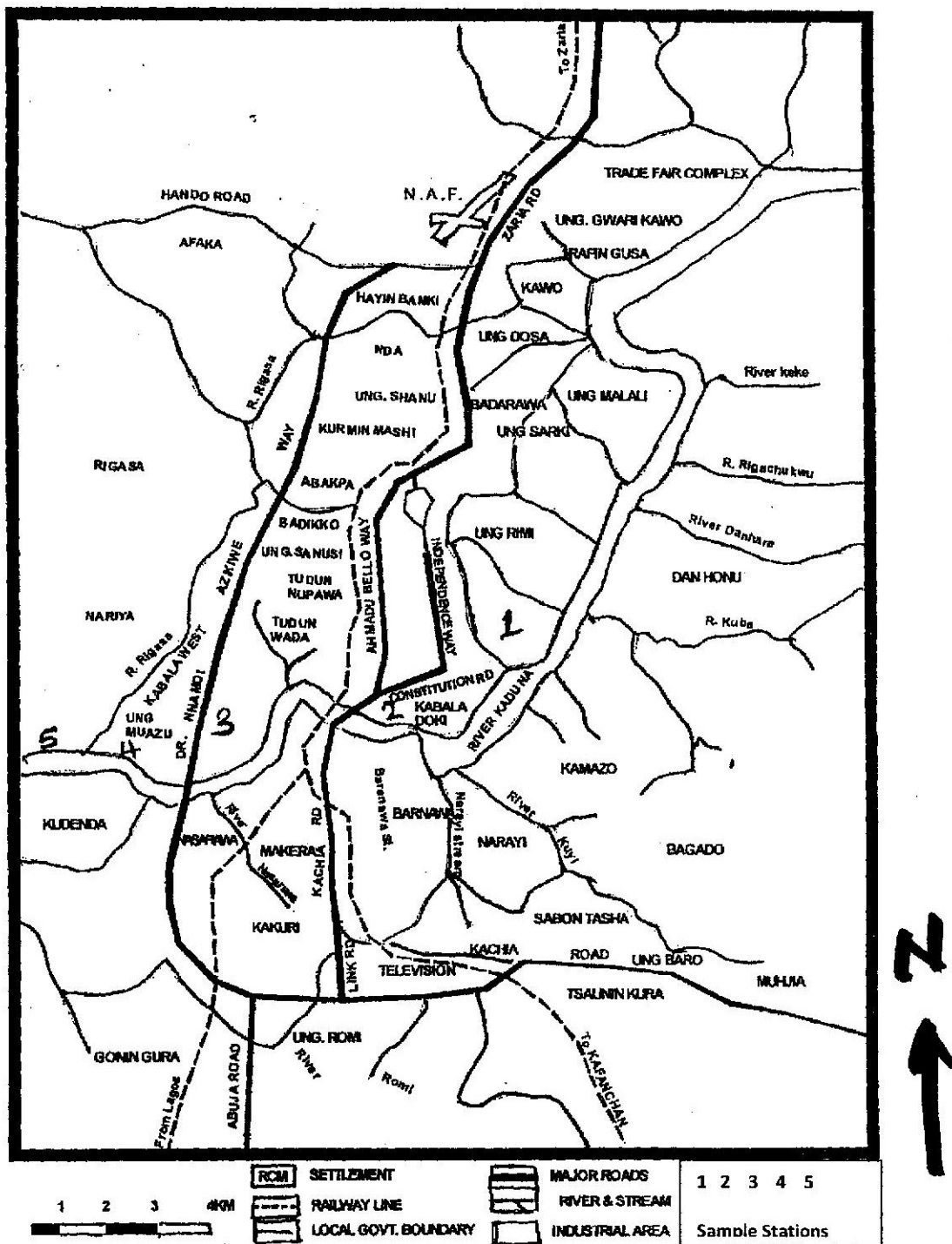


Figure 1: Settlement Distribution in Kaduna Town showing the 5 sampling stations along The Kaduna River.

Source:[15]



Risks assessment factors

Estimated daily intake of metal (EDIM)

The EDIM was calculated as a product of concentration of metal in *Amaranthus hybridus*, conversion factor and daily vegetable intake per average body weight using equation 1 [11].

$$EDIM = \frac{C_{\text{metal}} \times C_{\text{factor}} \times C_{\text{foodintake}} (DIM)}{\text{Averagebodyweight}} \quad (1)$$

Where EDIM is the estimated daily intake of metal, C_{metal} is the heavy metal concentration in vegetable (mg/kg); C_{factor} is the conversion factor (0.085); DIM is the daily vegetable intake, 65g/day; average body weight of 60 kg.

Hazard index

Hazard index (HI) is a vital index that measurestotal likely impacts that can be posed by exposure to more than one contaminant[4]. When the HI is greater than 1, the exposure is likely to cause apparent health impact from ingesting pollutants contain in food stuff. The HI is the arithmetic sum of the HQs for each pollutant as in equation 3 [4].

$$HI = \sum HQ \quad (3)$$

Statistical analysis

Data from the chemical analysis were subjected to descriptive statistics. Results were presented as mean \pm standard deviation of the mean.

Targeted hazard quotient

Hazard quotient is a fraction of the possible exposure to an element and level at which no negative effects are anticipated. When the hazard quotient (HQ) is < 1 , it means no potential health effects are expected from exposure, but when the HQ exceeds 1, it signifies potential health risks due to exposure and it was calculated using equation 2[11].

$$THQ = \frac{EF \times ED \times FIR \times C \times 10^{-3}}{RfD \times BW \times AT} \quad (2)$$

EF = 365 days/year; ED = 55 years, FIR = 65g/person/day; C = metal concentration (mg/kg); RfD = oral reference dose (Cd, Ni, Pb, Zn, Cu, Fe were 0.001, 0.020, 0.0035, 0.300, 0.040, 0.700 respectively (USEPA, 2016); WAB is the average body weight (60kg) and TA is average time for non-carcinogens (ED = 365 days/year).

Results and Discussion

Concentration of heavy metals in *Amaranthus hybridus* from sampling stations

The heavy metal concentrations in the studied *Amaranthus hybridus* showed significant variations (Table 1). The metal concentration ranged from 1.20-2.06mg/kg for Cd, from 2.60-10.00mg/kg for Ni, from 3.10-3.80mg/kg for Pb, from 0.10-0.45mg/kg for Zn, from 0.08-1.60mg/kg for Cu, from 0.60-1.50mg/kg for Fe. By comparing the concentrations of metals among samples from all stations, Ni concentrations were highest in all the samples under study from all stations.



Table 1: Mean Concentration (\pm SD) of Metals in the Experiment Sample of *Amaranthus hybridus* Compared with the WHO/FAO Standards (mg/kg)

Heavy Metal	Station					WHO/FAO
						Standard
	1	2	3	4	5	
Cadmium	1.60 \pm 0.36	1.80 \pm 0.14	1.20 \pm 0.29	2.06 \pm 0.04	1.60 \pm 0.31	0.20
Nickel	8.00 \pm 0.31	10.00 \pm 0.82	8.00 \pm 1.42	2.60 \pm 0.31	2.80 \pm 0.24	67.9
Lead	3.10 \pm 0.14	3.20 \pm 0.57	3.70 \pm 0.45	3.80 \pm 0.14	3.70 \pm 0.16	0.30
Zinc	0.15 \pm 0.08	0.10 \pm 0.03	0.45 \pm 0.04	0.40 \pm 0.22	0.25 \pm 0.04	99.4
Copper	0.08 \pm 0.01	0.70 \pm 0.17	0.90 \pm 0.28	1.60 \pm 0.24	0.90 \pm 0.21	73.3
Iron	0.80 \pm 0.08	0.90 \pm 0.29	0.70 \pm 0.22	0.60 \pm 0.22	1.50 \pm 0.25	425

Estimated daily intake of heavy metals from consuming *Amaranthus hybridus* from all stations

The total estimated intake rate for *Amaranthus hybridus* calculated was shown in Table 2. The estimated daily intake

of Cd, Ni, Pb, Zn, Cu, and Fe through consumption of the vegetable ranged from 0.11-0.18mg/kg/day, 0.23-0.92mg/kg/day, 0.28-0.34mg/kg/day, 0.01-0.04mg/kg/day, 0.01-0.14mg/kg/day and 0.05-0.13mg/kg/day respectively.

Table 2: Estimated Daily Intake (mg/kg/day) of Heavy Metals from Consumption of *Amaranthus hybridus* from the Respective Station

Heavy Metal	Station					WHO/FAO
	1	2	3	4	5	PMTDI
Cadmium	0.1473	0.1658	0.1105	0.1897	0.1373	0.064
Nickel	0.7367	0.9208	0.7367	0.2394	0.2578	5.000
Lead	0.2855	0.2947	0.3407	0.3499	0.3407	0.210
Zinc	0.0138	0.0092	0.0414	0.0368	0.023	15.000
Copper	0.0073	0.0644	0.0828	0.1473	0.0828	2.000
Iron	0.0725	0.0828	0.0644	0.0553	0.1381	15.000

Targeted HQ and HI from metal exposure from the studied samples

The calculated target HQ (THQ) and HI values were presented in Table 3. The findings showed that the THQ

values of all heavy metals were < 1 in all samples except for Cd in samples from station 4. The result for HI showed that all samples have HI values > 1.



Table 3:THQ of Individual Metals and their Health Index (HI) from Consumption of *Amaranthus hybridus* from the Respective Station

Heavy			Station		
Metal	1	2	3	4	5
Cadmium	0.8667	0.8667	0.8667	1.6250	0.8667
Nickel	0.2167	0.5417	0.2167	0.0542	0.0542
Lead	0.4643	0.4643	0.4643	0.4643	0.4643
Zinc	0.0002	0.0002	0.0014	0.0007	0.0004
Copper	0.0011	0.0108	0.0108	0.0217	0.0217
Iron	0.0006	0.0006	0.0007	0.0007	0.0009
HI	1.5496	1.8843	1.5606	2.1666	1.4082
THQ and HI > 1 indicates potential health risk.					

Concentration of metals

The various analyzed heavy metals were found to have bioaccumulated in the whole tissue of *A. hybridus* sampled in the order of magnitude Ni>Pb>Cd>Cu>Fe>Zn. In all the 45 samples of *A. hybridus* from the five sampling stations, the Ni concentration in all the 45 samples, the Zn concentration in all the 45 samples, the Cu concentration in all the 45 samples, the Fe concentration in all the 45 samples, were below the recommended maximum levels of contaminants in food as set by [19] except for Cd and Pb which were higher. The lowest level of Cd was found in Station 3, the lowest level of Ni was found in Station 4, the lowest level of Pb was found in Station 1, the lowest level of Zn and Cu were found in station 2, and the lowest level of Fe was found in Station 4. The result has shown that *A. hybridus* grown on all stations are good for consumption except it prevailing Cd and Pb whose presence is above the threshold level of tolerance. The presence of Cd and Pb above recommended levels could be as a result of their presence in refuse and sewage dump in river water used for irrigation at station 1 and 2 and industrial effluents discharged at station 3. This result agree with the work of [17] which assessed the heavy metal levels in selected vegetables obtained from irrigated farmlands in North central Geo-political Zone of Nigeria in which Cd and Pb were found to be above the recommended maximum levels of contaminants in Spinach and Okro. Cadmium (Cd) pollution of soil and food crops is a worldwide environmental problem that has arisen from unrestricted industrial development, flawed settlement expansion and rigorous agricultural practices [20]. Being a poisonous element, Cd poses high hazards to soil value, food security, and human wellbeing. Land is the ultimate avenue of waste disposal and utilization therefore, Cd discharged from different sources, ultimately reaches soil,

and then later bio-accumulates in food crops [21]. Cadmium poisoning has been reported from many parts of the world. It is one of the global health problems that affect many organs and in some cases it can cause deaths annually. Long-term exposure to cadmium through air, water, soil, and food leads to cancer and organ system toxicity such as skeletal, urinary, reproductive, cardiovascular, central and peripheral nervous, and respiratory systems [22]. Lead can be found in soil from active industry or in the environment from disposal of lead-containing products, such as batteries [23]. Lead exposure can have serious consequences for the health of children. At high levels of exposure lead attacks the brain and central nervous system, causing coma, convulsion and even death. Children who survive severe lead poisoning may be left with intellectual disability and behavioural disorders [24]. Lead exposure also causes anaemia, hypertension, renal impairment, immunotoxicity and toxicity to the reproductive organs. The neurological and behavioural effects of lead are believed to be irreversible [25].

Health risk assessment

The dietary exposure approach is a reliable tool for investigating a population's diet in terms of intake levels of nutrients, bioactive compounds and contaminants, providing important information about the potential nutritional efficiencies or exposure to food contaminants [4]. The health risk assessment was calculated to assess the level of exposure from ingestion of heavy metal in *A. hybridus* grown at the bank of River Kaduna. Different routes of exposure of heavy metals to human do exist, yet the most important route is the food chain [26]. The estimated daily intake of metals (EDIM), THQ and Health Index (HI) were calculated and the EDIM showed that Cd and Pb (0.11- 0.18mg/kg,



0.28-0.34mg/kg) were consumed above the PMTDI endorsed by WHO/FAO of 0.064mg and 0.21mg/person/day respectively. This was in agreement with the work of [4] where the estimated daily intake of Cadmium was 0.11-0.33mg/kg. It is however in contrast with the work of [27] where the estimated daily intake of Cadmium (0.00003) in lettuce consumed at Chalawa Area, Kano was below the recommended standard. The Targeted Hazard Quotient is a proportion of the probable exposure to an element and level at which no negative impacts are expected. When the hazard quotient (HQ) is < 1 , it means no potential health effects are expected from exposure, but when the HQ exceeds 1, it signifies potential health risks due to exposure [11]. The parameter defines the exposure duration and the risk with that period. This finding showed that HQ values of all heavy metals were < 1 in all vegetable samples except for Cd at Station 4 having THQ > 1 . The highest THQ observed in Station 4 is 1.6250. The high HQ observed in Cd for *A. hybridus* at station 4 has significant carcinogenic health effect to it consumers [4]. High HQ for Cd was also reported by [4] in irrigated vegetable and fruits cultivated in selected farms around Kaduna metropolis. Lower THQ for Cd, Pb, Cu, Zn and Ni was reported by [28] in vegetables from waste water irrigated area in Lagos metropolis. Hazard index (HI) is a vital index that assesses overall likely impacts that can be posed by exposure to more than one contaminant. When the HI is greater than 1, the exposure is likely to cause obvious health effect from consuming pollutants contain in food stuff. The hazard index population through consumption of *A. hybridus* grown along the bank of River Kaduna indicated HI greater than one ($HI > 1$) for all the five (5) stations. Therefore, the health risk of heavy metals exposure through the food chain is considered relatively high. This is similar to the work of [4] in which Health Index (HI) population through consumption of

selected vegetables in Kaduna metropolis indicated HI greater than one ($HI > 1$). This indicates the consumer's health and quality of life may be affected in the near future as the heavy metals accumulation in long term can lead to bio-magnification.

Conclusion

All the heavy metals found in *A. hybridus* were below FAO/WHO standard except for Cd and Pb whose concentrations were found to be above standard. The estimated daily intake of metals (EDIM) showed that Cd and Pb were consumed above the PMTDI endorsed by WHO/FAO. This findings shows that HQ values of all the heavy metals studied were < 1 in all samples except for Cd having THQ > 1 . The high HQ observed in Cd for *A. hybridus* has significant carcinogenic effects to it consumers. The hazard index (HI) through consumption of *A. hybridus* grown along the bank of River Kaduna is greater than one. Leafy vegetable produced on open field or with contaminated irrigation water are known to have high concentration of heavy metals that pose high risk for healthy living. Hence, there should be continuous monitoring of heavy metals in vegetables consumed by the populace in order to safeguard human health. Awareness about the health implications of consuming such vegetables should be carried out by appropriate authorities since such samples were also considered as bio indicators of environmental pollution. Waste water irrigation for vegetables and food crops should be discouraged as it serves as the major route for heavy metal accumulation in vegetables.

Declaration of conflicting interests

The authors declared no potential conflicts of interest

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Cite this article

Isah M.H., Ameh S.M., Banyigyi A.H. and Tanko D. (2023). Metals by Consumption of African Spinach (*Amaranthus hybridus*.) Grown along the Bank of River Kaduna .FUAM Journal of Pure and Applied Science, **3(1)**:79-87



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