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Abstract: This study was conducted to determine the presence, concentration and bioaccumulation of selected heavy metals in amaranths grown on soils from waste dump sites. The selected heavy metals were analysed using AAS. There was no clear trend on the values for the concentrations of the heavy metals in both the amaranths and their soils from the three fields. When compared with literature reports, the values for the concentrations of the heavy Metals in *Amaranthus caudatus* and their soil samples were generally low. Fe had the highest mean values of 20.17, 17.14 and 18.81 $\mu\text{g g}^{-1}$ in the vegetable samples and 28.63, 34.53 and 34.51 $\mu\text{g g}^{-1}$ in the soil samples from sites A, B and C, respectively, while Co had the lowest mean values of 00.52, 00.02 and 00.06 $\mu\text{g g}^{-1}$ in the vegetable samples and 00.38, 00.53 and 00.35 $\mu\text{g g}^{-1}$ in the soil samples from sites A, B and C, respectively. Significant differences were observed at $P < 0.05$ between the mean values of Cu and Cr in amaranth samples and Fe in the soil samples from the three sites which indicated lack of relationship. The Transfer Factor values were generally less than 1 except for Cr in samples from sites B and C and for Co in samples from site A. Therefore, the bioaccumulation of the selected heavy metals by amaranths were very low and as such, the use of soils from waste dump sites for cultivation of vegetables can be encouraged.

Keywords: Amaranths, bioaccumulation, heavy metals, soils, transfer factor, waste dumps

Introduction

The utilization of vegetables is part of Africa's cultural heritage and they play important roles in the customs, traditions and food culture of the African household (Birnin-Yauri *et al.*, 2011). Amaranth (*Amaranthus caudatus*), a quick – growing green leafy vegetable grows on a wide variety of soils. It is listed among the C4 plant as it can efficiently use CO_2 and suppress its photosynthesis loss (ICAR, 2007). The vegetable can photosynthesize at high rate even under high temperature. Hence it is grown successfully in hot summer and humid conditions (Mensah *et al.*, 2008; ICAR, 2007). It can be uprooted when it is 8 – 10 cm tall (3 – 4 weeks after sowing) or cut and subsequent cuttings are made at 10 – 15 days interval depending on the vegetative growth. Its flowers mature in 90 – 95 days (ICAR, 2007).

Soil is the basic natural source of food production. Plants get most of their nutrients from the soil. In the process of absorbing these nutrients, some are absorbed in large amount depending on their concentrations, soil pH, organic matter content, plant species, age and available form in the soil. Soil contamination by heavy metals and other toxins is generally the result of human activity and this has a negative effect on the productivity, microbiological process of soils, plant growth and development as well as the quality of agricultural products. Although, the content of heavy metals in soils is an important indicator of soil contamination, it is not sufficient to characterize this as environmental hazard as it depends on the forms available, pH, organic matter content, texture, cation exchange capacity (CEC) and moisture condition of the soil.

Similarly, translocation of heavy metals from root system to shoot is also another important factor as it differs from one plant to another and the type of element involved (Amusan *et al.*, 2005; Karezewska *et al.*, 1998; Nirmal *et al.*, 2009). Increase in pH, organic content and CEC has shown to reduce the availability of metals. Similarly, existence of carbonate, sulphate and phosphate in a soil creates an increase in a metal precipitation and consequently decreases the metal availability to the plant (Natasa *et al.*, 2015). The rapid increase in the population of humans in urban areas of Northern Nigeria has made solid waste handling and disposal a major environmental challenge. Most solid wastes contain paper,

food wastes, glasses, synthetic products, batteries, paints, pesticides and metallic containers which are good source of heavy metal accumulation to the soil (Mbong *et al.*, 2014). As a result of high level of poverty, most farmers have resorted to the use of waste dump sites for cultivation of crops or transfer of such soils to farmlands as alternative to industrial fertilizer and manure (Uba and Uzairu, 2008).

The uptake of heavy metals by plants results in the bioaccumulation of metals in plant tissues. Bioaccumulation Factor (BAF) also called Transfer Factor (TF) which is the ratio of the metal concentration in plant to the metal concentration in the soil environment is used to quantify the relative differences in the bioavailability of metals to plants (Uba and Uzairu, 2008). Previous studies on the levels of heavy metal transfer from soils treated with sewage sludge to plants reported highest TF values for Fe reported by Alino *et al.* (2012) and Zn and Fe (Uwah *et al.*, 2009). In both cases, lowest values were reported for Pb. Similarly, Amusan *et al.* (2005) reported highest TF values for Zn and Fe as well as lowest for Pb and Cd in vegetables grown in municipal waste dump sites. Jega local area, Kebbi State, has an area of 891 km² and a population 193,352 as at 2006 census. The geographical coordinates of Jega are 12° 13' 3" North, 4° 22' 45" East. Considering the fact that *Amaranthus caudatus* form the major part of the diet of people of Jega and that the farmers make use of domestic waste as substitute for fertilizer and local manure for its cultivation, there the need to investigate the correlation between the amount of heavy metals in the soil and their uptake by the plant with particular emphasis on the leaves. This research work aimed at evaluating the heavy metal composition in amaranths grown on soils collected from domestic waste dump sites and their level of bioaccumulation, with the view to make appropriate recommendations on the safety of its consumption as well as growing vegetables on waste dump soils.

Materials and Methods

Materials

Sample collection and preparation

At the 8th week of sowing, about 1kg each of the vegetable leaves and 1kg of soils (0 – 30 cm depths) were randomly

collected from three different agricultural fields in which soils from dump sites were freshly deposited. In the laboratory, the vegetables were washed before air drying and pulverized in a porcelain mortar, sieved through 20-mesh sieve and stored in plastic containers for metal analysis (Miroslav and Vladimir, 1999; Hassan *et al.*, 2005). The soils were air-dried, crushed and sieved to separate the fine earth fractions (2 mm) from coarse materials and stored in clean polyethylene bags for metal analysis (Aiboni, 2001).

Quality assurance

All reagents used in this work were of analytical grades and double distilled water was used throughout the analyses. The glass wares, plastic containers, crucibles, mortar and pestle were washed with liquid soap, rinsed with water and then soaked in 15% HNO₃ for 48 h before rinsing with distilled water and dried in an oven at 55°C for 5 h (Haw-Tarn *et al.*, 2004; Uba and Uzairu, 2008).

Methods

Analysis of heavy metals in amaranths

The process was carried out in triplicates by weighing out 1.0 g of each of the air dried and powdered sample in to separate digestion tubes, 30 cm³ of 69.5% (w/w) HNO₃ acid was added to each and heated until about 10 cm³ was left. This was followed with addition of 10 cm³ of 69.5% (w/w) HNO₃ acid and 2 cm³ of 60% HClO₄ acid and the heating process continued until clear solutions were obtained. Each of the digests was diluted with about 20 cm³ of distilled water, boiled for another 15 min, allowed to cool, filtered in to separate 50 cm³ volumetric flasks and made to the mark with distilled water. The solutions were stored in separate screw capped polyethylene bottles (Audu and Lawal, 2006; John, 2000). Blank solution was prepared in the same way but without any sample. The determination of the heavy metals was carried out using AAS at National Research Institute for Chemical Technology (NARICT), Zaria.

Analysis heavy metals in soil samples

The soil samples were prepared in triplicate for heavy metal analysis by refluxing 1.0 g of air dried sample with 10 cm³ of HNO₃ for 45 min. Heating was continued with 10 cm³ of aqua-regia and finally with 10 cm³ HNO₃. The filtrates were diluted to the marks of 50 cm³ volumetric flasks and the determinations were carried out using AAS (Uba and Uzairu, 2008). The Transfer Factor (TF) for each metal was computed using the formula below (Uwah *et al.*, 20009).

Transfer Factor values >1 indicates that the plant has high chance of accumulation of a given heavy metal. For values around 1 indicate that the plant is not influence by the metal. Similarly, for values <1 indicates that the plant exclude the element from uptake. If the plant has higher TF values, it can be used for phytoremediation (Natasa, *et al.*, 2015).

Statistical analysis

The mean and standard deviation of results of 3 x 3 measurements obtained in this work were on dry weight basis and expressed in µg g⁻¹. One way analysis of variance (ANOVA) was used to test for significant difference at a confidence level of P<0.05 between the means of the vegetables as well as those of the soils (John, 2000; Daniel, 2003).

Results and Discussion

Heavy metal composition in amaranths

Table 1 presents the selected heavy metal concentrations in the amaranth samples from the three waste dump sites converted to agricultural fields in Jega. The trends for the contents of the micro nutrient elements were Fe>Zn>Cu>Mn>Cr>Co>Pb, Fe>Cr>Zn>Mn>Pb>Cu>Co and Fe>Cr>Zn>Mn>Cu>Pb>Co as observed in amaranths of sites A, B and C, respectively. The leaves of amaranths generally

indicated low concentration of the heavy metals tested for. The Fe values of 28.63, 34.52 and 18.81 µg g⁻¹ for sites A, B and C, respectively were higher than those of other metals in the amaranth samples from the three sites. Similar observation was made by Audu and Lawal (2006) and BirinYauri *et al.* (2011). This could be related to the role of Fe as a constituent of heme and non-heme proteins in plants (BirinYauri, 2011). The Fe values (17.44 and 18.81 µg g⁻¹) were slightly below the recommended range of 20 – 200 µg g⁻¹ in plant tissues (Audu and Lawal (2006), but all were within the range of 18 - 1000 µg g⁻¹ natural Fe content in folder plants (Adeyeye, 2005).

The observed values were also lower than the values of 100.40 µg g⁻¹ (for bitterleaf), 125.40 µg g⁻¹ (for lettuce), 150.40 µg g⁻¹ (for spinach) 58.80 µg g⁻¹ (for pumpkin leaves) and 75.40 µg g⁻¹ (for water leaf) as reported by Idris and Ndamitso (2009). There was no significant difference at P<0.5 between the means values for Fe in the vegetable samples. Only the value of 6.95 µg g⁻¹ for Zn in samples from site C compared well with 6.63 and 6.86 µg g⁻¹ in dry and rainy spinach samples respectively, reported by Audu and Lawal (2006). Similarly, the value of 7.17 µg g⁻¹ for Zn in samples from site B compared well with the value of 7.71 µg g⁻¹ in tube well water spinach, but lower than the values of 26.17 and 16.38 µg g⁻¹ in sewage water spinach and combination of sewage and tube water grown spinach respectively (Lone *et al.*, 2003). The values were also lower than the values of 70.70 µg g⁻¹ (bitter leafs), 104.30 µg g⁻¹ (lettuce), 81.60 µg g⁻¹ (spinach), 46.70 µg g⁻¹ (pumpkin leaves) and 108.60 µg g⁻¹ (water leaf) as reported by Idris and Ndamitso (2009). Generally, the values for Zn in samples from the three sites were lower than the permissible limit of 15 – 100 µg g⁻¹ for Zn set by European Commission as reported by Uba and Uzairu (2008). There was no significant difference at P<0.05 between the means values for Zn in the vegetables. For Mn, the values of 1.18, 1.40 and 1.83 µg g⁻¹ as reported for samples in sites A, B and C respectively were generally much lower when compared with the values of 109.14 - 832.83 µg g⁻¹ as reported by Uba and Uzairu (2008) in amaranth samples grown in selected dumpsites areas of Zaria.

Similarly, the values were slightly lower than 3.69 – 5.79 µg g⁻¹ and 2.90 – 4.17 µg g⁻¹ ranges of values as reported by Audu and Lawal (2006) in dry and rainy season samples from three areas in Kano. There was no significant difference at P<0.05 between the mean values of Mn in the vegetable. The values of 1.96, 0.54 and 0.24 µg g⁻¹ for sites A, B and C respectively observed for Cu in the amaranth samples were lower than the values of 11.68, 15.06, 10.72, 8.71 and 11.35 µg g⁻¹ as reported by Afshin and Masoud (2008). The values were also lower than the values of 6.20 µg g⁻¹ (bitter leaf), 11.90 µg g⁻¹ (lettuce), 8.10 µg g⁻¹ (pumpkin leaves), 2.10 µg g⁻¹ (spinach) and 16.40 µg g⁻¹ (water leaf) as reported by Idris and Ndamitso (2009). Generally, the values were lower than the range of 5 – 20 µg g⁻¹ recommended as the normal Cu concentration in plants by ICAR (2006). There was significant difference at P<0.05 between the mean values of Cu in the vegetable samples. The values of 0.70 µg g⁻¹, 11.86 µg g⁻¹ and 14.39 µg g⁻¹ were observed for Cr in the amaranths for sites A, B and C respectively. The values for samples from sites B and C were higher than the values of 8.73 µg g⁻¹, 8.18 µg g⁻¹, 8.81 µg g⁻¹, 7.50 µg g⁻¹ and 6.3 µg g⁻¹ reported in selected vegetables (Afshin and Masoud, 2008) and much higher than the value of 0.60 µg g⁻¹ as reported by Audu and Lawal (2006) and <0.01 µg g⁻¹ in spinach as reported by Anthony *et al.* (2007). Significant difference at P<0.05 was observed between the mean values for Cr in the vegetable. The values of 0.52, 0.02, and 0.06 µg g⁻¹, respectively observed for Co in amaranths from sites A, B and C, were higher than 0.68 µg g⁻¹ as reported by Audu and Lawal (2006). No significant difference was

Heavy Metal Composition in *Amaranthus caudatus* from Waste Dump Soils

observed between the mean values for Co in the vegetables. The values for Pb in amaranths from sites A, B and C were 0.47, 0.69 and 0.41 $\mu\text{g g}^{-1}$, respectively. The values were higher than the value of <0.01 as reported by Anthony and Esther (2007), but much lower than the values of 11.23, 14.88, 11.33, 13.11 and 16.99 $\mu\text{g g}^{-1}$ reported in vegetables (Afshin and Masoud, 2008). Similarly, the values were lower than the

normal concentration of Pb (0.1 – 10 $\mu\text{g g}^{-1}$) in plants (Anthony and Balwant, 2009). Similarly, no significant difference was observed between the mean values of Pb in the vegetable samples. The low values observed for the tested heavy metals were indication that the leaves of amaranths from the study areas are safe for consumption.

Table 1: Heavy Metal Concentration in $\mu\text{g g}^{-1}$ dry weight samples of Amaranth

Site	Fe	Zn	Cu	Mn	Cr	Co	Pb
VA	20.17±0.32	9.57±3.15	01.96±0.14	01.92±0.18	00.70±0.05	00.52±0.42	00.47±0.20
VB	17.44±1.62	07.17±1.29	00.54±0.33	01.41±0.29	11.86±1.76	00.02±0.02	00.69±0.14
VC	18.81±0.98	06.95±1.08	00.24±0.06	01.86±0.71	14.39±2.63	00.06±0.03	00.41±0.04

VA, VB and VC represent *Amaranthus caudatus* from fields A, B and C, respectively

Table 2: Heavy metal concentration in $\mu\text{g g}^{-1}$ dry weight samples of soils of Amaranths

Site	Fe	Zn	Cu	Mn	Cr	Co	Pb
SA	28.63±0.84	14.59±5.90	02.88±1.63	11.73±0.47	07.24±1.53	00.38±0.07	04.67±0.34
SB	34.53±0.92	11.79±1.82	02.86±0.28	14.48±0.69	06.94±1.42	00.53±0.08	05.16±0.22
SC	34.51±0.64	12.79±0.60	02.04±0.25	12.09±2.13	05.76±1.16	00.35±0.11	04.28±0.43

SA, SB and SC represent soil samples from fields A, B and C respectively

Heavy metal composition in soils

Table 2 present the heavy metal composition in soil samples, the trend of Fe>Zn>Mn>Cr>Pb>Cu>Co was observed in samples from sites A and C, while the trend of Fe>Mn>Zn>Cr>Pb>Cu>Co was observed in samples from site B. Generally, the values for heavy metals in the soil samples were very low. Like in the vegetables, Fe had the highest mean values (28.63, 34.53 and 34.51 $\mu\text{g g}^{-1}$) which were much lower than 925.93 and 2527.34 $\mu\text{g g}^{-1}$ as reported for soils from dump sites by Amusan *et al.* (2005). Also, they were lower than the ranges of 63.75 – 663.12 $\mu\text{g g}^{-1}$ but were within 1.28 – 488.75 $\mu\text{g g}^{-1}$ (Buszewski *et al.*, 2000). Significant difference was observed in the mean values for Fe in the soils samples. This is an indication that the concentrations of Fe in the soil samples from the three sites were not related. This could be due to the effect of the presence of Fe containing waste materials in one of the waste dump site. The values (14.59, 11.79 and 12.79 $\mu\text{g g}^{-1}$) for Zn were within the range of 1.60 – 120.87 $\mu\text{g g}^{-1}$, but lower than the ranges of 71.25 – 375.00 $\mu\text{g g}^{-1}$ as reported by Buszewski *et al.*, (2000) and 45 – 4014 $\mu\text{g g}^{-1}$ by Anthony and Balwant (2009). The values were also lower than the 63.20 and 102.11 $\mu\text{g g}^{-1}$ as reported by Amusan *et al.* (2005), but were within the range of 3 – 100 $\mu\text{g g}^{-1}$ normal Zn concentration in German soils (Kretzschmar *et al.* (1998). No significant difference was observed at P<0.05 between the mean values for Zn in the soil samples from the three sites. The values (11.73, 14.48 and 12.09 $\mu\text{g g}^{-1}$) observed for Mn were lower when compared with those reported by Uba and Uzairu (2008) and the range of 20 - 800 $\mu\text{g g}^{-1}$ reported as normal Mn concentration in German soils by Kretzschmar *et al.* (1998).

Also no significant difference was observed in the mean values for Mn in the soils. This indicated that the concentrations of Mn in the soil samples were related. The values (7.24, 6.94 and 5.76 $\mu\text{g g}^{-1}$) for Cr were much lower than the values of 65.50 and 76.18 $\mu\text{g g}^{-1}$ (Uwahet *et al.*, 2009). No significant difference was observed at P<0.05 between the mean values for Cr in the vegetable samples. The values for Cu were much lower than the range 30 – 330 $\mu\text{g g}^{-1}$ in Costa Rica soils but were within the range of 1 - 40 $\mu\text{g g}^{-1}$ as normal Cu concentration in German soils (Kretzschmar *et al.*, 1998). The values compared well the values of 1.36 and 3.78 $\mu\text{g g}^{-1}$ reported in soils (Uwah *et al.*, 2009). There was no significant difference in the mean values for Cu in the soils. The values of 0.38, 0.53 and 0.35 $\mu\text{g g}^{-1}$ observed for Co in soils from sites A, B and C respectively were much lower than the values of 36.00 $\mu\text{g g}^{-1}$ and 132.14 $\mu\text{g g}^{-1}$ in soils from dump sites

(Amusan *et al.*, 2005). The values of 4.67, 5.16 and 4.28 $\mu\text{g g}^{-1}$ for Pb observed in soils of sites A, B and C, respectively were lower than the values of 63.58 and 418.58 $\mu\text{g g}^{-1}$ (Amusan *et al.*, 2005), but were within the ranges of 4.80 – 60.25 $\mu\text{g g}^{-1}$ and 0.50 – 15.45 $\mu\text{g g}^{-1}$ (Buszewski *et al.*, 2009). They values were slightly higher than the values of 2.95 and 3.58 $\mu\text{g g}^{-1}$ (Uwahet *et al.*, 2009). Like in the values for Zn, Cu, Mn, Co and Cr, there was no significant difference in the mean values for Pb in the soil samples. The low values for the selected heavy metals observed in the soil samples were indications that the wastes (mostly domestic) contained little quantities of the heavy metals.

Mobility of heavy metals from soil to amaranths

The Transfer Factor (TF) values for the heavy metals presented in Table 3 are indicators of the bio-mobility and transportation of the metals to the upper shoot of amaranths from the soil. The factors were based on the root uptake of the metal and discount the foliar absorption of atmospheric metal deposits. From the values obtained for TF in this work, Fe had values that were lower than 1 but slightly higher than 0.5 which indicated that the amaranths had less chance of Fe accumulation. According to Sajjad *et al.* (2009), if the transfer factor of a metal is greater than 0.5, the plant may have a greater chance of the metal contamination by anthropogenic activities. The TF values for Zn were also lower than 1 and slightly higher than 0.5. Values ranging from 0.4 – 1.2 were reported in selected vegetables by Kashif *et al.* (2009). In accordance with the observation made by Natasaet *et al.* (2015), the values obtained in this work indicated that Zn may have the chance of accumulation in amaranths; and therefore amaranths can be used as possible bio-indicator of Zn pollution. The TF values for Cu from the three sites were lower than 1, while only for samples from site A was slightly greater than 0.5. The values for samples from sites B and C compared well with the reported values of 0.10, (for Zaria dump sites H and GL) and 0.18 (for dump site R) as reported by Uba and Uzairu (2008) as well as 0.18 as reported by Kashif *et al.* (2009).

Table 3: Transfer factor (TF) for the heavy metals from soil to Amaranth samples

Sites	Fe	Zn	Cu	Mn	Cr	Co	Pb
A	0.71	0.66	0.68	0.16	0.10	1.37	0.10
B	0.51	0.61	0.19	0.10	1.71	0.04	0.13
C	0.55	0.54	0.12	0.15	2.50	0.17	0.10

On the other hand, the values from the three sites were lower than the values of 11.43, 9.87, 4.02, 4.78, 1.13, 2.30, and 0.78 samples from Zaria dumpsites G, K, J, AB, NTC, D and B, respectively as reported by Uba and Uzairu (2008). This indicated low Cu mobility from soil to amaranth and therefore it cannot be used as a bio-indicator of Cu pollution. The TF values for Mn from the three sites were lower than 0.5 which indicated that its mobility from soil to amaranth is very low. Except for samples from site A, the TF values for Cr were the highest when compared with those of other elements in this study. Similarly, the values of 1.71 for samples from site B and 2.50 for site C were >1 which indicated high bio-mobility of Cr in amaranth. The values were much higher than the value of 0.1 as reported by Kashif *et al.* (2009). Therefore amaranth can be used as possible bio-indicator of Cr pollution. Except for samples from site A, the TF values for Co were less than 0.5. The observed TF value of 1.37 in samples from site A could be because Co was in a much available form to the vegetable. The TF values for Pb were much lower when compared with the values for other samples and were also lower than 1. This also is good indication that Pb accumulation in *Amaranthus caudatus* is very low. The TF values for Pb supported the findings made by Kashif *et al.* (2009) that, its accumulation in most plants is very low.

Conclusion

The results obtained in this study revealed the presence of Fe, Zn, Cu, Mn, Cr, Co and Pb in amaranths and soils samples from three agricultural fields of Jega, Kebbi State. The levels of the heavy metals in both the vegetable and their soils were generally low when compared with literature values. This is an indication that the vegetable is likely to be safe for human consumption. The lack of significant difference at $P < 0.05$ observed between the mean values of the heavy metal except Cu and Cr in amaranth samples from the three sites indicates that the set of values for each of the metals were related. Similarly, with the exception of the values for Fe, there was no significant difference at $P < 0.05$ between the mean values of the individual metals in the soil samples from the sites which also indicated close relation between the values. The TF values obtained for each of the metals from the three sites, except for Cr from sites B and C as well as Co from site A, indicates that, the mobility of the metals from soil to Amaranths (*Amaranthuscaudatus*) is very slow. The chances of heavy metal accumulation in Amaranth grown on soils treated with waste dumps are very slim. Therefore, the consumption of amaranths from the study sites is likely to be safe in terms of heavy metal toxicity.

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Heavy Metal Composition in Amaranthus caudatus from Waste Dump Soils

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