



Monitoring of heavy metals in vegetables and soils of Lokoja riverside, Kogi State, Nigeria

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Abstract

The purpose of this study was to assess the accumulation of heavy metals in riverside soils of rivers Niger and Benue and beyond the confluence and their uptake by *Amarantus hybridus* and *Corchorus olitorius L* grown on these soils. Four agricultural areas around the confluence point were selected. A total of nine samples each of soils, were collected from the selected areas and were analyzed for pH, textural class, percentage organic carbon and matter, moisture content, manganese, nickel, copper, zinc, lead and cadmium. Soil pH ranged from 6.4 to 6.7. There was no significant difference in the mean values of the organic matter, organic carbon and moisture contents of the soils, while the total metal content ranges from 3.0 - 8.4mg/kg for cadmium; 10.2 - 20.2mg/kg for copper; 170.0 - 205.2mg/kg for manganese; 201.0 - 269.4mg/kg for nickel; 23.5 - 33.4mg/kg for lead and 48.7 - 77.8mg/kg for zinc. Nickel and chromium were in levels higher than the European Union Standards. The levels of nickel, zinc, lead and Cadmium in the vegetables were higher than the World Health Organisation permissible value in plants. The total metal contents in *A. hybridus* and *C. olitorius L* grown on the riverside soils follow the ranking: Ni > Mn > Zn > Pb > Cu > Cd. Pb had the highest bioaccumulation factor, 0.5691 and 0.6301 in the soil from CN site for *A. hybridus* and *Corchorus olitorius L*, respectively. This indicated that the highly toxic metal lead has been entering our food chain through vegetables.

Keywords: Rivers Niger and Benue, Heavy Metals, Soils, Vegetables, Pollution index

1. Introduction

Heavy metal contamination refers to the excessive deposition of toxic heavy metals in the soil caused by human activities. These include some significant metals of biological toxicity like mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As) etc. Others are zinc (Zn), copper (Cu), nickel (Ni), stramonium, vanadium and so on [1].

Currently, irrigation farming along rivers side soils of rivers Niger and Benue help to provide vegetable crops for the people of Lokoja, Kogi State and its environs during the dry season and early part of the rainy season. However, with the flooding problems faced by the State in 2012, large items were washed into the water bodies. Therefore, the level of heavy metals in both soils and plants grown on the river side soils are expected to be elevated beyond the threshold levels [2].

It is worthy of note, that these two rivers come from far distance where, the domestic, industrial, mining, metallurgical and agricultural activities can contribute to the heavy metal loading of the water and riverside soils being irrigated with the water from these rivers. Thus, the determination of the heavy metal levels of the riverside soils post flooding becomes imperative [2].

Determination of the heavy metal uptake is further justified, since these metals are taken up by plants and from there enter into the food chain where they may cause health hazards. The pollution indices of the

riverside soil will help to determine the level of pollution loading after the flooding of 2012 when data is compared to that in literature before the flood.

It is based on these facts that this study is aimed at determining the levels of some heavy metals in riverside soils of River Niger, River Benue and beyond the confluence point, and to assess the heavy metal uptake by some crops planted on the soils.

2. Materials and methods

The river side soils for total metal determination were collected from the bank of river Niger, river Benue and beyond the confluence point at about 0 - 15cm and 15 - 30cm depth. The collection site was 50m away from the bank of the river and each point of collection was 10 m away from the other (n = 60).

Another set of soil samples (0 - 30cm) were collected during the dry season 50 m from the river bank (n = 10) for pot culture experiment to determine the amounts of Cd, Cu, Mn, Ni, Pd and Zn absorbed by *Amarantus hybridus* and *Corchorus olitorius L*.

The soil samples for control experiment were collected from a farmland 1 km away from the two rivers since this part is not affected by water from the river.

2.1 Pot culture experiment for the plants

In order to study the Phyto availability of the Cd, Cu, Mn, Ni, Pd, Zn in the two plants, seeds of spinach (*Amarantus hybridus*) called "alayyaho" in Hausa,

“Inine” or “Opotoko” in Igbo and “Efo” in Yoruba and jute (*Corchorus olitorius L.*) called “Laalo” or “Malafia” in Hausa, “Arira” or “Ahihara” in Igbo and “Oyoyo” or “Ewedu” in Yoruba, were planted separately on 5kg of the soil in pots having no hole at the bottom (Figure 2.1). Three seedlings per pot after germination were plant cultured (watering twice a day, weeding manually, exposure to sunlight and with adequate plant protection measures).

The pot culture experiment was carried out in a glass house at Crop Protection Department, Institute for Agricultural Research, Ahmadu Bello University, Zaria, Nigeria. They were uprooted after six (6) weeks. Identification of the plant was done at the Herbarium of the Department of Botany, Ahmadu Bello University, Zaria, Nigeria. This was carried out in the month of August 2014. The *Amarantus hybridus* was identified with Herbarium number; V/no.: 2400 and *Corchorus olitorius L.* with Herbarium number; V/no.: 2649.



Figure 2.1: Pot culture experiment for the plants

2.2 Pre-treatment of the soil and plant samples

Soil samples from each site were homogenised in an agate mortar and then air dried overnight in circulating air in an oven at 30°C. It was then allowed to pass through a 2 mm sieve. The sieved soils were placed in polythene bags for analysis.

The plant samples *Amarantus hybridus* and *Corchorus olitorius L.* 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°C for 48hours in order to remove moisture. The dried plant samples were ground into fine particles using a clean acid-washed agate mortar and pestle.

The glass wares were washed with liquid soap, rinsed with distilled water and then soaked in 10% HNO₃ solution for 24 hours [3]. The wares were then rinsed with enough distilled water and later dried in a Memmert drying oven at 80°C for 5 hrs.

2.3 Digestion of Samples

2.3.1 Digestion of soil samples

The soil samples were digested in order to carry out heavy metal analysis on them using the method of [4]. 1.0 g sample of the soil sample was digested in a Teflon cup with 30 cm³ aqua-regia (HCl: HNO₃, 3:1) on a thermos started hotplate at 150°C. After, about 2 hours of digestion, the Teflon cup with its content was brought down from the hot-plate to simmer. Then, 5 cm³ HF was added to the mixture and heated further for 30 min. The Teflon cup with its content was then allowed to cool to room temperature and filtered. After which the filtrate was transferred into 50 cm³ volumetric flask and made to mark with distilled water.

2.3.2 Digestion of plant samples

The plant samples harvested after six weeks from the pot experiment conducted in the procedure 3.4.2 were digested according to [5]. A 0.5g dried plant sample each of *Amarantus hybridus* and *Corchorus olitorius L.* was weighed into 100cm³ beaker, a mixture of 5ml concentrated HNO₃ and 2ml HClO₄ was added and digested at low heat using a hot plate until the content was about 2cm³. The digest was allowed to cool and then filtered into 50cm³ standard flask. The beaker was then rinsed with small portions of distilled-deionised water and then filtered into the flask.

Each digest was carried together with blank for triplicate determination of As, Cd, Cu, Mn, Pb and Zn contents using atomic absorption spectrophotometer (AAS).

3. Results and discussion

3.1 Physicochemical Parameters of the Farmland Soils near the Rivers and beyond Confluence point

Physicochemical properties as well as heavy metal concentrations in the soil samples collected from the riverside soils are presented in Table 3.1. The soil pH ranged from 6.4 to 6.7 for the farmland soils of River Niger, River Benue and beyond the confluence for the contaminated soils. These lower pH values may be attributed to acid effluent coming from nearby industrial operations as well as high organic content. Also, the organic matter content was low as a result of intensive use of these soils and the rapid mineralization of organic matter under semiarid conditions. The organic matter contents of the soil play an important role in absorption reaction in the soil, hence prevents pollutants from reaching ground water sources [6].

Table 3.1: Physicochemical parameters and heavy metal contents of riverside soil of Rivers Niger and Benue in wet season 2014

Soil property	N soil(mg/kg)	B soil(mg/kg)	CN soil(mg/kg)	CB soil(mg/kg)
pH	6.7	6.5	6.5	6.4
% sand	84	50	62	76
% clay	6	34	26	10
% silt	10	16	12	14
Textural class	Loamy sand	Sandy clay loam	Sandy loam	Sandy loam
Organic carbon (%)	0.249	0.958	0.563	0.822
Organic matter (%)	0.533	1.859	1.311	1.034
Moisture content	81.20 ± 0.01	73.50 ± 0.10	68.10 ± 0.12	73.75 ± 0.030
Total Cd				
15cm (mg/kg)	7.3 ± 0.0009	8.4 ± 0.0003	7.6 ± 0.0003	8.4 ± 0.00050
30cm (mg/kg)	3.3 ± 0.0007	4.2 ± 0.0004	3.0 ± 0.0005	3.4 ± 0.00040
Total Cu				
15cm (mg/kg)	11.60 ± 0.0004	20.20 ± 0.0005	18.30 ± 0.0003	18.00 ± 0.0005
30cm (mg/kg)	10.20 ± 0.0003	18.70 ± 0.0013	19.40 ± 0.0004	17.50 ± 0.0004
Total Mn				
15cm (mg/kg)	179.30 ± 0.0036	205.20 ± 0.0041	195.20 ± 0.0032	171.00 ± 0.0028
30cm (mg/kg)	176.30 ± 0.0032	201.10 ± 0.0039	193.30 ± 0.0035	170.00 ± 0.0030
Total Ni				
15cm (mg/kg)	269.40 ± 0.0004	267.40 ± 0.0005	201.00 ± 0.0004	220.80 ± 0.0005
30cm (mg/kg)	262.90 ± 0.0005	211.70 ± 0.0003	206.70 ± 0.0005	210.40 ± 0.0007
Total Pb				
15cm (mg/kg)	23.5 ± 0.0002	33.4 ± 0.0003	24.6 ± 0.0006	28.1 ± 0.00020
30cm (mg/kg)	23.5 ± 0.0003	32.2 ± 0.0003	25.1 ± 0.0005	28.0 ± 0.0004
Total Zn				
15cm (mg/kg)	63.10 ± 0.0025	77.80 ± 0.0012	50.00 ± 0.0014	51.60 ± 0.0026
30cm (mg/kg)	61.7 ± 0.0030	74.1 ± 0.0021	48.7 ± 0.0021	50.0 ± 0.0010

***N = Niger riverside soil, B = Benue riverside soil, CN = Niger riverside soil after confluence, CB = Benue riverside soil after confluence

Table 3.2: Permissible limits of heavy metals in soils and plant.

Elements	Threshold Conc. of soil (mg/kg) (EU 2002)	Permissible value of plants (mg/kg) (WHO 1996)
Ni	75	10
Cu	140	10
Zn	300	20
Pb	300	2
Cd	3	0.2
Mn	2000	300

While the heavy metal concentrations of the elements in the soil samples collected from riverside soils of River Niger, Benue and after the confluence point (see Table 3.1) would be compared with European Union Standards [7], the heavy metals concentrations of these elements in *Amarantus hybridus* and *Corchorus olitorius L* would be compared to World Health Organisation permissible value in plants [8].

3.2 Heavy metal content in the riverside soil samples used for Agricultural purposes

Cd concentrations of the studied area as shown in Table 3.1 indicated that Cd concentration of 8.4mg/kg obtained in both sites B and CB was the highest, while the Cd concentration (3.0mg/kg) at CN sampling site was the lowest. The Cd concentrations obtained were higher than the European Union Standards of 3 mg/kg [7] as seen in table 3.2. Cadmium is regarded as one of the most toxic trace elements in the environment. Cadmium occurs naturally in soils as a result of the weathering of the parent rock [6]. Although most natural soils contain less than 1 mg/kg cadmium from weathering of parent materials, those developed on black shales and those associated with mineralised

deposits can have much higher levels [6]. Cadmium is higher in the studied area, probably due to the use of phosphatic fertilisers, irrigation by untreated water of the river and due to the soil of the study area being from deposits of the flooding of 2012, and the soils have been derived from sediments (sand, silt and clay) of Rivers Niger and Benue. Surface soils commonly contain higher concentrations of Cd than subsurface horizons. The higher concentrations of Cd in surface horizons are probably due to the cycling of Cd from lower depths to the surface by plants [9].

Copper content was reported to be lower than that of European Union Standard limit [7] of 140 mg/kg (Table 3.2). Copper had relatively low values ranging from 10.2mg/kg in the soil at N to 20.2mg/kg in B. The concentrations of copper are higher in some soil samples due to the irrigation of agricultural lands with untreated river water which could lead to accumulation of Cu in soils. The Cu concentrations are lower due to the continuous removal of heavy metals by the food crops grown in the area and also due to leaching of heavy metals into the deeper layer of the soil and to the ground water.

As seen in Table 3.1, Mn concentration in the soil was generally higher than all the other metals recorded but was generally lower than the European Union Standards of about 2000mg/kg [7]. It ranges from 170.00mg/kg to 205.20mg/kg. The observed large concentration of Mn in the soil samples might have been due to background concentration of Mn in the soil and sediment of the river. Dara [10] reported that manganese may be found in most soil since it is one of the elements in the earth crust.

Ni concentrations in the soil samples of the study area are higher than that of European Union Standards [7] of 75mg/kg. It ranges from 201.0 to 269.4mg/kg. Nickel occurs naturally in soils as a result of the weathering of the parent rock [11]. The underlying geology and soil forming processes strongly influence the amount of nickel in soils with higher median concentrations reported in clays, silts, and fine-grained loams relative to coarser grained loams, sandy and peaty soils [12]. Agricultural fertilizers, especially phosphates, are also a significant source of nickel in soil but it is unlikely to build-up in soil in the long term from their use [11]. The irrigation of the farmland in riverside of Rivers Niger and Benue by the river water and use of agricultural fertilizers may account for the increase in the Ni concentrations of the farmland.

Lead contents were found to be highest (33.4mg/kg) in the soil sample from B and lowest (23.5mgkg⁻¹) at N sampling site. The value of Pb in the soil samples were generally low compared to the European Union Standards of about 300mg/kg [7]. Lead particles are deposited in the soil from flaking lead paint, from incinerators (and similar sources), and from motor vehicles that use leaded gasoline. Waste disposal is also a contributory factor to increased Pb in soil. Urban environments in general have received higher depositions of lead from vehicular emissions than rural areas; though Pb in antiknock additives used in gasoline has been banned and not currently used in many countries. When lead is deposited in soil from anthropogenic sources, it does not biodegrade or decay and is not rapidly absorbed by plants, so it remains in the soil at elevated levels. Lead is toxic to humans, and poisoning can occur either through ingestion of lead or by breathing in lead dust. Both long-term low-dose and short-term high-dose exposures can permanently damage the nervous, renal (kidney), and haematopoietic (blood-forming) systems.

The Zn contents as presented in Table 3.1 indicated that the soil samples in site CN (48.7mg/kg) was the lowest while the sample from B (77.80mg/kg) had the highest Zn concentration. The highest Zn concentrations of the studied area were lower than that of European Union Standards of 300mg/kg [7]. Zn is released to the environment from both natural and anthropogenic sources. However, releases from anthropogenic sources are greater than those from natural sources. The most important sources of anthropogenic zinc in soil come from discharges of smelter slag and wastes, mine tailings, coal and bottom fly ash, and the use of commercial products such as fertilizers and wood preservatives that contain zinc. The lower concentrations of Zn than the safe limits of EU at most sites might be due to the continuous removal of heavy metals by the food crops grown in the area and also due to leaching of heavy metals into the deeper layer of the soil and to the ground water.

3.3 Level of Heavy Metal in *Amarantus hybridus* and *Corchorus olitorius* L

Heavy metal concentrations in spinach (*Amarantus hybridus*) called “alayyaho” in Hausa, “Inine” or “Opotoko” in Igbo and “Efo” in Yoruba and jute (*Corchorus olitorius* L.) called “Laalo” or “Malafia” in Hausa, “Arira” or “Ahihara” in Igbo and “Oyoyo” or “Ewedu” in Yoruba, were found to be generally lower than that levels of each of the heavy metals in the soil, as shown in Figures 3.1 to 3.6 for *Amarantus hybridus* and *Corchorus olitorius* .L.

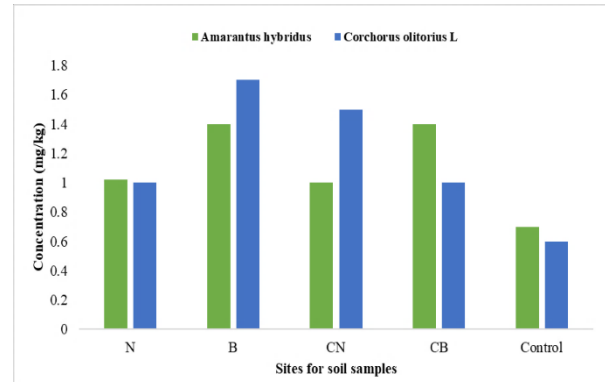


Figure 3.1: Cadmium content in the two plants grown on riverside soils in the pot experiment

The Concentrations of cadmium (Figure 3.1) in *A. hybridus* was found to be lowest (1.0mgkg⁻¹) in the plant from N and CN, and was highest (1.4mgkg⁻¹) in the crop planted on B and CB soil samples. For *Corchorus olitorius* L., the lowest Cd level was 1.0mgkg⁻¹ in the plant from N and CB and the highest level was 1.7mgkg⁻¹ in the crop planted on site B soil sample. The plant in the control soil had relatively lower value both for *A. hybridus* and *Corchorus olitorius* L. compared to the experimental soils. There was significant difference in the values recorded in *A. hybridus* compared to *Corchorus olitorius* L.

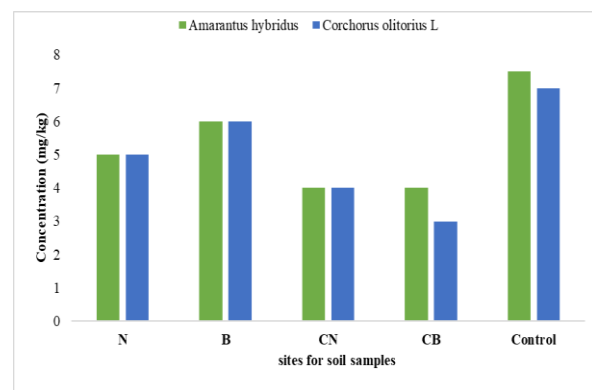


Figure 3.2: Copper content in the two plants grown on riverside soils in the pot experiment

Copper contents in *A. hybridus* as presented in Figure 3.2 ranged from 4.1 in the crop harvested from CN to 6.0mg/kg in the plant from site B; while in *Corchorus olitorius* L., it ranged from 3.2 in CB to 6.2mgkg⁻¹ in B. The extremely high value obtained in site B both in *A. hybridus* and *Corchorus olitorius* L., could be due to

the decomposition of solid wastes containing high copper contents, which are drain into the rivers and subsequently in the soil. In the control sites low values were recorded in both the *A. hybridus* and *Corchorus olitorius L.* This could be due to the fact that the site is not affected by the untreated water of the river. These values are however above the tolerance limit (10 mg/kg) set by WHO (8) as seen in Table 3.2. There was no significant difference in the values recorded in *A. hybridus* compared to *Corchorus olitorius L.*

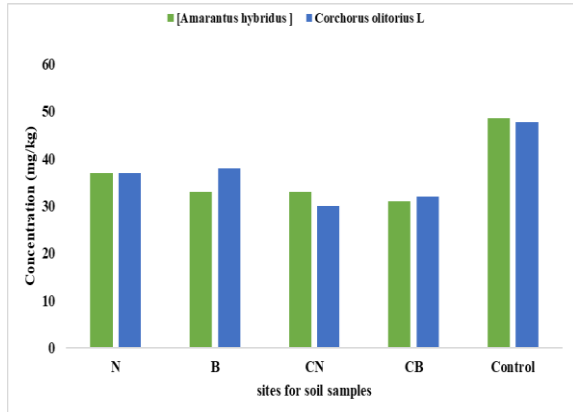


Figure 3.3: Manganese content in the two plants grown on riverside soils in the pot experiment

Manganese contents as presented in Figure 3.3, had the lowest value in *A. hybridus* planted on the soil of site CB (30.6mgkg^{-1}) and was highest in the plant harvested from the soil of N (37.4mgkg^{-1}). On the other hand, for *Corchorus olitorius L.* the lowest level of Mn was 30.3mgkg^{-1} for the ones from CN soil and 37.8mgkg^{-1} the highest Mn level recorded in the plant from B soil sample. From the Figure 3.3, it is indicated that the plant from the control site had relatively high level of Mn for both *A. hybridus* and *Corchorus olitorius L.*, which is as expected. In addition, there was little significant difference in the values obtained for both *A. hybridus* and *Corchorus olitorius L.*

Nickel contents (Figure 3.4) was relatively higher than manganese, and was the highest level recorded among all the metals studied, the lowest value of Ni in *A. hybridus* was recorded in the ones planted on the soil from CN (36.7mgkg^{-1}) and the highest Ni was recorded in the plant harvested from the soil of B (51.2mgkg^{-1}). For *Corchorus olitorius L.* 28mgkg^{-1} was the lowest level of Ni in the crop from site CB and 40.3mgkg^{-1} was the highest Ni level recorded in the plant harvested from site N soil. Figure 4.4d indicated that the plant from the control site had relatively low level of Ni in both the *A. hybridus* and *Corchorus olitorius L.* In addition, there was no significant difference in the values obtained for both *A. hybridus* and *Corchorus olitorius L.*

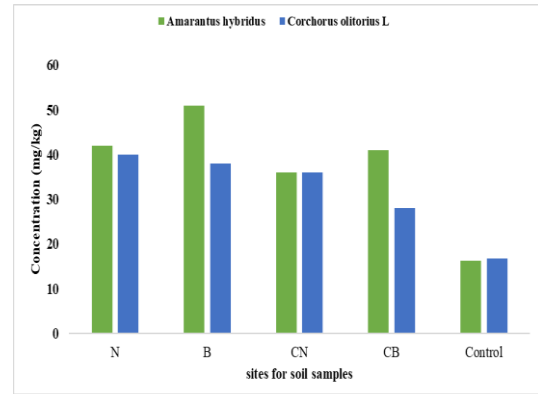


Figure 3.4: Nickel content in the two plants grown on riverside soils in the pot experiment

Lead contents (Figure 3.5) measured was lowest in *A. hybridus* planted on the soil from N (12.5mgkg^{-1}) and was highest in the plant from CB and CN soils (14mgkg^{-1}). For *Corchorus olitorius* the lowest level of Pb was 12.3mgkg^{-1} obtained in the plant from N soil. The highest amount of Pb was 15.7mgkg^{-1} recorded in the plant from CB soil. The control plant had relatively lower value both for *A. hybridus* and *Corchorus olitorius L.* compared to the experimental plants. There was no significant difference in the values recorded in *A. hybridus* compared to *Corchorus olitorius L.*

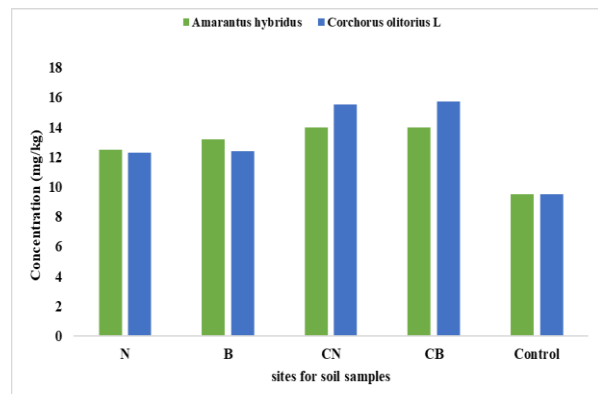


Figure 3.5: Lead content in the two plants grown on riverside soils in the pot experiment

Zinc contents (Figure 3.6) in *A. hybridus* planted on the soil ranged from 17.4 in soil from B to 18.9mgkg^{-1} in the soils from N and CB; for *Corchorus olitorius L.* Zn level ranged from 16.2 in the sample planted on B soil to 17.4mgkg^{-1} in the one from N. The concentration of zinc in the control site was higher than those in the sample area, this could be attributed to the background zinc present in the soil [10]. These zinc values recorded in the experimental plant are above the tolerance limit of zinc in plant and could be harmful to man if accumulated over time through the food chain.

The ranking of these metals in *A. hybridus* and *Corchorus olitorius L.* planted on the riverside soils is in the order: Ni > Mn > Zn > Pb > Cu > Cd, while the pattern in the control site was Mn > Zn > Ni > Pb > Cu > Cd.

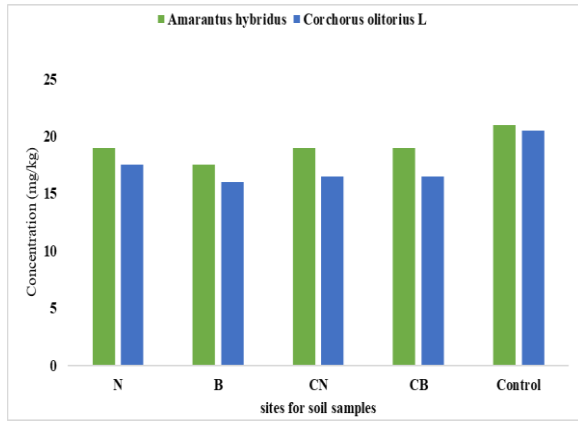


Figure 3.6: Zinc content in the two plants grown on riverside soils in the pot experiment

3.4 Bioaccumulation factor (BF) of the Heavy Metals in *A. hybridus* and *Corchorus olitorius*

In order to determine the extent of contamination content of the heavy metals in soil, an enrichment factor was computed called the transfer factor of bioaccumulation factor (BF). This was expressed as the ratio of the concentration of the metals in the plants to that in the soil [13]. Table 3.3 presents the BF for *Amarantus hybridus*, while Table 3.4 presents for *Corchorus olitorius L.* bioaccumulation factor (BF) varied significantly among the soil species of the heavy metals. Of all the metals studied, the BF of Pb from the soil to the plant was highest, being 0.5691 and 0.6301 considering the soil from CN to *A. hybridus* and *Corchorus olitorius L.*, respectively.

Table 3.3: Bioaccumulation factor (BF) of the heavy metals in *Amarantus hybridus*

Metals	N	B	CN	CB
Cd	0.1370	0.1667	0.1316	0.1667
Cu	0.3879	0.2970	0.2240	0.2389
Mn	0.2086	0.1598	0.1670	0.1789
Ni	0.1496	0.1410	0.1801	0.1268
Pb	0.5319	0.3952	0.5691	0.4982
Zn	0.2995	0.2236	0.3760	0.3663

Table 3.4: Bioaccumulation factor (BF) of heavy metals in *Corchorus olitorius L.*

Metals	N	B	CN	CB
Cd	0.1370	0.2024	0.1974	0.1190
Cu	0.3879	0.3069	0.2350	0.1778
Mn	0.2070	0.1842	0.1552	0.1895
Ni	0.1496	0.1410	0.1801	0.1268
Pb	0.5234	0.3712	0.6301	0.5587
Zn	0.2757	0.2082	0.3300	0.3178

The Bioaccumulation Factor obtained for Ni with *A. hybridus* and *Corchorus olitorius L.* was the lowest with the exception of the values using soil from CN (0.1801). Similar trend was observed for Cd except in *Corchorus olitorius L.* using soil from B (0.2024) where transfer factor was relatively high. These results

indicate that *A. hybridus* and *Corchorus olitorius L.* have potential to accumulate more of Pb and Cu from the riverside soil compared to Ni and Cd. There is tendency of Pb and Cu in the soil of the farmland from River Niger and Benue in Lokoja 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 overtime may cause some health hazards as reported by [1]. It was also observed that the transfer factor or bioaccumulation factor values recorded for the metals show reverse trend compared to the total metal content obtained across the seasons $Pb > Cu > Zn > Mn > Cd > Ni$. According to [14] some factors such as pH, exchange binding capacities, climate change and morphology of the plant might have contributed to low transfer factor values obtained in the riverside soils to the plant.

4. Conclusions

From the present study it can be concluded that in some agricultural fields, the concentration of, Ni and Cd are above the normal soil value and reflect the possibility of soil pollution. Accumulation of nickel, zinc, lead and cadmium in the vegetables in both leafy *A. hybridus* and *Corchorus olitorius L.* which are higher than the WHO permissible value of plants (1996), indicated that the highly toxic metal Pb has been entering food chain through vegetables. Although the green vegetables are good sources of Zn, Cu, Fe necessary for good health, but by the accumulation of toxic metals like Ni, Pb and Cd, the essential micronutrients would be deficient in our daily diet. In heavy metal contaminated areas, leafy vegetables which are good accumulator should be avoided for commercial farming and should be substituted by non-accumulator plant like potato.

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