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Heavy Metal Levels in Plants Growing on Abandoned Coal Ash Dumpsite in Oji, Enugu State, Nigeria

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Abstract

The levels of thirteen metals; Fe, Mn, Ni, Cd, Pb, Cr, Co, As, Zn, Cu, Mo, Se and Hg in the leaves of five common plant species (Abelmoschus esculenta, Aspilia africana, Manihot esculenta, Panicum maximum and Zea mays), growing around the coal ash dump site at Oji, Enugu State were evaluated. The leaves were collected from the plants at the four cardinal points of the study area and analyzed for heavy metals using Atomic Absorption Spectrometer (AAS) Varian 240AA. The results showed that the concentration of the metals; Ni, Pb, Cd, Co, As, Mo and Se were above the USEPA set limits for the selected plant leaves, and varied with the following sequence; Ni (1.10±0.57to 7.05±12.86 mg/kg), Pb (6.45±5.75 to 9.25±5.43 mg/kg), Cd (1.13±0.34 to 5.23±6.55mg/kg), Co (0.05±0.10 to 1.55±1.84mg/kg), Cr (0.025±0.04 to 0.05±0.09mg/kg), As (4.13±6.54 to 22.53±30.69mg/kg), Mo (7.03±12.96 to 25.45±20.96 mg/kg), and Se (7.93±9.63 to 15.45±10.70 mg/kg). Also, the result showed that the metals concentration were higher in the study area than the control except iron (Fe). Considering the importance of plants in the food chain, we recommend for soil remediation if the study area must be used for farming or as grazing ground.

Keywords

Heavy Metals, Plant Leaves, Soil Remediation, Atomic Absorption Spectrometer

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1. Introduction

The study area contains a huge amount of coal ash generated from forty years operations of a contemporarily non-operative coal based thermal power plant. The power plant operated by the former National Electric Power Authority (NEPA), now Power Holding Company of Nigeria (PHCN), was commissioned in 1956 at Oji, to supply electricity to the former Eastern region. Coal ash deposit has the ability to pollute an environment with its attendant health risks, as it contains various categories of pollutants ranging from organic to in-organic [4]. This is due to the fact that coal ash contains significant amounts of fine powdered ferro-alumino-silicate material with Al, Ca, Mg, Fe, Na and Si as the predominant elements and toxic metals such as As, Ba, Hg, Cr, Ni, V, Pb, Zn and Se [10]. Many heavy metals such as Cu, Ni, Fe, Co, Zn are well known as essential trace elements for plants. The contamination of soil by heavy metals increases plants uptake thereby causing their accumulation in different plant tissues including the leaves [15]. During the process of absorption of the trace elements, plants can as well accumulate other 'non essential' metals (As, Pb, Hg, Cd, Cr, etc) which have no known biological function. At high concentrations, all heavy metals have strong toxic effects and are regarded as environmental pollutants [11], because they bio-

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accumulate in the plant cells [5].

High concentration of heavy metals in the leaves of the plant may directly or indirectly affect the nutritional health of the people that consume it [16]. Phytotoxicity also results in chlorosis, weak plant growth, yield depression, and may even be accompanied by reduced nutrient uptake disorders in plant metabolism and, in leguminous plants, a reduced ability to fixate molecular nitrogen [2]. However, deficiency in the supply of certain essential elements especially Zn is a serious problem for agriculture in many parts of the world. In heavy metal polluted soils, plant growth can be inhibited by metal absorption. However, some plant species are able to accumulate fairly large amounts of heavy metals without showing any stress [5]. Essentially, heavy metal uptake by crops growing in contaminated soils is a potential hazard to human health because of transmission in the food chain [1]. The extensive use of the coal ash dump and its surroundings for cultivating plant-based foodstuff including vegetables and animal grazing, without proper assessment of the associated health risks may be catastrophic. This study therefore, was aimed at providing a baseline data that will fill these scientific gaps especially in Oji, Enugu State.

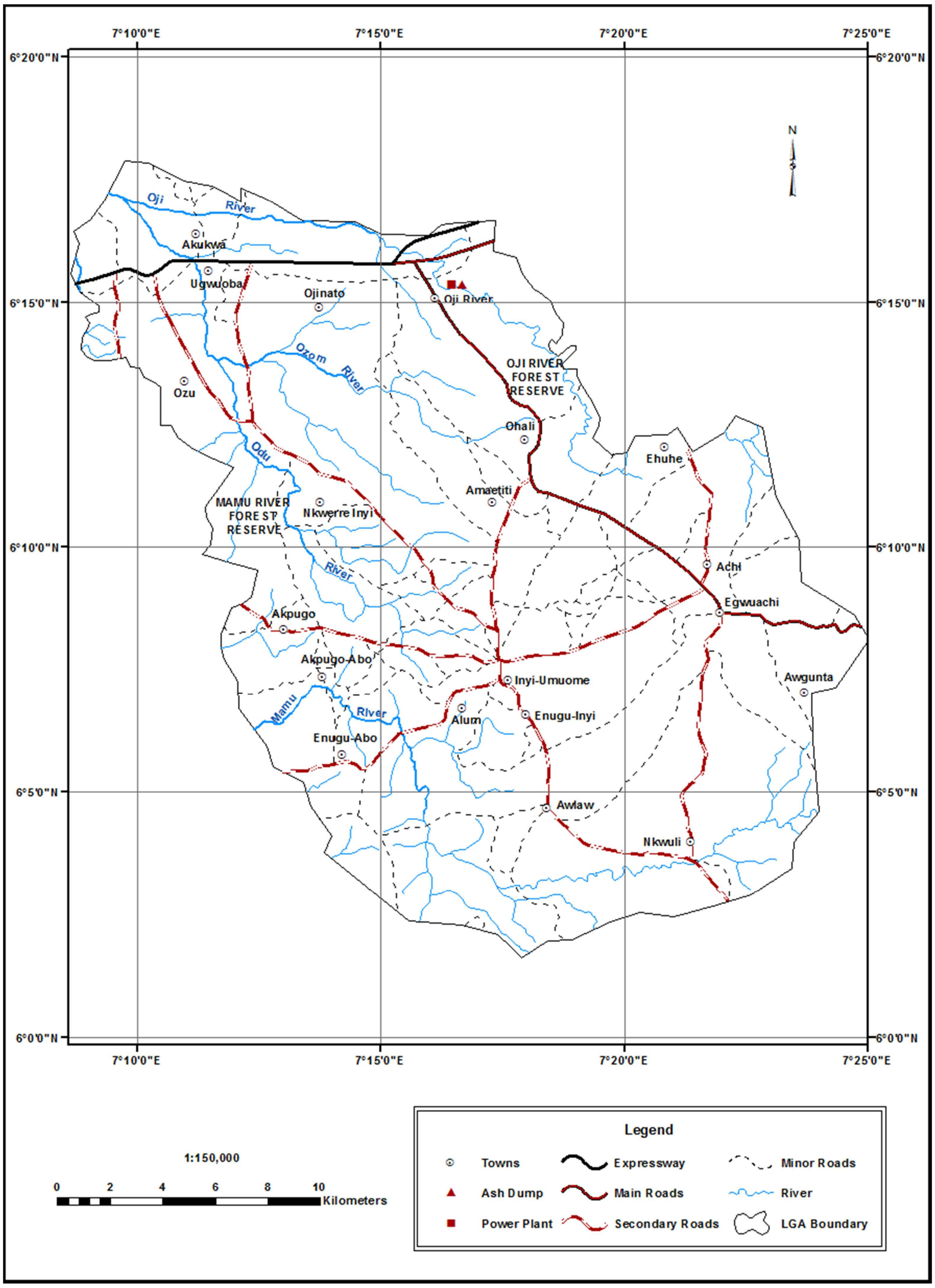

Figure 1. Map of Oji River Local Government Area showing the study Area.

2. Materials and Method

2.1. The Study Area

The area under study is in Oji town, Oji River Local Government Area of Enugu State (Figure 1). The coal ash dump site and the power generating plant are separated by a distance of about 800m. The location of the study area measured with GPS (etrex 30) model, shows that the coal ash dump (Figure 2), lies on the elevation of 89m, at latitude 6° 15' 21.996" N and longitude 7° 16' 40.08" E. The place was originally owned by Umubo village in Agbalaenyi Ward Nachi in Udi Local Government Area of Enugu Statebefore it was declared urban, following the commissioning of the power plant in 1956.

Figure 2. Side View of Coal Ash Dump Site from the East Axis.

2.2. Materials

Sample Collection of Leaves

Leaves from five different plant species (*Manihot esculenta, Abelmoschus esculenta, Aspilia Africana, Panicum maximum* and *Zea mays*) which were common to the study area were sampled along each axis. The samples were collected within the hundred meter range from the coal ash dump. Each of the cardinal points was divided into five sampling points at twenty meter intervals. At each sampling point, leaves were collected from the required available plant in each cardinal point. Also leaves from the same plant species as the study area were collected from each of the background of the four cardinal points. Three of the plants (*Abelmoschus esculenta, Manihot esculeta and Zea mays*) are edible crops. The remaining two plants (*Aspilia Africana and Panicum maximum*) are widely consumed by herbivorous animals. The plants were selected based on their peculiar natural characteristics, and they were collected under the same conditions. The samples were placed in polyethene bags properly labelledand taken to the laboratory.

Preparation of the plant leaves

The leave samples were air driedunder room temperature for one week. The leaves were further dried in an oven at a temperature of 100^{o}C for one hour to remove the remaining moisture content and for easy grinding. The leaves were ground into powdered form and properly labelled. One (1) gram of each of the powdered samples of the same plant specie collected at different sampling points (1-5) in the same axis were mixed to get a composite sample of the particular leaf. After the blending, twenty grab sample representatives of the study area was obtained. A weight of 1g of the dry powdered leaves samples were weighed into 125cm^3 glass beaker to which 4cm^3 perchloric acid, 25cm^3 concentrated nitric acid, and concentrated sulfuric acid were added. The content were mixed and kept for about two hours for the samples to dissolve. The beakers were then heated on the hot plates in the fume chamber, the samples were heated until white fumes appeared, then, the temperature was raised to 100^{o}C and heated again for 30 minutes. The sample solutions were allowed to cool, and filtered into 100cm^3 volumetric flasks and made upto the mark with deionized water. The solutions were analyzed for heavy metals using Atomic Absorption Spectrometer (AAS) varian 240AA.

3. Results and Discussion

Heavy metal concentration in five plants leaves common to the study area

Concentrations of metals in five plants leaves common to the soil of the study area were determined and the results are presented in Table 1 and Figure 3 The results revealed that themost abundant metal in the leaves of sampled plants is zinc (Zn), followed by iron (Fe) and managanese (Mn) while the least accumulated were chromium (Cr) and mercury (Hg).

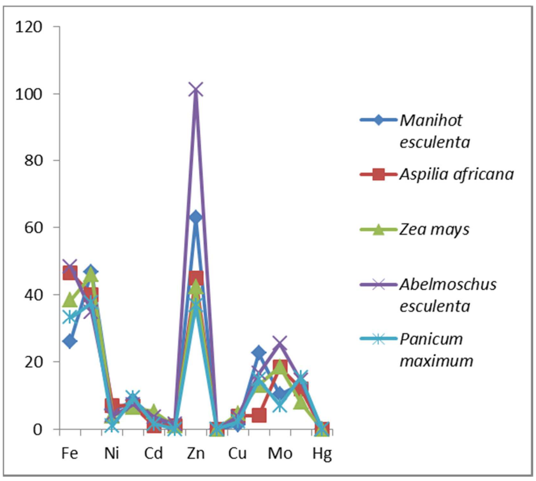

Figure 3. Comparison of Heavy Metals concentration in the five plant leaves from the study area and the control.

Table 1. Heavy Metals concentration (mg/kg) in sampled plant leaves.

Metals	*Manihot esculenta*	*Aspilia africana*	*Zea mays*	*Abelmoschus esculenta*	*Panicum maximum*
Fe	26.1±26.81	46.65±7.91	38.38±25.75	48.5±24.50	33.18±19.35
Mn	46.93±20.91	40.00±27.53	45.95±48.79	34.85±22.54	37.60±22.58
Ni	5.68±9.25	7.05±12.86	3.98±3.46	4.03±5.90	1.10±0.57
Pb	8.48±5.33	6.85±1.84	6.45±5.75	7.38±5.18	9.25±5.43
Cd	3.58±5.97	1.13±0.34	5.23±6.55	3.65±1.86	1.60±1.96
Co	0.73±1.02	1.05±0.82	0.93±1.04	1.55±1.84	0.05±0.10
Zn	62.85±55.10	44.93±20.50	42.35±25.26	101.13±70.30	36.88±31.86
Cr	BDL	0.025±0.04	0.05±0.09	0.03±0.05	BDL
Cu	1.28±1.47	3.95±3.72	4.58±4.58	3.70±4.61	2.28±1.47
As	22.53±30.69	4.13±6.54	13.08±12.26	16.63±17.50	14.73±27.34
Mo	10.33±12.00	18.35±22.32	18.48±11.93	25.45±20.96	7.03±12.96
Se	13.38±10.51	12.03±9.00	7.93±9.63	14.43±20.22	15.45±10.70
Hg	0.03±0.04	BDL	0.05±0.05	0.03±0.03	BDL

Footnote: BDL= Below Detectable Limit

The comparison of heavy metal concentration in five plant leaves from the study area and the control, are shown in Table 2.

Table 2. Comparison of Heavy Metal Accumulation in five Plant Leaves.

Metals		*Manihot esculenta*	*Aspilia africana*	*Zea mays*	*Abelmoschus esculenta*	*Panicum maximum*
Fe	A	26.1±26.81	46.65±7.91	38.38±25.75	48.5±24.50	33.18±19.35
	B	52.95±21.44	56.18±36.21	62.38±32.85	42.48±7.76	48.98±13.95
Mn	A	46.93±20.91	40.00±27.53	45.95±48.79	34.85±22.54	37.60±22.58
	B	20.30±17.12	8.80±8.13	5.78±7.48	6.68±10.80	18.80±17.78
Ni	A	5.68±9.25	7.05±12.86	3.98±3.46	4.03±5.90	1.10±0.57
	B	1.3±0.87	1.30±1.06	1.45±1.58	0.58±0.81	0.88±0.84
Pb	A	8.48±5.33	6.85±1.84	6.45±5.75	7.38±5.18	9.25±5.43
	B	0.80±0.32	0.30±0.17	1.05±0.35	0.38±0.29	0.43±0.39
Cd	A	3.58±5.97	1.13±0.34	5.23±6.55	3.65±1.86	1.60±1.96
	B	0.83±0.86	0.50±0.73	0.95±0.58	0.45±0.46	0.65±0.30
Co	A	0.73±1.02	1.05±0.82	0.93±1.04	1.55±1.84	0.05±0.10
	B	0.93±0.64	0.63±1.20	1.18±0.85	0.08±0.10	1.00±0.95
Zn	A	62.85±55.10	44.93±20.50	42.35±25.26	101.13±70.30	36.88±31.86
	B	16.40±16.64	26.83±27.70	16.38±13.67	15.08±16.16	19.10±8.65
Cr	A	BDL	0.025±0.04	0.05±0.09	0.03±0.05	BDL
	B	BDL	BDL	BDL	0.20±0.39	BDL
Cu	A	1.28±1.47	3.95±3.72	4.58±4.58	3.70±4.61	2.28±1.47
	B	3.03±0.25	4.00±3.15	2.25±1.15	2.33±1.65	2.30±1.15
As	A	22.53±30.69	4.13±6.54	13.08±12.26	16.63±17.50	14.73±27.34
	B	BDL	0.05±0.05	0.03±0.04	0.15±0.30	0.05±0.07
Mo	A	10.33±12.00	18.35±22.32	18.48±11.93	25.45±20.96	7.03±12.96
	B	2.98±1.58	1.58.48±1.18	0.15±0.15	0.70±0.62	1.15±1.34
Se	A	13.38±10.51	12.03±9.00	7.93±9.63	14.43±20.22	15.45±10.70
	B	2.40±1.34	1.33±0.93	1.38±0.69	1.33±0.85	2.03±2.23
Hg	A	0.03±0.04	BDL	0.05±0.05	0.03±0.03	BDL
	B	0.08±0.09	0.05±0.09	0.03±0.06	0.1±0.07	0.05±0.05

A = Study area, B = control

The highest level of Arsenic was found in *manihot esculenta* 22.525mg/kg followed by *Abelmoschus esculenta* 16.625mg/kg, *Panicum maximum* 14.725mg/kg, *Zea mays* 13.075mg/kg, the least concentration of 4.125mg/kg was found in *Aspilia africana* (Table 1 and Figure 3). The trend showed that arsenic was a possible toxicant to the five selected plant leaves and probably had adverse health implication for the consumers of such plants since its concentrations were above the standard limit of 1-1.7mg/kg reported by [6]. The results of this study were higher than the ones obtained by [16] and [14]. It was also observed that Arsenic concentrations in the control leaves were below the normal range (Table 2). The high level of Arsenic in the plant leaves from the study area may be related to the impact of coal ash deposit.

Molybdenum accumulated highest in *Abelmoschus esculenta* 25.45mg/kg, followed by *Zea mays* 18.475mg/kg, *Aspilia africana*18.35mg/kg, *Manihot esculenta*10.325mg/kg and the least *Panicum maximum* 7.025mg/kg (Table 1, Figure 3). The result showed that the five selected plant leaves may experience toxic effects as a result of molybdenum contamination since its concentrations were above the WHO permissible limit of 0.0-5mg/kg reported by [6]. The results obtained in this study was higher than the ones obtained by [3] in their study of *Diodia Scandeus* leaves, the results of the control samples were below the recommended range (Table 2). Molybdenum is essential to plant nutrition, as it is involved in nitrogen fixation, nitrate reduction and valence changes [7]. Molybdenum is also essential in animal nutrition [9] and can result in copper toxicity if present in deficient amount. In this study the results are still within the toxic limit but there is tendency of accumulating molybdenum in the tissues and organs ofanimals that feed regularly on the leaves of such plants.

It was observed in Table 1 and Figure 3 that the highest level of mercury was found in *Zea mays* (0.05mg/kg) followed by *Abelmoschus esculenta* and *Manihot esculenta* each having a concentration of (0.03mg/kg). In *Aspilia africana* and *Panicum maximum*, mercuryconcentration were below detectable limit of the instrument, while in *Zea mays* a concentration of 0.05mg/kg was recorded (Table 1 and Figure 3). The mean value of mercuryin the sampled plants leaves from the study area and the control in Table 2 were below the toxic range of 1-3mg/kg. There were no clear differences between the results from the study area and the control samples. In some of the plant leaves, the level of mercury were higher in the control samples than the study area (Table 2). Hence the mercury observed in this result may not be attributed exclusively to coal ash deposit in the study area. Mercury is not essential to plants, animals or humans, translocation of mercury is generally limited as mercury accumulates in the roots, thereby reducing problems caused by consumption of plant foliage [17].

Highest concentrations of managanese were found in *Zea mays* 46.925mg/kg, followed closely by *Manihot esculenta* 45.95mg/kg, *Aspilia africana* 40.00mg/kg, *Panicum maximum* 37.6mg/kg, and the least *Abelmosehus esculenta* 34.85mg/kg (Table 1 and Figure 3). The result suggested that Mn did not pose any contamination problem to any of the five selected plant leaves and no adverse health implications to consumers of the plants were expected since the results were either below or within the normal range of 30–300mg/kg reported by [7]. The results obtained in this work were however lower than the results obtained by [3] in *Diodia scandeus*. Manganese is essential for the production of oxygen in plant chloroplasts and it affects plant nutrition indirectly through its involvement in nitrate reduction [7]. Since plants require manganese for development, they absorb manganese even at unfavourable conditions.

The highest concentration of selenium was found in *Panicum maximum* 15.45mg/kg followed by *Abelmoschus esculenta* 14.425mg/kg, *Manihot esculenta* 13.375mg/kg, *Aspilia africana* 12.025mg/kg and the least *Zea mays*7.925mg/kg (Table 1 and Figure 3). The mean value of seleniumin the sampled leaves of the study area were all above the normal range of 0.01-2mg/kg reported by [6]. It was also observed that selenium concentration in the control samples were above the normal range in *Manihot esculenta* and *Panicum maximum*, others were within the normal range (Table 2). The results obtained in this work were higher than the ones reported by [3] in their study of *Diodia scandeus* leaves. The high level of selenium in plant leaves of the study area may be related to the impact of coal ash deposit and the composition of the parent soil materials.

Lead (Pb) accumulated most in *Panicum maximum* 9.25mg/kg followed closely by *Manihot esculenta* 8.475mg/kg, *Abelmosehus esculenta* 7.375mg/kg, *Aspilia africana* 6.85mg/kg and *Zea mays* 6.45mg/kg (Table 1, Figure 3). The result suggested that Pb posed a toxicity threat to the five selected plant leaves and possible Pb poisoning to people who eat the plants, if no precautionary measure is put in place. The mean lead value in the sampled plant leaves of both the study area and the control were within the normal range of 5-10mg/kg reported by [6] for plants growing on natural soil. The results showed that lead concentration in the leaves from the study area were all higher than those of the control (Table 2). Lead is a non essential element for plants, animals and humans. It is toxic to plants at leaf levels of 30-300ppm (dry weight basis) at which point plants exhibit dark green leaves, wilting and stunted foliage and roots [6].

Highest concentration of iron (Fe) was found in *Abelmosehus esculenta* (48.5mg/kg) followed by *Aspilia africana* (46.65mg/kg), *Zea mays* (38.375mg/kg), *Panicum maximum* (33.175mg/kg) and *Manihot esculenta* (26.1mg/kg). Iron was neither a possible toxicity threat to the plants or to their consumers since its concentration was below the WHO/FAO safe limit of 450mg/kg for naturally growing plants (Table 1 and Figure 3). It was observed that apart from *Abelmoschus esculenta* in which the concentration of iron was higher in the leaf from the study area, reverse were the cases in *Manihot esculenta*, *Aspilia africana*, *Zea mays* and *Panicum maximum (Table 2)*. Iron (Fe) plays an important role in photosynthesis and Nitrogen fixation [7].

It was observed from Table 1 and Figure 3 that the highest concentration of cobalt (Co) was found in *Abelmoschus esculenta*1.525mg/kg followed by *Aspilia africana* (1.05mg/kg), *Zea mays* (0.925mg/kg), *Manihot esculenta* (0.725mg/kg) and the least *Panicum maximum* (0.05mg/kg). Comparing the results from both the study area and the control sites (Table 2) revealed the following variations of cobalt concentrations: 0.725mg/kg and 0.925mg/kg for *Manihot esculenta*, 1.05mg/kg and 0.625mg/kg in *Aspilia africana*, 0.925mg/kg and1.175mg/kg in *Zea mays*, 1.525mg/kg and 0.075mg/kg in *Abelmoschus esculenta* and 0.05mg/kg and 1.00mg/kg in *Panicum maximum*. These results revealed that the concentration of cobalt were higher in *Manihot esculenta*, *Zea mays* and *Panicum maximum* from the control site. However, the concentrations of Co in *Aspilia africana* and *Abelmoschus esculenta* were higher in the study area. The result also suggested possible Co poisoning through eating of *Abelmoschus esculenta* and *Aspilia africana* from the study area. Invariably, the Co content of the selected plant leaves may be attributed to both the parent soil materials and some level of contributions from the coal ash dump.

Table 1 and Figure 3 above shows that the highest concentration of copper (Cu) was found in *Zea mays* 4.575mg/kg, followed by *Aspilia africana* 3.95mg/kg, *Abelmosehus esculenta* 3.7mg/kg, *Manihot esculenta* 0.725mg/kg and the least *Panicum maximum* 0.05mg/kg. The results revealed that copper concentration in the leaves from both the study area and the control sites varied between 1.275mg/kg and 3.035mg/kg in *Manihot esculenta*, 3.95mg/kg and 4.00mg/kg in *Aspilia africana*, 2.075mg/kg and 2.25mg/kg in *Zea mays*, 3.70mg/kg and 2.325mg/kg in *Abelmoschus esculenta* and 2.275mg/kg and 2.30mg/kg in *Panicum maximum* (Table 2). This result showed that the level of copper content in the selected plant leaves cannot be attributed to coal ash dump, nor a toxicity threat in any of the plant leaves studied.

The highest level of concentration of cadmium was found in *Zea mays* 5.225mg/kg (Table 1 and Figure 3), followed by *Abelmoschus esculanta* (3.65mg/kg), *Manihot esculenta* (3.575mg/kg), *Panicum maximum* (1.60mg/kg) and *Aspilia africana* (1.125mg/kg). The five selected plant leaves were at danger of Cd contamination and possible adverse health effect to their consumers since the level of Cd in each of the plant leaves exceeded its permissible limit. The concentration of cadmium in the leaves from the study area and the control sites varied between 3.575mg/kg and 0.825mg/kg in *Manihot esculenta*, 1.125mg/kg and 0.50mg/kg in *Aspilia africana*, 5.225mg/kg and 0.95mg/kg in *Zea mays*, 3.65mg/kg and 0.45mg/kg in *Abelmoschus esculenta* and 1.6mg/kg and 0.65mg/kg in *Panicum maximum* (Table 2). It is observed that concentration is higher in all the leaves from the study area than the control. Invariably, the level of cadmium content in the selected plant leaves of the study area may be attributed to coal ash dump.

Chromium concentration was most abundant in *Zea mays* (0.05mg/kg), *Aspilia africana* and *Abelmoschus esculenta* had concentrations of 0.025mg/kg each, while *Manihot esculenta* and *Panicum maximum* concentrations were below detectable limit of the instrument (Table 1 and Figure 3). Also chromium concentration varied between 0.025mg/kgand 0.20mg/kgin *Abelmoschus esculenta* for the study area and the control (Table 2). The result showed that eating of *Zea mays, Aspilia africana* and *Abelmoschus esculenta* from the study area may result to chromium poisoning.

Nickel (Ni) accumulated highest in *Aspilia africana* 7.05mg/kg (Table 1 and Figure 3), followed by *Manihot esculenta* 5.675mg/kg, *Abelmoschus esculenta* 4.025mg/kg, *Zea mays* 3.975mg/kg, and *Panicum maximum* 2.35mg/kg. The result showed that *Aspilia africana* and *Manihot esculenta* may be at danger of nickel contamination and possible adverse health implication to their consumers. The mean nickel valuein the sampled leaves were within the normal range of 0.1 – 5mg/kg reported by [6] for plants growing on natural soils, while *Manihot esculenta* and *Aspilia africana* had Ni concentrations beyond the normal range (Table 2). The results were similar to sample A of [12]. Nickel concentration in the leaves of the sampled plants from the study area and the control varied between 5.675mg/kg and 1.30mg/kg in *Manihot esculenta*, 7.05mg/kg and 13.00mg/kg in *Aspilia africana*, 3.975mg/kg and 1.45mg/kg in *Zea mays*, 4.024mg/kg and 0.575mg/kg in *Abelmoschus esculenta* and 1.1mg/kg and 0.875mg/kg in *Panicum maximum* (Table 2). The results showed that nickel concentration was higher in all the plant leaves from the study area than the control. Consequently, the level of nickel content in the selected plant leaves in the study area can be attributed to coal ash dump.

Highest concentration of zinc (Zn) was found in *Abelmoschus esculenta* 101.125mg/kg followed by *Manihot esculenta* 62.85mg/kg, *Aspilia africana* 44.925mg/kg *Zea mays* (42.35mg/kg) and *Panicum maximum* 36.875mg/kg (Table 1 and Figure 3). The mean value of zincin the sampled plant leaves from both the study area and the control are either below or within the normal range of 27 -150mg/kg reported by [6]. It was also observed that all the plants from thestudy area have higher level of zinc than the control samples (Table 2). Similar results were obtained by [13] in the study of *Solenum nigrum* L. Zinc is essential for plants in lipid and carbohydrate metabolism [6]. It is required for several enzymes in animals and is also essential for energy metabolism in humans [8].

4. Conclusion

The high level concentration of the metals Ni, Pb, Cd, Co, As, Mo, and Se in the sampled plant leaves were linked to the coal ash deposit in the study area, since their concentrations were more in the study area than the background. Meanwhile the selected plants were considered on the basis of their consumption either by man or animals. Consequently, the regular dependence on the food crops cultivated on the soil of the study area may be a threat to the food chain.

5. Recommendations

Based on the conclusions drawn from this study, it is recommended that more studies be carried out which will include the analysis of human blood of those who depend mostly on food crops and water sources from the study area for twenty years or more. Soil amendment and remediation should be applied if the place must be cultivated. The drinking water sources from the area should undergo proper treatment before use. More so, as the Federal Government of Nigeria is planning to resuscitate the coal industry, heavy metal remediation program should be incorporated into the original plant design of the Oji River power station.

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