Assessment of Heavy Metals (Zn, Cu, Pb, Cr, Cd and Ni) Concentration in the Leaves, Stems and Tubers of *Manihot esculenta* (Cassava) Harvested from the Egi Community, Rivers State

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Abstract: Heavy metals are usually associated with oil and gas exploration and exploitation activities. This study determined the levels of Zn, Cu, Pb, Cr, Cd and Ni in cassava (leaves, stems and tubers) grown in Egi. Samples of cassava collected from four locations, Control (Ohali-Elu) Location 1 (New Elf Road), Location 2 (Ugada) and Location 3 (Egita Land) were analysed using the AA500 model Atomic Absorption Spectrophotometer. Results of heavy metals concentration (mg/kg) in cassava leaf, stem and tuber from the study showed that all the metals were present in the plant tissues in both wet and dry season. Furthermore, their values were below the permissible limit in food crops by WHO/FAO/DPR (2018) except Cd which were recorded as 0.057 (Control), 0.375 (Location 1), 0.061 (Location 2) and 0.126 (Location 3) for Leaf, 0.345 (Control), 0.661 (Location 1), 0.348 (Location 2) and 0.191 (Location 3) for Stem and 0.924 (Control), 1.461 (Location 1), 0.893 (Location 2) and 0.393 (Location 3) for Tuber, in the wet season. This indicated that Cd levels in leaf, stem and tuber in the wet season were above the permissible limit of 0.02mg/kg for food crops. The elevated levels of Cd in cassava tissues implied consequences of oil-related activities and other anthropogenic contaminants in the study area. The pollution consequences of Cd together with its imminent hazards on human and animals have been discussed based on the result; therefore constant monitoring programs should be put in place to further safeguard the environment from other contamintants.

Keywords: Heavy Metals, Manihot esculenta, Pollution, Concentration, Contaminants

1. Introduction

Environmental pollution has been a major challenge confronting societies, scientists and regulators globally. It happens in both aquatic and terrestrial environments. A day hardly passes without a reported incident of environmental contamination resulting from anthropogenic activities (Osuji et al., 2004). Some cases have been reported to have occurred as a result of equipment failure, while others are attributed to personnel negligence and sabotage (Osuji et al., 2004). However, each pollution case, presents a serious concern to the environment as both biotic and abiotic components are either directly or indirectly affected in the process (Ekweozor, 1985). The aggressive manner of crude oil exploration and exploitation by the International Oil Companies (Total E&P, Shell Petroleum Development Corporation, Exxon Mobil, Chevron Oil Company, Nigeria Agip Oil Company etc.) for over five decades in the oil rich Niger Delta has undeniably transformed the area into an arena of environmental degradation such that visible signs of improvement in the quality of life of the local communities are rarely recorded (UNEP, 2011).

A great quantity of heavy metals and other chemical compounds, especially produced for industries, agriculture, mining, combustion of fossil fuels and traffic are often released to the atmosphere, soil and water, they aggressively manifest on terrestrial and aquatic flora and fauna (Celiket et al., 2005; Okafor and Opuene 2007; Mahvi 2008; Yasar et al., 2010). Heavy metals easily accumulate in large quantities in plant tissues with no visible phyto toxicity, but exceed human and animal tolerance level over time (Kovalchuk et al., 2001; Frasad and Freitas, 2003).

*Manihot esculenta* (cassava) is a perennial woody shrub in the *Euphorbiaceae* purge family native to South America but now grown in tropical and sub-tropical areas worldwide for the edible starchy roots (tubers), which are a major food source in the developing world, in equatorial regions including Africa, South America and Oceania.

The cassava shrub may grow to 2.75m (9 feet) tall, with leaves deeply divided into 3–7 lobes. The shrub is often grown as an annual plant and propagated from stem cuttings after tubers have been harvested. The fruit is small, roughly 1cm (1/2 inch) in diameter, but root tubers in cultivated varieties can be 5-10cm in diameter. Fresh roots and leaves contain cyanide compounds including linamarin (cyanogenic glucoside) and hydrocyanic acid at levels that may be toxic, but properly treated, the cyanide content is negligible. “Bitter” varieties contain more of these compounds than “sweet” varieties.

Cassava originated in Western and Southern Mexico and tropical South America (likely Brazil). It was introduced to West Africa in the 16th Century and became a major food crop there and in Asia. Cassava tubers are prepared in various forms as a food, and are an important source of carbohydrates; they also contain significant amount of phosphorus and iron, and are relatively rich in vitamin C. The leaves, which must also be treated to remove cyanide compounds before eating, contain 20-30% protein and are used as vegetables. Cassava is also used as livestock feed (Balley, 1976; FAOSTAT, 2012; Sadik, 1988).

The main objective of this study was to determine the content of Zn, Cu, Pb, Cr, Cd and Ni in cassava plant grown...
in selected locations in Egi community over wet and dry seasons.

2. Materials and Methods

2.1 Description of the Study Area

This study was carried out in Egi Community in Ogbá/Egbema/Ndoni Local Government Area. The area is located in the northern part of Rivers State sharing boundaries with Imo and Delta State respectively. It is a growing city with an estimated population of about 40,000 people EPNL (2005). The economy of the area relies mainly on agriculture and oil and gas, being one of the highest oil and gas producing communities in Rivers State. The climate is typically tropical with dry (November – March) and wet (June – October) seasons. Average temperature of the area ranges between 27°C – 32°C, while average humidity is between 69% and 96%, EPNL (2005).

Description of Sample Location

**Location 1 (New Elf Road)** - Situated at latitude 05°16'51.3” and longitude 006°37'56.8”, is 20 meters away from Total E&P Nigeria Ltd flare pit and flow station, and 50 meters to OB 29 Oil and Gas wells. The flare pit receives waste water from all injection wells around Ogbogu flow station. Members of the community farm annually on the land around the sample Location for commercial and domestic purposes.

**Location 2 (Ugada Imeagi)** - situated at latitude 05°16’51.3” and longitude 006°36’39.0”. It is 10 meters away from OB 38 and OB 64 Oil and Gas wells belonging to Total E&P Nigeria Ltd. OB 38 has a waste pit that receives drill cuttings and other industrial waste from Total E&P Nigeria Limited facilities. The land also serves as community farm land.

**Location 3 (Egita Land)** - situated at latitude 05°14’39.5” and longitude 006°37’10.8”. It is 10 meters away from OB 38 and OB 64 Oil and Gas wells belonging to Total E&P Nigeria Ltd. Location 3 is 50 meters away from the Ibewa gas clusters locations. This is where the gas eruption of 2012 took place. The location is also 100 meters away from the Obite gas plant which witnessed an explosion in 1998.

**Control Location (Ohali-Elu)** - Situated at latitude 05°16’51.3” and longitude 006°37’10.8”, 8km away from Location 3, 6.2km from Location 2 and 6km away from Location 1. The Control borders with the Orashi River from the North. The area is completely agrarian with no known records of Oil and Gas exploration and production activities. However, there is high vehicular and human activities in the area. Also, worthy of note is that the 2012 flood which submerged all the sample Locations including oil and gas facilities came from the Control.

Sampling Procedure

**Plant Sample Collection**

Samples of leaves, stem and tubers of *Manihot esculenta* were collected randomly six months after planting using vinyl gloves and carefully packed into polyethylene bags (Alam et al., 2003; Osma et al., 2012) for both wet and dry seasons. Samples collected were properly labeled showing locations, sample types, plant species and date of sampling, then taken to the Department of Plant Science and
Biotechnology, for proper botanical identification and thereafter to the Institute of Pollution Studies Laboratory, Rivers State University, Port Harcourt (RSU, PH) for preparation and analysis.

Plant Sample Preparation
All samples were taken to the Institute of Pollution Studies Laboratory, RSU, PH. All plant samples (leaves, stems and tubers) were washed in fresh running water to eliminate dust, dirt, possible parasites or eggs. The samples were then cut into small pieces and air dried for two weeks. The dried plant samples were homogenized by grinding using grinder and stored in polythene bags until used for acid digestion (Faruq et al., 2009).

Analysis of Heavy Metals
1g of prepared dried plant matter was added to 10ml of well mixed nitric, perchloric, and sulphoric acid. The mixture was heated using a heating mantle for 10-20 minutes. This was allowed to cool and thereafter, 20ml of distilled water was added. The mixture was then boiled to bring metals into solution. Thereafter, the solution was filtered after cooling through Whatmann filter paper into 100ml standard flask. It was then made up to the mark and content transferred into a plastic container. Each metal was thereafter ran using a AAS 500 calibrated daily with specific metallic standard.

3. Results

Heavy metal Concentration in the Leaf (mg/kg) of Manihot esculenta
The concentration of heavy metals in the leaf of Manihot esculenta sampled during the wet and dry season are shown in Table 1 and 2.

Table 1: Showing the concentration of heavy metals in the leaf of Manihot esculenta sampled during the Wet season

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Loc 1 (mg/kg)</th>
<th>Loc 2</th>
<th>Loc 3</th>
<th>Control</th>
<th>WHO/FAO/DPR (2017)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.375*</td>
<td>0.061*</td>
<td>0.126*</td>
<td>0.057*</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>0.028*</td>
<td>0.017*</td>
<td>0.039*</td>
<td>0.014*</td>
<td>1.30</td>
</tr>
<tr>
<td>Pb</td>
<td>0.033*</td>
<td>0.021*</td>
<td>0.027*</td>
<td>0.010*</td>
<td>2</td>
</tr>
<tr>
<td>Cu</td>
<td>0.000*</td>
<td>0.005*</td>
<td>0.005*</td>
<td>0.007*</td>
<td>10</td>
</tr>
<tr>
<td>Zn</td>
<td>0.000*</td>
<td>0.000*</td>
<td>0.000*</td>
<td>0.000*</td>
<td>0.60</td>
</tr>
<tr>
<td>Ni</td>
<td>0.009*</td>
<td>0.000*</td>
<td>0.000*</td>
<td>0.000*</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 2: Showing the concentration of heavy metals in the leaf of Manihot esculenta sampled during the Dry season

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Loc 1 (mg/kg)</th>
<th>Loc 2</th>
<th>Loc 3</th>
<th>Control</th>
<th>WHO/FAO/DPR (2017)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.002a</td>
<td>0.001a</td>
<td>0.002a</td>
<td>0.001a</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>0.005a</td>
<td>0.010a</td>
<td>0.005a</td>
<td>0.007a</td>
<td>1.30</td>
</tr>
<tr>
<td>Pb</td>
<td>0.002a</td>
<td>0.005a</td>
<td>0.002a</td>
<td>0.002a</td>
<td>2</td>
</tr>
<tr>
<td>Cu</td>
<td>0.030a</td>
<td>0.014a</td>
<td>0.026a</td>
<td>0.035a</td>
<td>10</td>
</tr>
<tr>
<td>Zn</td>
<td>0.367a</td>
<td>0.103a</td>
<td>0.256a</td>
<td>0.253a</td>
<td>0.60</td>
</tr>
<tr>
<td>Ni</td>
<td>0.012a</td>
<td>0.000a</td>
<td>0.000a</td>
<td>0.020a</td>
<td>10</td>
</tr>
</tbody>
</table>

The trends in the concentration of heavy metals in the leaf of Manihot esculenta sampled revealed thating the wet season, Cd (0.375) > Cr (0.028) > Ni (0.009) > Pb (0.003) > Zn and Cu (0.000) in Location 1 (Table 1) (Fig. 2); Cd (0.061) > Pb (0.021) > Cr (0.017) > Cu (0.007) > Zn (0.000) > Ni (0.000) in Location 2; Cd (0.126) > Cr (0.030) > Pb

Figure 2: Concentration of Heavy Metals in the Leaf of Manihot esculenta during the Wet Season

Figure 3: Concentration of Heavy Metals in the Leaf of Manihot esculenta during the Dry Season

Heavy metal Concentration in the Stem (mg/kg) of Manihot esculenta
The levels of heavy metal concentration in the stem of Manihot esculentasampled during the wet and dry season are shown in Table 3 and 4.

Table 3: Showing the concentration of heavy metals in the stem of Manihot esculenta sampled during the Wet season

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Loc 1 (mg/kg)</th>
<th>Loc 2</th>
<th>Loc 3</th>
<th>Control</th>
<th>WHO/FAO/DPR (2017)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.661*</td>
<td>0.348*</td>
<td>0.191*</td>
<td>0.345*</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>0.084*</td>
<td>0.025*</td>
<td>0.030a</td>
<td>0.051*</td>
<td>1.30</td>
</tr>
<tr>
<td>Pb</td>
<td>0.003a</td>
<td>0.010a</td>
<td>0.014a</td>
<td>0.011a</td>
<td>2</td>
</tr>
<tr>
<td>Cu</td>
<td>0.002a</td>
<td>0.005*</td>
<td>0.006a</td>
<td>0.005*</td>
<td>10</td>
</tr>
<tr>
<td>Zn</td>
<td>0.000*</td>
<td>0.000*</td>
<td>0.000*</td>
<td>0.000*</td>
<td>0.60</td>
</tr>
<tr>
<td>Ni</td>
<td>0.000*</td>
<td>0.000*</td>
<td>0.000*</td>
<td>0.000*</td>
<td>10</td>
</tr>
</tbody>
</table>

The trends in the concentration of heavy metals in the leaf of Manihot esculenta sampled revealed that during the wet season, Cd (0.375) > Cr (0.028) > Ni (0.009) > Pb (0.003) > Zn and Cu (0.000) in Location 3 and Cd (0.057) > Cr (0.014) > Pb (0.010) > Cu (0.007) > Zn (0.000) and Ni (0.000) in the Control (Table 1) (Fig. 2). Cd recorded the highest concentration of 0.375mg/kg at Location 1.

Dry season showed that Zn (0.367) > Cu (0.03) > Ni (0.012) > Cr (0.005) > Pb and Cd (0.002) in Location 1 (Table 2) (Fig. 3); Zn (0.103) > Cu (0.014) > Cr (0.01) > Pb (0.005) > Cd (0.001) > Ni (0.000) in Location 2 and Zn (0.256) > Cu (0.026) > Cr (0.005) > Pb and Cd (0.002) > Ni (0.000) in Location 3 and Zn (0.253) > Cu (0.035) > Ni (0.02) > Cr (0.007) > Pb (0.002) > Cd (0.001) in the Control (Table 2) (Fig. 3). Zn recorded the highest concentration of 0.367mg/kg at Location 1.
The values recorded during the wet season followed a trend which reveals, Cd (0.661) > (0.084) > Pb (0.003) > Cu (0.002) > Zn and Ni (0.000) in Location 1 (Table 3) (Fig. 4); Cd (0.348) > Cr (0.255) > Pb (0.010) > Cu (0.005) > Zn and Ni (0.000) in Location 2, Cd (0.191) > Cr (0.030) > Pb (0.014) > Cu (0.006) > Zn and Ni (0.000) in Location 3 and Cd (0.345) > Cr (0.051) > Pb (0.011) > Cu (0.005) > Zn and Ni (0.000) in the Control (Table 3) (Fig. 4). Cd had the highest concentration of 0.661mg/kg in the stem of Manihot esculenta at Location 1. The values were however not significantly different (P<0.05).

The values followed a different pattern during the dry season which reveals Zn (0.241) > Cu (0.023) > Cr (0.003) > Pb (0.002) > Ni (0) for Location 2, Zn (0.215) > Cu (0.024) > Cr (0.004) > Cd (0.003) > Pb (0.002) > Ni (0) for Location 3 and Zn (0.029) > Cu (0.014) > Cr (0.004) > Pb (0.002) > Cd (0.001) > Ni (0) for Control (Table 4) (Fig. 5). Statistically the values were also not significantly different (P<0.05).

Table 4: Showing the concentration of heavy metals in the stem of Manihot esculenta sampled during the Dry season

<table>
<thead>
<tr>
<th>Heavy metals (mg/kg)</th>
<th>Loc1</th>
<th>Loc 2</th>
<th>Loc 3</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.003*</td>
<td>0.002*</td>
<td>0.003*</td>
<td>0.001*</td>
</tr>
<tr>
<td>Cr</td>
<td>0.005*</td>
<td>0.003*</td>
<td>0.004*</td>
<td>0.004*</td>
</tr>
<tr>
<td>Pb</td>
<td>0.002*</td>
<td>0.002*</td>
<td>0.002*</td>
<td>0.002*</td>
</tr>
<tr>
<td>Cu</td>
<td>0.203*</td>
<td>0.019*</td>
<td>0.024*</td>
<td>0.014*</td>
</tr>
<tr>
<td>Zn</td>
<td>0.241*</td>
<td>0.297*</td>
<td>0.215*</td>
<td>0.298*</td>
</tr>
<tr>
<td>Ni</td>
<td>0.000*</td>
<td>0.000*</td>
<td>0.000*</td>
<td>0.000*</td>
</tr>
</tbody>
</table>

The trend in the concentrations of heavy metals in the tubers of Manihot esculentas sampled during the wet and dry season are shown in Table 5 and 6.

Table 5: Showing the concentration of heavy metals in the tuber of Manihot esculenta sampled during the Wet season

<table>
<thead>
<tr>
<th>Heavy metals (mg/kg)</th>
<th>Loc1</th>
<th>Loc 2</th>
<th>Loc 3</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>1.461</td>
<td>0.893</td>
<td>0.393</td>
<td>0.924</td>
</tr>
<tr>
<td>Cr</td>
<td>0.908</td>
<td>0.088</td>
<td>0.160</td>
<td>0.010</td>
</tr>
<tr>
<td>Pb</td>
<td>0.001</td>
<td>0.009</td>
<td>0.010</td>
<td>0.009</td>
</tr>
<tr>
<td>Cu</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Zn</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Ni</td>
<td>0.049</td>
<td>0.040</td>
<td>0.040</td>
<td>0.026</td>
</tr>
</tbody>
</table>

Table 6: Showing the concentration of heavy metals in the tuber of Manihot esculenta sampled during the Dry season

<table>
<thead>
<tr>
<th>Heavy metals (mg/kg)</th>
<th>Loc1</th>
<th>Loc 2</th>
<th>Loc 3</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.002</td>
<td>0.001</td>
<td>0.008</td>
<td>0.103</td>
</tr>
<tr>
<td>Cr</td>
<td>0.009</td>
<td>0.001</td>
<td>0.004</td>
<td>0.005</td>
</tr>
<tr>
<td>Pb</td>
<td>0.007</td>
<td>0.006</td>
<td>0.003</td>
<td>0.005</td>
</tr>
<tr>
<td>Cu</td>
<td>0.012</td>
<td>0.010</td>
<td>0.023</td>
<td>0.016</td>
</tr>
<tr>
<td>Zn</td>
<td>0.089</td>
<td>0.060</td>
<td>0.087</td>
<td>0.077</td>
</tr>
<tr>
<td>Ni</td>
<td>0.000</td>
<td>0.000</td>
<td>0.010</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The trend in the concentrations of heavy metals in the tubers of Manihot esculentas sampled during the wet and dry season are shown in Table 5 and 6.

Wet season followed a trend which reveals that Cd (1.461) > Cr (0.098) > Ni (0.049) > Cu (0.002) > Pb (0.001) > Zn (0.000) in Location 1 (Table 5) (Fig. 6): Cd (0.893) > Cr (0.088) > Ni (0.040) > Pb (0.009) > Cu (0.002) > Zn (0.000) in Location 2, Cd (0.393) > Cr (0.160) > Ni (0.040) > Pb (0.010) > Cu (0.002) > Zn (0.000) in Location 3 and Cd (0.924) > Cr (0.110) > Ni (0.026) > Pb (0.009) > Cu (0.002) > Zn (0.000) in Control. The values recorded were not significantly different (P<0.05).

Dry season showed a different trend which further revealed that Zn (0.089) > Cu (0.012) > Cr (0.009) > Pb (0.007) > Cd (0.002) > Ni (0.00) in Location 1 (Table 6) (Fig. 7). Zn (0.06) > Cu (0.01) > Pb (0.006) > Cr (0.001) > Ni (0.00) in Location 2 and Zn (0.087) > Cu (0.023) > Cd (0.008) > Cr (0.004) > Pb (0.003) > Ni (0.01) in Location 3 and Cd (0.103) > Zn (0.077) > Cu (0.016) > Pb (0.005) > Cr (0.005) > Ni (0.00) in the Control (Table 6) (Fig. 7). Cd recorded the highest concentration of 0.103mg/kg in the tuber at the Control Location however the values were also not significantly different (P<0.05).

Figure 4: Concentration of Heavy Metals in the Stem of Manihot esculenta during the Wet Season

Figure 5: Concentration of heavy metals in the stem of Manihot esculenta during the Dry Season

Figure 6: Concentration of Heavy Metals in the Tuber of Manihot esculenta during the Wet Season
Calabar” reported higher values than those obtained in this study. Okereke et al., (2006) reported similar range of value for Cu in a study carried out on vegetables and tubers in Alakiahia and Eleme communities of Rivers State, Nigeria. The higher values of Cu recorded in the dry season could be attributed to the strong affinity of Cu with organic matter (Novell, 1991). This therefore suggest that the amount of organic matter dissolved in the soil solution especially in soil high in organic matter in the wet season could play a very important role in determining Cu solubility and availability.

4. Discussion

Zinc (Zn) mg/kg
Result of Zn obtained from the present study showed that while Zn was found to be below detection limit in the wet season, it was detected in the dry season with the highest value recorded in the leaf of M. esculenta as 0.253 in the Control. However, all values obtained in all plant tissues were below permissible limit of 0.60mg/kg for food crops. Concentration of Zn varied statistically significant at P<0.05 between wet and dry seasons in the leaf, stem and tuber respectively.

However, Osakwe et al., (2015) reported higher values of Zn in cassava leaves and tubers than those reported in the present study. Idoho-Umeh et al., (2010) also reported mean concentration of 3.39mg/kg of Zn in epicarp of plantain fruit. Furthermore, Nwajei et al., (2013) reported a mean concentration of 4.89±0.5mg/kg of Zn in tomato leaves and 3.33±0.52mg/kg of Zn in tomato fruit. Ano et al., (2007) and Nabulo (2006) in their studies reported similar range of values as those reported by Osakwe et al., (2015). The non-detection of Zn in the leaf, stem and tuber in the wet season may be attributed to its strong affinity with organic matter which may have accumulated as a result of slow degradation process occasioned by low temperature associated with wet season.

Moreso, complexes between organic matter and Zn may have also made Zn non-bioaccessible for M. esculenta during the wet season. Furthermore, Moraghan and Macaigu Jnr (1991) reported that Zn forms precipitation with oxides of Fe, Al and Mn in waterlogged soils under reducing condition. This could also suggest Zn non-availability for plant uptake.

Copper (Cu) mg/kg
Cu concentration observed from the results obtained showed that Cu was not detected in all Locations in the wet season. Highest value of Cu was recorded in the leaf of M. esculenta in the dry season as 0.035 in the Control. Values recorded for Cu in the present study showed statistical significant difference at P<0.05 between wet and dry season.

However, all the values obtained in this study were found to be lower than the permissible value of 10mg/kg recommended for Cu in food crops by WHO/FAO/DPR (2017). Edem et al., (2009) in a study titled, “distribution of heavy metals in leaves, stems and roots in fluted pumpkin in Calabar” reported higher values than those obtained in this study. Okereke et al., (2006) reported similar range of value for Cu in a study carried out on vegetables and tubers in Alakiahia and Eleme communities of Rivers State, Nigeria. The higher values of Cu recorded in the dry season could be attributed to the strong affinity of Cu with organic matter (Novell, 1991). This therefore suggest that the amount of organic matter dissolved in the soil solution especially in soil high in organic matter in the wet season could play a very important role in determining Cu solubility and availability.

Lead (Pb) mg/kg
Results of Pb concentration obtained in stem vary significantly between and dry seasons at P<0.05. while that of the leaf and tuber did not show any significant difference at P>0.05. However, the highest value of Pb was recorded in the leaf in the wet season as 0.027 in Location 3. The result of Pb concentration obtained in this study are below the permissible limit of 2mg/kg for food crops.

Values of Pb obtained in the present study agrees with those reported for Pb in root/tubers from Alakiahia and Eleme by Okereke et al., (2006). Edem et al., (2009) reported elevated values of Pb in leaves, stems and roots of T. occidentalis. Osakwe et al., (2015) reported high values of Pb in cassava tubers. Ano et al., (2007) and Nabulo (2006) in their studies reported values similar to those reported by Osakwe et al., (2015).Ogboi (2012) also reported that the concentration of Pb in both the root and stem of groundnuts have exceeded permissible levels for human and animal consumption as recommended by FAO and WHO (2012). Furthermore, in a similar study, Essiet et al., (2010) reported a concentration of 0.36mg/kg for Pb, which is higher than those reported in the present study. The results obtained in this study agrees with those of Akanivwor et al., (2005) who reported the absence of Pb in raw and processed Nigerian staple foods from oil producing areas of Rivers and Bayelsa State of Nigeria. Higher concentration values obtained in the wet season in this study could be attributed to reduced soil pH which favors Pb solubility, thereby making them more bioavailable than in the dry season.

Pb could be introduced to the soil through oil spill, fertilizers, fossil fuel and other domestic and industrial waste disposed into the soil. This increases the soil-plant-man pathway which may eventually lead to accumulation of Pb. In children, Pb is most damaging at the age of six years and younger. At low levels, Pb can be harmful and is associated with learning disabilities resulting in decreased intelligence, attention deficit disorder, behavior issues, nervous system damage, speech and language impairment, decreased muscle growth, decreased bone growth and kidney damage (International Cadmium Association, 2013). WHO (2010) also stated that chronic Pb poisoning as characterized by neurological defects, renal tubular dysfunction and anemia. In men, Pb affects male gametes resulting in sperm abnormalities and decreased sexual desires as well as sterility Needlemen et al., (1981). In women, Pb poisoning is associated with abnormal ovarian cycles and menstrual disorders in addition to spontaneous abortion Needelemen et al., (1984). Pb toxicity has been associated with inhibited synthesis (Harmon et al., 2004).
Chromium (Cr) mg/kg
Cr concentration obtained showed statistically significant between wet and dry seasons at P<0.05. Highest values of Cr were recorded in the tuber of *M. esculenta* in the wet season as 0.160 in Location 3. Cr concentration in the tissues of *M. esculenta* analyzed in the wet and dry season were found to be lower than the permissible limit of 1.30mg/kg set for Cr in food crops by WHO/FAO/DPR (2017).

The values of Cr obtained in this study during the wet season are consistent with those reported by Nkwocha and Duru (2010)in a study to analyze the effect of oil pollution on local plant species and food crops. Okereke *et al.,* (2006) also reported similar range of values for Cr as those recorded in the present study. In a similar study, Osakwe *et al.,* (2015) reported higher concentration of Cr in the leaves and tubers of cassava. Ano*et al.,* (2007) and Nabulo, 2006also reported similar values as those reported by Osakwe *et al.,* (2015). Edemet *et al.,* (2009) reported similar values of Cr in the leaves, stems and roots of *T. occidentalis* in Calabar. Possible sources of Cr contaminated into soil include Chromium plated vehicle part used for corrosion preservation, Al-Rhasman (2007).Cr is also used as anticrosive material in the installment of crude oil pipes. Variability in Cr concentration between wet and dry seasons observed in the present study could be as a result of reduced soil pH which favors metal solubility. Cr is carcinogenic resulting in the cancer of respiratory organs in workers exposed to Cr contaminating dust (Langard, 1980).Cr has also been reported of having epidemiological effects on the urogenital system, cardiovascular problems and carcinogenic effect (Costa and Klein, 2006).

Cadmium (Cd) mg/kg
Cd concentration in the leaf and stem varied statistically at P<0.05. Highest value of Cd was recorded in the tuber of *M. esculenta* in the wet season as 1.461 in Location 1. Cd concentration levels obtained were above Cd permissible levels of 0.02mg/kg for food crops in all Locations in the wet season and in Control in the dry season. Higher concentration of Cd in the wet season may have been favoured by both pH of the soil and the absence of Zn. Since according to Isirimah, 2004 Zn and Cd have geochemical association, therefore Cd being directly below Zn in the Periodic Table, will tend to mimic Zn in its absence.

Concentration of Cd recorded in the present study is higher than those reported in cassava leaves and tuber by Nkwocha and Duru (2010). Okereke *et al.,* (2006)in a similar study reported lower values of Cd than those recorded in the present study in the root/tubers at Alakahia and Eleme. Essiet *et al.,* (2010) also obtained in a study, mean concentration of 0.05mg/kg in plants grown in oil polluted soil. Kihampa *et al.,* (2011)stated that the level of Zn, Cr, Pb and Cd were above the permissible levels of heavy metals in food as outlined in WHO guidelines and Tanzania Bureau of Standards. Ogboi (2012) stated that the concentration of Cd and Pb in both the root and stem of groundnuts have exceeded permissible levels for human and animal consumption as recommended by FAO and WHO. Sources of Cd to the soil and plant include phosphate fertilizers, detergent and refined petroleum products. Also, application of pesticides and biosolids (sewage sludge) and the disposal of industrial waste or the atmospheric contaminants increased the total concentration of Cd in soils and the bioavailability of Cd determines whether the plant Cd uptake occur to a significant degree (Weggler *et al.,* 2004).Cd in the body is known to affect several enzymes. It is believed that the renal damage that result in proteinuria is the result of Cd adversity affecting enzymes responsible for reabsorption of proteins in kidney tubules (Manahan, 2003).Cd toxicity induces tissue injury through creating oxidative stress, epigenetic changes in DNA expression, inhibition or up regulation of transport pathways particularly in proximal segment of the kidney tubule (Dufresne and Fransworth, 2001).

Nickel (Ni) mg/kg
Ni was only detected in leaf of *M. esculenta* harvested from Location 1 and tuber harvested in all Locations in wet season. In the dry season, Ni was only present in the Control and Location 1. Highest value of Ni was recorded in the tuber in the wet season as 0.049 in Location 1.

Onder *et al.,* (2017) reported airborne particles emitted by brakes and wears from vehicle tyres as possible sources of Nickel to the soils. The absence of Ni in the leaf, stem and tuber of *M. esculenta* analysed in both wet and dry seasons in most of the Locations agrees with Akaniwor *et al.,* (2005)who reported the absence of Ni and Pb in raw and processed Nigerian staple foods from oil producing areas of Rivers and Bayelsa State of Nigeria. Some of the values obtained in this study are consistent with those reported by Nkwocha and Duru, (2010)but lower than those reported by Okereke *et al.,* (2006), Osakwe *et al.,* (2015), Ano *et al.,* (2007) and Nabulo, 2006, Ni level recorded in this study is below the permissible limit of 10mg/kg in food crop as recommended by WHO/FAO/DPR (2017). Exposure to intake of large amount of Ni from plants, grown in Ni rich soils lead to higher chances of developing cancer of the lungs, nose, larynx and prostrate as well as respiratory failure, birth defects and heart disorders (Duda-Chodale and Blaszzyk, 2008;Lentech, 2009).

5. Conclusion

Heavy metals in plants are essential for the total wellbeing and growth of animals and human beings, but their levels should fall within tolerance limits. As shown in the results of the investigation, the concentration values of Zn, Cu, Pb, Cr and Ni were below permissible limit in food crops as set by WHO/FAO/DPR. The exception was the concentration of Cd which was above the permissible limit of 0.02mg/kg for food crops. As a result, the pollution status of cassava in the study area with respect to Cd is significant. Consequently, humans and animals in the study area are under the threat of Cd contamination. From the data obtained from this study, it will be expedient to conduct a follow up study to assess the levels of the toxic element for other food crops that are cultivated and sold in different markets in Egi community. Also, management measures to reduce the transfer of Cd from contaminated soils into the food chain should be developed.
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References


