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Research Article

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Assessment of Heavy Metals in Soils and *Manihot esculenta* of Some Selected Communities in Niger Delta

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Abstract

The study to evaluate the concentration of heavy metals in soils and *Manihot esculenta* in some selected communities in Niger Delta: Umuechem (S1), Ebocha (S2), Ofuoma (S3), and Ndashi (control)(S4). Heavy metals were analyzed following standard methods using Perkin-Elmer model 403 Atomic Absorption Spectrophotometer. Data revealed that the levels of heavy metals in soil samples from the selected stations vary significantly ($P<0.05$). Heavy metals such as Cd was above permissible limit (WHO), Cu, Ni and Pb were all below detectable limit, while Cr was below detectable limit in the Dry season and below permissible limit in the wet season. The study further revealed that heavy metals such as Cd, Cu, Ni and Pb in *Manihot esculenta* were all above permissible limit (WHO) while Cr was above permissible limit in all stations except in the control Station (Ndashi) in the wet season and below detectable limit in the dry season. This study established that there should be constant monitoring of anthropogenic activities in the study area.

Keywords: *Manihot esculenta*, soil, Heavy metals, Niger Delta

1.0 Introduction

One of the greatest environmental problems that pose a grave challenge to the residents of Niger Delta is oil pollution. Oil pollution is defined as the poisoning of the land, air and sea (Akpofuro *et al.*, 2000; Ako and Okonmah, 2009). Oil pollution is also seen as the introduction of substances into the physical environment which causes hazards and general discomfort to man, plants and animals, as have been witnessed in the Niger Delta Region of Nigeria in recent times (Clark, 2005).

In 1946, one year after the war had ended; the exploration of oil began in the Niger Delta region of Nigeria. Shell D'Arcy drilled several exploration wells and discovered the first commercial oil in Oloibiri fields in January 1956 and the second one in Afam (Ite *et al.*, 2013).

Over the years, the Nigerian economy has survived majorly on the exploration, production and exportation of petroleum from the Niger Delta region of the country. This has led to great improvements in the economy over the past few decades. The economy has been dominated by the petroleum industry and this has resulted in a decline in the contribution recorded by the agricultural sector of the economy in the 1970 (Ite *et al.*, 2013). According to Phil-eze and Okoro (2009), there is evidence to indicate that crude oil sales income as a proportion of foreign exchange earnings escalated from 2.5% to 58.1% in 1970, to 93.6% in 1975 greater than 98% through the first half of the 1980s. Over 85% of Nigeria's GDP can be associated with oil and gas resources. This sector also represents over 95% of foreign exchange revenues from Nigeria and contributes over 80% of the revenues required in the running of the government of Nigeria (Aaron, 2005).

In addition to the poverty ravishing the area, the activities that are part of petroleum exploration, production and operations have significantly impacted negatively on the environment. Over these years there are remarkable changes to the sediments and soil, groundwater, atmosphere, surface water, marine and estuarine ecosystems, biological integrity and diversity in both the terrestrial and aquatic ecosystems (Ite *et al.*, 2013). There may be paucity of records to confirm in this trend over the years as these changes and pattern to directly be subtle; however, there are drastic changes due to catastrophic events arising from petroleum exploration in the Niger Delta (Aaron, 2013).

Other human-related sources of pollution exist within the oil producing states in Nigeria, effluents discharge from petroleum production into the environment have led to pollution of the environment leading to the disadvantageous implication of the social and economic life of the people, regional economy and general environmental degradation in the Niger Delta region.

The activities of the Oil Companies instead of improving have impoverished its people by causing a serious decline in their marine and agricultural resources, which constitute their economic main stay (UNEP, 2006). Environmental pollution drasticaly declines in the region’s biodiversity and ecological resources, which are the main sources of their income and the people’s mode of survival (Nwilo and Badejo, 2005).

Excessive accumulation in agricultural soils may result not only in soil contamination, but has also consequences for food quality and safety. So, it is essential to monitor food quality, given that plant uptake is one of the main pathways through which heavy metals enter the food chain (Atuanya, 2005).

Tubers and fruits take up heavy metals and accumulate them in their edible and non-edible parts at quantities high enough to cause clinical problems to both animals and human beings (Thomas, 2018). Onojake and Frank (2013), reported that soil and vegetables contaminated with Pb and Cd in Copsa Mica and Baia Mare, Romania, significantly contributed to decrease human life expectancy (9-10 years) within the affected areas.

2.0 Materials and Methods

2.1 Description of the study area

Niger Delta is the delta of the Niger River sitting directily on the Gulf of Guinea on the Atlantic Ocean in Nigeria. The Niger Delta extends over about 70,000 km^2 (27,000 sq mi) and makes up 7.5% of Nigeria's land mass, (Frank, 2013). It is the largest wetland and maintains the third-largest drainage basin in Africa. The Delta's environment can be broken down into four ecological zones: coastal barriers islands, mangrove swamp forests, freshwater swamps and lowland rainforests. The region has an estimated regional population of nearly 30 million people (Frank, (2013) and comprise of

9 States including Rivers, Bayelsa, Akwa Ibom, Delta, Imo, Abia, Ondo, Cross River and Edo (Frank, 2013). However, majority of the oil pollution and gas flaring occur in the core Niger Delta states of Bayelsa, Rivers, Delta, and Akwa-Ibom states respectively. It is also the region of Nigeria where majority of the oil exploration activities are carried out. The area host a number of International Oil Companies (IOC'S) including Shell whose activities is more prominent in the region.

Niger Delta is linked to all parts of the world through its international air and sea ports. Niger Delta climate falls within the sub equatorial climate belt. Temperature and humidity are high throughout the year. The area is marked by two distinct seasons the wet and the dry seasons –with 70 percent of the annual rains falling between April and August, while 22 percent is spread in the two months of September to October. The driest months are from November to March (Ayotamuno et al., 2000). The soil type consists mainly of poorly-drained silt clays mixed with sand, which is geologically classified under the Benin formation.

This study was carried out in Umuechem land in Etche Local Government of Rivers State, Ebocha in Ogba/Egbema/Ndoni Local Government of Rivers State, Ofuoma, Ughelli North Local Government Area of Delta State and a control site in Ndashi in Etche Local Government of Rivers State. The three communities under study have petroleum flow stations apart from Ndashi community which serves as control site has none. Therefore, this study to assess the levels of heavy metals in soil and *Manihot esculenta* of some selected communities in Niger Delta.

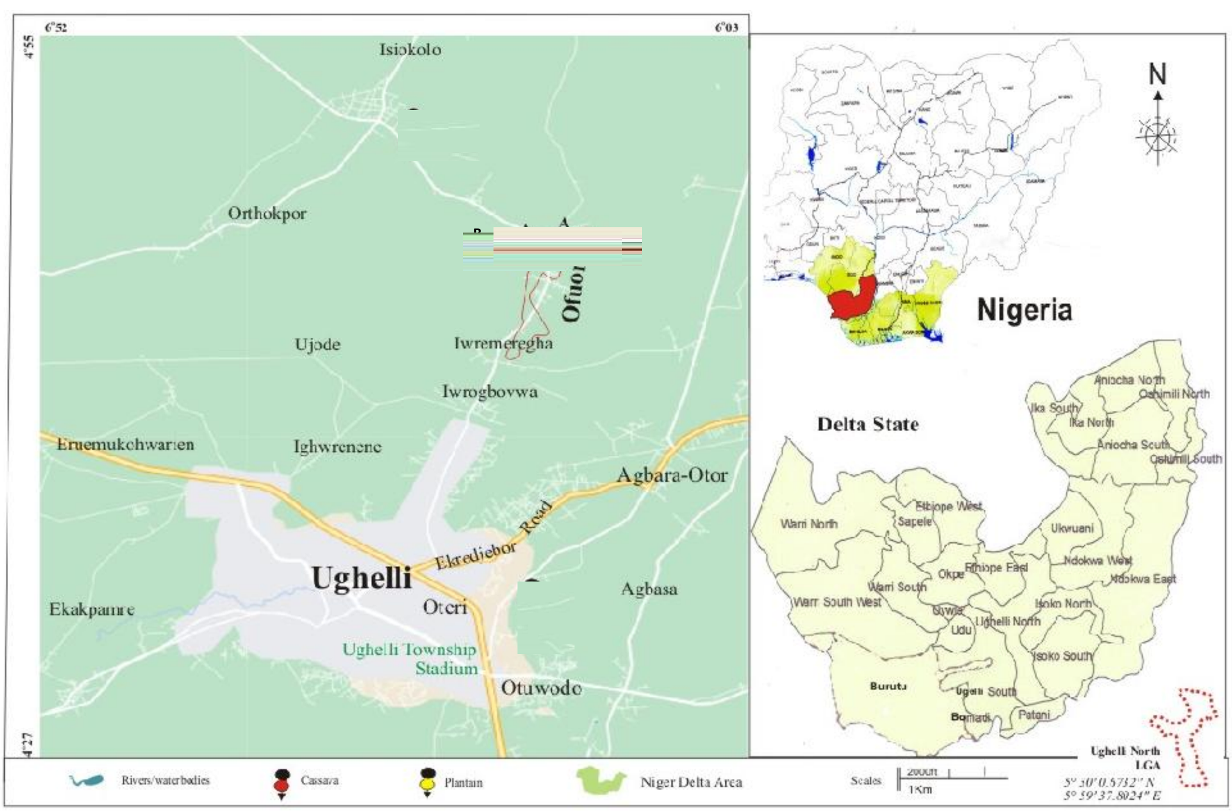

Fig. 1 Map of Rivers and Delta State Showing the Study Areas.

2.2 Analysis of Heavy Metals in Soil (mg/kg)

Soil samples were air-dried, ground to fine dust, sieved through a 2mm sieve, then digested and heavy metal concentrations determined using the Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer according to the method described by Bates (2006). The Atomic Absorption Spectrophotometer was calibrated using standard solution of the respective metals of interest (Cd, Cu, Ni, Pb and Ni). The concentration values were extrapolated from a calibrator graph of Absorbance and Concentration which gave the concentration of heavy metals in mg/kg.

2.2.1 Extraction and Analysis of Heavy Metals in *Manihot esculenta*

The samples of *Manihot escaulenta* were brought out of refrigerator and kept in clean polythene bags and allowed to attain room temperature. The piliferous layers of *Manihot escaulenta* tubers were carefully removed. The cortex of *Manihot esculenta* was cut into pieces and oven dried at 85°C to constant weight. The dried samples were ground into powdery form and labelled. One gram of each ground sample was weighed into 100 ml beaker. 5ml concentrated nitric acid and 2mL perchloric acid was added and heated in a fume cupboard to almost dryness. Then, 10mL of deionised water was added and the solution was properly, stirred and filtered with Whatman filter paper No. 42. Blank samples were prepared in the same procedure with deionised water instead of *Manihot escaulenta*. The filtrate of each sample was aspirated into the flame of Absorbed Atomic Spectrophotometer (AAS) along with standard solution. Readings were taken and recorded in mg/kg.

2.2.2 Soil to Plant Transfer Assessment

Soil to plant metal transfer was computed as transfer factor (TF) which was defined by equation 1.

$$TF = C_{plant} / C_{soil} \qquad (1)$$

(Chary et al., 2008)

Where (C_{plant}) is the concentration of heavy metals in plants and (C_{soil}) is the concentration of heavy metals in soil.

2.3 Health risk assessment

For the assessment of health risks through consumption of cassava produce by the local inhabitants, the daily intake of metal (DIM), health risk index (HRI), and the target hazard quotient (THQ) were evaluated using equations 2, 3, and 4 respectively.

$$\text{Daily Intake Metal (DIM)} = \frac{Cmetal\ x\, Cfood\ \mathrm{int}\, ake}{B\, average\ weight} \qquad \text{(Chary et al., 2008)} \qquad (2)$$

$$\text{Health Risk Index (HRI)} = \frac{DIM}{Rfd} \qquad \text{(Jan et al., 2010)} \qquad (3)$$

$$\text{Target Health Quatient (THQ)} = \frac{10^{-3}\,(EF\ ED\, FIR\, C)}{RFD\, Baverage\, weight\, TA} \qquad \text{(Chien } et\ al. \text{ 2002)} \qquad (4)$$

Where, C_{metal}, $C_{foodintake}$, and B average weight represent the heavy metal concentrations in cassava tuber (mg kg-1), daily intake of cassava produce, and average body weight respectively.

The average daily intake of cassava produce (garri) was gotten by conducting a survey where 323 people (males and females) having an average body weight of 60 kg were asked for their daily intake of garri. RFD represents reference oral dose (mg kg-1 day-1). Value for Cr, Ni, Cu, Pb and Cd, is 1.5, 0.02, 0.04, 0.004 and 0.001, (mgkg-1 bw day-1) respectively (USEPA IRIS, 2006). EF is exposure frequency (365 days year-1), ED is the exposure duration (70 years), equivalent to the average life time (Bennett et al. 1999), FIR is the food ingestion rate (kg person-1 day-1), C is the metal concentration in food (mg /kg) and TA is the average exposure time for noncarcinogens (365 days year-1).

3.0 Results and Discussion

3.1 Heavy Metal Concentrations in the Soils of the Sampled Stations

The Concentration of heavy metals in the soils from the sampled stations in the wet and dry season are shown in Table 1 below.

The mean concentrations of Cadmium in the soil in this study showed that Umuechem (2.75±0.21, 15.04±4.59mg/kg), Ebocha (5.95±1.34, 11.15±3.29mg/kg), Ofuoma (8.45±1.06, 14.53±5.73mg/kg) and Ndashi (1.91±1.64, 2.79±1.39mg/kg) for wet and dry season respectively. The least came from the control site (Ndashi) in wet season while the highest came from Umuechem in dry season, statistically the values were not significantly different in both seasons ($P<0.05$). This could be attributed to the presence of spilled crude-oil at Umuchem, Ebocha, Ufuoma sites, which must have been washed by rain from nearby flow stations, gas compressors, giant electric generators and numerous oil wells. The low concentrations of heavy metals found in control site (Ndashi) from oil polluted sites is a confirmation that spilled crude-oil was responsible for the higher values recorded at Umuechem, Ebocha and Ufuoma sites. This is expected since any area near petroleum activities has higher level of pollutants including heavy metals (Nkwocha and Duru, 2010). Udosen *et al.* (2012) reported values 1.12 mg/kg for Cd for soil samples obtained from the crude oil contaminated land of Mkpanak in Ibeno Coastal Area of Akwa-Ibom, State. This finding is in line with the assertion of Akubugwo *et al.* (2012) who recorded cadmium metal content in the soils ranging between 73.62 mg/kg to 226.39 mg/kg in Abia State. Similarly Tsafe *et al*. (2012) reported a value of 195.25 mg/kg in the soils studied. Other studies have reported higher values than those of this study. Awokunmi et al. (2010) reported values between 1100 to 10,920 mg/kg in Itaogbolu Area of Ondo State while McGrath *et al.* (2008) reported Cadmium metal content of 80000 mg/kg in Western Europe and Kimani (2007) reported a mean concentration of 57100mg/kg on uncontaminated soil in Kenya. The transfer factor of Cadmium between the soil, fruits and tubers was only significant for those fruits and tubers grown at the control site.

Chromium in this study are presented in Table 1, Umuechem (2.75±0.21, BDL), Ebocha (6.83±96.17mg/kg, BDL), Ofuoma (353.7±3.13, BDL) and Ndashi (7.45±3.46 mg/kg, BDL) in both wet and dry season respectively. The least came from Umuechem wet season while the highest came from Ofuoma wet season, dry season is below dictation limits in all the stations. The Cr in wet season is below the permissible limit of 100mg/kg (WHO/DPR, 2004) in all the sample stations, the values were also not significantly different ($P<0.05$). This finding is below the observations made from the ealier work by Banka-Coker and Ekundayo (2018) who had reported a significant build up of heavy metals in crude oil contaminated soils collected from Niger Delta. Futher studies by Inengite *et al.* (2010) had similarly shown the relatively abundance of Cr in oil contaminated soils.

The mean concentrations of Cu are presented in Table 1, Umuechem (26.5±13.41, 29.54±1.46), Ebocha (31.9±9.63, 5.68±3.02 mg/kg), Ofuoma (14.58±15.10, 7.84±3.72 mg/kg) and Ndashi (27.25±7.21, 2.91±1.51 mg/kg) in wet and dry seasons respectively. The least came from Ndashi dry season while the highest came from Ebocha wet season, the result at all the stations were below the permissible limits of 36mg/kg

(WHO/DPR, 2004). Statistically the values were significantly different in the dry season.

The values are below those reported in literature for uncontaminated soils. Kabata-Pendias and Pendias (1992), Haluschak *et al.* (1998), McGrath *et al.* (2001) in Western Europe and EPA (1995) reported soils with the higher limits of 140 mg/kg, 68 mg/kg, 100 mg/kg and 750 mg/kg, respectively for copper in uncontaminated soils. Awokunmi *et al.* (2010) reported even higher levels of copper from 95 to 6726 mg/kg from soils collected from several oil polluted sites in Itaogbolu Area of Ondo State, Nigeria.

The transfer of copper from the soils to the fruit and tubers in this study was almost zero. This could be because copper contents do not mobilize in plants and remain stagnant in roots, which would explain the lower content of the metal in leaves as compared to the soils (Bakere et al., 1994). Yang *et al.* (2002) showed that copper mainly accumulated in roots while a small fraction (10%) of absorbed copper was transported to the shoots. The results by Bakere *et al.* (1994) and Yang *et al*. (2002) could explain why there were similar copper levels among the four sites in all the fruits and tubers. Indeed, when copper ends up in soils, it strongly attaches to organic matter and minerals. As a result, it does not travel very far after release and consequently copper tends to accumulate in soil (Slooff *et al*., 2009; Alloway, 2005). Perhaps, this explains why the soil had high levels of copper while the fruits and tubers had very little.

The mean levels of Ni in the soil in this study are recorded in Table 1. Umuechem (24.78±10.70, 14.00±6.70 mg/kg) Ebocha (47.47±9.66, 3.98±2.52 mg/kg), Ofuoma (24.22±17.52, 4.85±3.37) and Ndashi (20.20±8.62, 1.50±1.02) in wet and dry seasons respectively. The lowest came from the control site (Ndashi) (1.50±1.02) dry season and the highest came from oil polluted site, Ebocha (47.47±9.66 mg/kg) wet season and this is above WHO (2004) permissible limits of 35mg/kg but other stations are within permissible limit. Statistically the values were significantly different (P<0.05) in both wet and dry season

The trend and findings of this study is similar to the work of Banka-Coker and Ekundayo (1995) where oil spill led to the significant built-up of heavy metals in the contaminated soil in Niger Delta Area of Nigeria. Global input of nickel to the human environment is from natural and anthropogenic sources including emissions from fossil fuel consumption, industrial production, use and disposal of nickel compounds and alloys (Kasprzak *et al.*, 2003). Soils in this study recorded concentrations that were lower than those reported in literature with values ranging from 5250.62 – 11968.76 mg/kg which may account for the high metal content found in the vegetables. Literature report values of 450 mg/kg, 98 mg/kg, 100 mg/kg, 1650 mg/kg and 2360mg/kg recorded by Kabata-Pendias and Pendias (1992), Haluschak *et al.* (1998), McGerath et al. (2001), Awokunmi *et al.* (2010) and Adefemi and Awokunmi, (2009), respectively. Udosen *et al.* (2012) reported values of 21.76 mg/kg, Ni, for soil samples obtained from the crude oil contaminated land of Mkpanak in Ibeno Coastal Area of Akwa Ibom State. Farm soils contain approximately 3 to 1000 mg/kg of nickel, but the concentration can reach up to 24,000 to 53,000 mg/kg in soil near metal refineries and in dried sludge, respectively (Denkhaus and Salnikow (2002); Sutherland and Costa (2002). Some areas of the United States may contain natural levels as high as 5000 mg/kg (ATDSR, 2005). Although literature shows that nickel in plants is highly mobile and is likely to accumulate in both leaves and seeds, in this study the transfer ratio of nickel between the soil, fruits and tubers was more than zero. Srinivas *et al.* (2009) reported that vegetables have more nickel than animal products.

The mean metal concentrations of Pb in the soil are presented in Table 1. Umuechem (16.95±2.21, 43.96±9.08mg/kg), Ebocha (31.7±6.66, 24.66±3.31mg/kg), Ofuoma (12.75±7.45, 24.49±4.52mg/kg) and Ndashi (33.53±25.04, 0.41±0.37mg/kg) in wet and dry season respectively. The lowest came from the control site (Ndashi) in dry season while the highest came from Umuechem dry season. Statistically the values were significantly different (P<0.05) in the dry season Lead is one of the more persistent metals and is estimated to have a soil retention time of 150 to 5000 years (Sobolev and Begonia, 2008). However, the observed Pb values were below the DPR target value of 85 mg/kg for a standard soil. These findings were consistent with the work of Inengite *et al*. (2010) who had reported that oil contaminated soils were relatively more spiked with Pb as compared to the control soils. Udosen *et al.* (2012) reported values of 21.76 mg/kg, Pb, for soil samples obtained from the crude oil contaminated land of Mkpanak in Ibeno Coastal Area of Akwa Ibom State. This is within the ranges of soils studied by Premarathna et al (2011) who reported a range of 15 to 311 mg/kg. Similarly, Kabata-Pendias and Pendias (1992), Haluschak et al. (1998), McGrath *et al*. (2001) in Amazonia, USA, and Kimani (2007) reported lead values of 189 mg/kg, 55 mg/kg, 80 mg/kg and 34.5 mg/kg in Kenya, respectively in uncontaminated soils of the temperate humid zone of Europe. However Awokunmi et al., (2010) reported very high levels of lead from soils collected from various oil polluted in sites in Osun State ranging between 3500-6860 mg/kg. Aluko *et al.* (2003) also reported high values of lead in soil at Ibadan ranging from 1340 - 1693 mg/kg.

The heavy metals present in the oil polluted soils when absorbed by plants are capable of making the plant potentially toxic and harmful to man and livestock if ingested or consumed as food (Ogri, 2008). Khan et al. (2008) also reported that accumulated of heavy metals in contaminated soils may pose health risks. This observation confirms the report by Benson and Ebong (2005) on vegetables where heavy metal accumulation in plants resulted in poor growth and in yield reduction. Similarly, Epstein (1972) reported that lead and cadmium prevent mineral uptake by either synergistic or antagonistic reactions.

Table 1: Heavy Metal Concentrations (mg/kg) in the Soils from the Sampled Stations in the wet and dry season from April 2021 – February 2022

Heavy Metal	Umuechem (S1)	Ebocha (S2)	Ofuoma (S3)	Ndashi (S4)	Maximum Permissible Limits (WHO/DPR)
Cd					0 .8 mg/kg
Wet	**2.75±0.21** ^{b}	**5.95±1.34** ^{ab}	**8.45±1.06** ^{a}	**1.91±1.64** ^{b}	
Dry	**15.04 ±4.59** ^{a}	**11.15±3.29** ^{ab}	**14.53±5.73** ^{a}	**2.97±1.39** ^{b}	
Cr					100 mg/kg
Wet	2.75±0.21 ^{a}	6.83±96.17 ^{a}	**353.7±3.13** ^{a}	7.45±3.46 ^{a}	
Dry	BDL ^{a}	BDL ^{a}	BDL ^{a}	BDL ^{a}	
Cu					36mg/kg
Wet	26.5±13.41 ^{a}	31.9±9.63 ^{a}	14.58±15.10 ^{a}	27.25±7.21 ^{a}	
Dry	29.51±1.46 ^{a}	5.68±3.02 ^{b}	7.84±3.72 ^{b}	2.91±1.51 ^{b}	
Ni					35 mg/kg
Wet	24.78±10.70 ^{ab}	**47.47±9.66** ^{a}	24.22±17.52 ^{ab}	20.20±8.62 ^{ab}	
Dry	14.05±6.70 ^{a}	3.98±2.52 ^{b}	4.85±3.37 ^{b}	0.89±1.02 ^{b}	
Pb					85 mg/kg
Wet	16.95±2.23 ^{a}	31.7±6.66 ^{a}	12.75±7.45 ^{a}	33.53±25.04 ^{a}	
Dry	43.96±9.08 ^{a}	24.60±3.31 ^{b}	24.49±4.52 ^{b}	0.41±0.37 ^{c}	

3.2 Heavy Metal Concentrations (mg/kg) in *Manihot esculenta*

The concentration of heavy metals in manihot esculenta is shown in Table 2.

Various sources of environmental contamination have been implicated as route for heavy metals in food. Waste water irrigation, air deposition, spillage are major pathway to heavy metals bioaccumulation in plants (Singh et al., 2010; Oluwole et al., 2013; Adesuyi et al., 2015). Plant is a major part of Nigerian diet and is very susceptible to environmental pollution due to the activities and processes going on or practiced in the area where it is cultivated or obtained from. The recommended maximum limit of cadmium, chromium, copper, Nickel and lead for plants by FAO/WHO 2001 is 0.2, 1.5, 0.3, 40 and 1.12 (mg/kg) respectively (Maleki and Zarasvand, 2008). The recommended limits for various heavy metals vary depending on the food. The concentrations of heavy metals in the cassava tubers grown in oil impacted and un-impacted soils of Umuechem, Ebocha, Ofuoma and Ndashi (control site) are presented in Table 2 along with the permissible limits set by SEPA (2006), FAO/WHO 2001.

The mean concentrations of *Manihot escaulenta* from oil impacted soil are higher then control in *Manihot escaulenta*. The result showed that Cd concentrations in *Manihot escaulenta* in all the sampled stations exceeded WHO (2004) permissible limit of 0.02mg/kg in plants and this can be toxic to the kidney (FAO/WHO, 2007), (Nkwocha et al, 2010; Okoronkwo et al, 2005; Hart et al, 2005 and Gideon – Ogero, 2008). Cadmium is a heavy metal with high toxicity and it is a non-essential element in foods and natural waters and it accumulates principally in the kidneys and liver (Divrikli *et al*., 2006; Adesuyi *et al*., 2015). Higher values have been previously reported for tubers cultivated in crude oil polluted soil (0.27 mg/kg) in Olomoro, Delta, State, Nigeria by Okoye *et al.* (2014). According to FAO/WHO (2001), the safe limit for Cd consumption in fruits tubers is 0.2 mg/kg**.**

Cr mean concentrations in *Manihot esculenta* are presented in Table 2. Umuechem (602.74±562.99, BDL), Ebocha (671.45±81.32, BDL), Ofuoma (549.15±241.66, BDL), and the control site Ndashi (BDL, BDL) in wet and dry seasons respectively. Cr was below dictation limits in the control site (Ndashi) both in dry and wet season. The highest came from Ebocha (wet season). Cr mean concentrations in *manihot escaulenta* is above the permissible limits 1.5mg/kg of FAO/WHO (2007) permissible limits in wet season and below dictation limits in dry season. However, the chromium levels obtained from this study are higher than that of Schumacher *et al.* (1993) in Western Europe where they reported a mean value of 0.1 mg/kg chromium found in fruits they worked with. Chromium depending on the valent state can be beneficial or harmful; the hexavalent state of chromium is harmful (Leopora, 2005). Chromium is known to help maintain normal blood glucose levels by enhancing the effects of insulin (Chove *et al.*, 2006). The most widespread human effect is chromium allergy caused by exposure to chromium (especially Cr (VI) compounds), and they are assumed to cause cancer (RTI, 2000). Therefore, there is also a likely threat to chromium poisoning if contaminated food is ingested. It is crucial for the body when high Cr levels are detected in body tissues (Taylor et al, 2006). Continual accumulation of Chromium in the body may lead to serious health problems. Symptoms of Cr poisoning include nausea, vomiting and headaches (Prasad, 1995).

Cu is an essential micronutrient necessary for hematologic and neurologic system (Tan et al., 2006). Table 2 shows the mean concentrations of Cu in *Manihot esculenta*. Umuechem (9.65±4.82, 25.25±2.59), Ebocha (7.33±7.45, 3.00±0.23), Ofuoma (23.93±13.24, 4.16±0.90) and Ndashi (4.2±1.05, 1.8±0.28) in wet and dry season respectively. The least came from the control site in dry season while the highest came from Umuechem in dry season. Cu in *Manihot esculenta* is below the maximuim tolerable limit copper in fruits and tubers is 40mg/kg (FAO/WHO, 2004). Therefore, values obtained from this work are within the acceptable limits.

Cu can produce adverse effects in the liver, gastrointestinal tract and kidney for humans and animals upon ingestion of toxic dose (Araya et al., 2003). Similar results have been reported by Uwah et al. (2011) who recorded copper values of between 0.81 mg/kg and 1.75 mg/kg in spinach and lettuce grown in Nigeria, respectively and Okoye et al. (2014) in Olomoro, Delta State, Nigeria were they dictated the mean concentrations of Cu, 14.72mg/kg,

Copper (Cu) is essential to human life as metalloproteins and function as enzymes, however, high doses leads to health risks such as anemia, diabetes, inflammation, kidney and liver dysfunction and vitamin C deficiency (Lokeshappa *et al*., 2012). JECFA (2005) suggested safe limits of 40 mg/kg in adults which was significantly higher than maximum copper levels in this study. Although toxicity of copper is rare, its metabolism is enhanced by molybdenum and zinc constituents in the body (Oladele and Fadare, 2015). Lower copper uptake in human consumption can cause a number of symptoms which include growth retardation, skin ailments, and gastrointestinal disorders. Copper deficiency impinges on iron metabolism, causing an anemia that does not respond to iron supplementation. Interactions between iron and copper seem to be impaired utilization of one in the absence of the other. Copper deficiency also exerts an effect on iodine metabolism resulting in hypothyroidism, at least in animal models (Michael et. al., 2009).

In particular, copper functions as an electron transfer intermediate in redox reactions. As well as a direct role in maintaining cuproenzyme activity, changes in copper status may have indirect effects on other enzyme systems that do not contain copper. The level of copper in the body are affected by the levels of zinc as it appears to exert an antagonistic effect on copper status through the induction of metallothionein synthesis by zinc in mucosal cells in the intestine. Metallothionein bound copper is not available for transport into the circulation and is eventually lost in the faeces (Gyorffy and Chan, 2002; Barone et. al., 1998; Zahir et. al., 2009). Copper is required for the proper functioning neurovascular system. It is a component of several enzymes, cofactors, and proteins in the body. In particular, copper functions as an electron transfer intermediate in redox reactions. As well as a direct role in maintaining cuproenzyme activity, changes in copper status may have indirect effects on other enzyme systems that do not contain copper.

The values of Ni recorded in *Manihot esculenta* were Umuechem (25.1±13.66, 2.8±0.23) Ebocha (16.68±2.01, 10.6±3.35) Ofuoma (28.16±14.99, 14.67±2.34mg/kg) and Ndashi (22.26±12.84, 1.78±0.53mg/kg) in wet and dry season respectively. The lowest came from Ndashi dry season while the highest came from Ofuoma in wet season. The mean concentrations of Ni in *Manihot escaulenta* were above the permissible limits (1.12mg/kg) of FAO/WHO (2007). Similarly, Premarathna et al. (2011) reported nickel levels ranging from 2.3 to 37.80 mg/kg in the various fruits. Okoronkwo et. al., (2005) reported values of Ni between 22.59 mg/kg and 24.47 mg/kg in the tubers studied. On the other hand, Naser et al. (2009) in Bangladesh reported lower levels of nickel than those of this study of 0.36mg/kg in the fruits. Literature report values of 450 mg/kg, 98 mg/kg, 100 mg/kg, 1650 mg/kg and 2360mg/kg recorded by Kabata-Pendias and Pendias (1992), Haluschak et al. (1998), McGerath et al. (2001), Awokunmi et al. (2010) and Adefemi and Awokunmi, (2009), respectively. Nickel in plants is highly mobile and is likely to accumulate in both tubers and seeds (Sengar et. al., 2008). There is also evidence of uptake and accumulation in certain plants (ATSDR, 2005a). Intake of too large quantities of nickel by humans from plants grown on nickel rich soils has higher chances of inducing the development of cancers of the lung, nose, larynx and prostrate as well as inducing respiratory failures, birth defects and heart disorders (Duda-Chodak and Blaszczyk, 2008; Lenntech, 2009).

Studies have shown that heavy metals such as nickel can stimulate cell growth in estrogen receptor (ER) positive breast cancer cells (Martin et. al., 2003). Indeed, Ionsescu et al. (2006) found highly significant nickel accumulation in 20 breast cancer tissue biopsies compared to controls. Although nickel is a toxic metal, it plays a role as a coenzyme in different enzymes (ATSDR, 1999a; Lyaka et. al., 2005). Similarly, Premarathna et al. (2011) reported nickel levels ranging from 2.3 to 37.80 mg/kg in the various vegetables. Okoronkwo et. al., (2005) reported values of between 22.59 mg/kg and 24.47 mg/kg in the vegetables under study. On the other hand, Naser et al. (2009) in Bangladesh reported lower levels of nickel than those of this study of 5.369 mg/kg in the vegetables. Nickel in plants is highly mobile and is likely to accumulate in both leaves and seeds (Sengar et. al., 2008). There is also evidence of uptake and accumulation in certain plants (ATSDR, 2005a). Intake of too large quantities of nickel by humans from plants grown on nickel rich soils has higher chances of inducing the development of cancers of the lung, nose, larynx and prostrate as well as inducing respiratory failures, birth defects and heart disorders (Duda-Chodak and Blaszczyk, 2008). Global input of nickel to the human environment is from natural and anthropogenic sources including emissions from fossil fuel consumption, industrial production, use, and disposal of nickel compounds and alloys (Kasprzak et al., 2003).

The mean concentrations of Pb in *Manihot escaulenta* are presented in Table 2. Umuechem (44.74±22.95, 21.55±4.21), Ebocha (16.89±3.21, 26.65±9.53), Ofuoma (12.40±6.26, 27.85±7.06) and Ndashi (30.56±17.07, 2.49±0.73) in wet and dry seasons respectively. The least came from Ndashi (control site) in the dry season while the highest came from oil polluted site (Umuechem) wet season. The mean concentrations of Pb in *Manihot escaulenta* was above FAO/WHO (2007) permissible limits of 0.3mg/kg in all oil polluted and control sites. Okoye and Okwute also reported high concentrations of Pb in cassava tubers and plantain fruits from Olomo community, Pb was above WHO (2004) acceptable limits for food (Okoye and Okwute, 2014). Symptoms including abdominal pain, nausea, vomiting, body pain, headache, dizziness and depression were also reportedly prevalent amoung the local population (Okoye and Okwute, 2014). A study by Gideon-Ogero on cassava harvested from Afiesere, Orogun and Ekiugho communities revealed that Pb was present above the WHO recommended limit (Gideon-Ogero, 2018). As reported by Casarett and Doull (1996), Pb has the tendency to cross the placenta and cause damage to foetal brain which could lead to the development of autoimmunity in which a person's immune system attacks its own cells leading to diseases such as rheumatoid arthritis, diseases of kidneys, nervous system, and circulatory system. It is on record (Boon and Soltanpour, 1992) that the population mostly affected by consumption of contaminated farm products is pregnant and young children. Cases of heavy metals orders reported are hemochromatosis, neurological disorders, central nervous system destruction, cancers of various body organs, low birth weight and severe mental retardation of newborn children (Forstner and Wittman, 1981; Mahaffey *et al.* 1981; Manahann, 1994; Van Vuren and Nussey, 1999).

Heavy metals found in food crops, have a potential hazard to man through the dietary pathway (Batra, 2012). Some heavy metals like Pb are toxic even in small concentrations. Pb was observed to be above WHO (2007) acceptable limits in *Manihot esculenta* (3.0mg/kg), therefore posing serious health risks to people who ingest these food crops.

General symptoms of Pb poisoning such as headache, abdominal pain, body pain, stomach disorder, nausea, vomiting, dizziness and depression (Mills, 2003) were commonly experience by the people of particular concern was the high prevalence of acute headache, body pain and stomach disorder sourced from the questioneer. The most vulnerable populations affected by consumption of contaminated products were women, Okwute (2014). In pregnant women, Pb can easily cross the placenta and damage foetal brain and may also cause development of auto-immunity in which a persons' immune system attacks its own cells, leading to diseases related to the nervous and circulatory system (Mills, 1971). Majority of the women (30.8%) complained of nausea as a common ailment, while 48.5% complained of dizziness. It was observed that although depression is a symptom of Ni and Pb poisoning, the people's social life were completely unaffected, and they seem to be very happy and friendly even with strangers. This was supported by the response majority of them gave when asked if they were depressed. Only about 23.8% strongly agreed to being depressed, while majority said that they were not.

In children, Pb poisoning may cause mental retardation and learning disorders (Curtis, 1999). This accounts for the reason why majority of the people are farmers and secondary school certificate holders, since they lack the mental capacity to attain a higher level of education. Only 7.7% strongly agreed to experiencing mental illness/learning disorder among their children, while majority (52.3%), strongly disagreed. This could be attributed to the fact that most people did not like to be affiliated among people whose households were known for mental illness. All these symptoms mentioned were commonly experienced among household members and were reported to be prevalently high by medical personnel. Pb and Ni accumulated in the body over long periods may result to cancer (Essien, 1992). Therefore, there is a possibility that a high percentage of people have cancer without knowing, cancer was prevalently low among the people. Lead values were not within the permissible levels for agricultural soils, the transfer factor of this metal to the fruits and tubers were significant and this could explain why the fruits and tubers had higher than permissible levels of lead. Indeed, lead accumulation in many plants can exceed several hundred times the threshold of maximum level permissible for human (Wierzbicka, 1995).

The high levels of lead in fruits, tubers and soils in this study could be attributed to the oil production, this is because in the past lead was used in gasoline and hence a major contributor to lead in soil, and automotive exhaust emitted when gasoline contained lead. Luilo and Othman (2006) found high levels of lead in both soil and couch grass grown along the oil region in Dares Salaam. Lead is released into the air during burning oil, or waste. Lead is removed from the air by rain and by particles falling to land or into surface water. Once lead falls onto soil, it sticks strongly to soil particles and remains in the upper layer of soil (ATSDR, 2007).

Lead has no beneficial biological function and is known to accumulate in the body (Zurera-Cosano et. al., 1984; Ellen et. al., 1990; Yargholi and Azimi, 2008). Lead exposure can cause adverse health effects, especially in young children and pregnant women, since lead is a neurotoxin that permanently interrupts normal brain development. It also accumulates in the skeleton and its mobilization from bones during pregnancy and lactation causes exposure to foetuses and breastfed infants (ATSDR, 2007; WHO, 2004). Lead on a cellular and molecular level may enhance carcinogenic events involved in DNA damage, DNA repair and regulation of tumor suppressor and promoter genes (Silbergeld, 2003).The high levels of lead in both vegetables and soils could be attributed to the dumpsite and the busy Roads. This is because in the past lead was used in gasoline and hence a major contributor to lead in soil, and automotive exhaust emitted when gasoline contained lead. Luilo and Othman (2006) found high levels of lead in both soil and couch grass grown along the road in Dar es Salaam. Lead is released into the air during burning oil, or waste. Lead is removed from the air by rain and by particles falling to land or into surface water. Once lead falls onto soil, it sticks strongly to soil particles and remains in the upper layer of soil (ATSDR, 2007).

Table 2: Mean Concentration of Heavy Metals (mg/kg) in *Manihot esculenta* Wet and Dry Seasons from April 2021 – February 2022

Heavy metal	Umuechem (S1)	Ebocha (S2)	Ofuoma (S3)	Ndashi (S4, Control)	Permissible Limit of Plants (FAO/WHO, 2007)
Cd					0.02 mg/kg
Wet	**5.94±1.97** [a]	**5.44±1.88** [a]	**3.59±2.62** [a]	**2.39±2.73** [a]	
Dry	**15.6±1.27** [a]	**15.33±1.13** [a]	**15.65±2.34** [a]	**4.36±23.90** [b]	
Cr					1.5 mg/kg
Wet	**602.74±562.99**[a]	**671.45±81.32** [a]	**549.15±241.66** [a]	BDL	
Dry	BDL [a]	BDL [a]	BDL [a]	BDL [a]	
Cu					40 mg/kg
Wet	9.65±4.82 [a]	7.33±7.45 [ab]	23.93±13.24 [a]	4.2±1.05 [b]	
Dry	25.55±2.59 [a]	3.00±0.23 [b]	4.16±0.90 [b]	1.80±0.28 [b]	
Ni					1.12 mg/kg
Wet	**25.1±13.66** [a]	**16.68±2.01** [a]	**28.16±14.99** [a]	**22.26±12.84** [a]	
Dry	**2.80±0.23** [b]	**10.60±3.35** [a]	**14.16±2.34** [a]	**1.78±0.53** [b]	
Pb					0.3 mg/kg
Wet	**44.74±22.95** [a]	**16.89±3.21** [a]	**12.40±6.26** [a]	**30.56±17.07** [a]	
Dry	**21.55±4.21** [a]	**26.65±9.53** [a]	**21.09±7.06** [a]	**2.49±0.73** [b]	

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