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Bioaccumulation of the Heavy Metals in Cassava Tubers and Plantain Fruits Grown in Soils Impacted with Petroleum and Non-Petroleum Activities

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Abstract: The values of Total Petroleum Hydrocarbons (TPH) and heavy metals in soils, plantain fruits and cassava tubers harvested from farms impacted with petroleum and non-petroleum activities at Olomoro, Isoko South Local Government Area, Delta State, Nigeria were investigated. The TPH was determined by Fourier transformed infrared spectrophotomer, while heavy metals were analyzed with atomic absorption spectrophotometer. The values of TPH in soil impacted with petroleum activities was 5251.99 mg kg^{-1} compared to below detection level in non-petroleum impacted soil. All heavy metals showed higher values in petroleum impacted soil than non-impacted soil. The order of abundance of heavy metals in petroleum impacted soil was Fe>Mn>Zn>Cu>Co>V>Pb>Cr while in non-impacted soil, it was Fe>Zn>Mn>Cu>Co. The values of heavy metals were higher both in epicarp and mesocarp of plantain fruits harvested from petroleum impacted soil than from non-petroleum impacted soil. In cassava tubers, the values of heavy metals in the cortex were all higher in the petroleum impacted soil than non-impacted soil. Cr, V, As and Hg were all below detection levels both in plantain fruits and cassava tubers from both soils. The values of Zn (3.39), Pb (2.44) in the epicarp of plantain fruits and Zn (4.385) in the cortex and (5.955) in the piliferous layer and Pb (1.75) in the cortex of cassava were higher than the values recorded in soils indicating hyperaccumulation.

Key words: Petroleum activities, heavy metals, TPH, soil, plantain, cassava, impact

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INTRODUCTION

Oil exploration and exploitation has uplifted Nigerian economy leading to rapid development but the impacts of oil exploration and exploitation on the environment are receiving less attention (Idodo-Umeh, 2002). One of the major anthropogenic sources of heavy metal enrichment in terrestrial habitats of oil producing areas of Niger Delta of Nigeria is the frequent spills of crude oil on land and gas flaring (Idodo-Umeh, 2002). Nigerian crude oil is known to contain heavy metals such as Al, Zn, As, Ba, Fe, Pb, Co, Cu, Cr, Mn, Ga, Sb, Ni and V (Unpublished data). Toxicity of ingested heavy metals has been an important health issue for decades (LeCoultre, 2001). High levels of accumulation of heavy metals from soil by common garden vegetables has been reported by many environmental researchers (Boon and Soltanpour, 1992; DePieri *et al.*, 1997; Xiong, 1998; Cobb *et al.*, 2000; LeCoultre, 2001). Some species of *Brassica* (cabbage) are high accumulators of heavy metals in the edible parts of the plants (Xiong, 1998) and this can be an important exposure pathway for people who consume vegetables grown in heavy metal contaminated soil (LeCoultre, 2001).

Certain plants can accumulate heavy metals in their tissues and uptake increases generally in plants that are grown in areas with increased soil contamination with heavy metals and therefore, many

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people could be at risk of adverse health effects from consuming common garden vegetables cultivated in contaminated soil (LeCoultre, 2001).

One of the major anthropogenic sources of heavy metal enrichment in terrestrial habitats in Niger Delta of Nigeria is oil spillage. Oil spillage and dumping of petroleum effluents on land are common phenomena. Gas flaring also contributes to heavy metal contamination of soil.

The aims of this study are to:

- Determine the levels of heavy metal concentrations in soils impacted with petroleum and non-petroleum activities in relation to accumulation of heavy metals in cassava tubers and plantain fruits obtained from both soils
- Compare the results obtained to internationally accepted limits for food
- Highlight the effects of consuming such contaminated tubers and fruits

MATERIALS AND METHODS

Study Area

The study was conducted in November 2007 at two sites of cultivated land in Olomoro, Isoko South Local Government Area of Delta State, Nigeria (Fig. 1). The area marks the geological boundary of the Sombreiro-Warri formation and the meader belts of the upper deltaic plains of the Niger Delta (Short and Stauble, 1967). The Sombreiro-Warri formation has been described by Allen (1965) as older sands of the Niger Delta comprising massive, generally fine to medium grained and fairly sorted but consolidated sand.

The two study sites fall within the tropical climate characterized by rainy and dry seasons (Ofune, 1979; Hare and Carter, 1984).

Site 1 is a farm land by the side of petroleum activities. It lies between latitude 5° 29’ 29”N and longitude 6°C 10’ 23 E. There are two flow stations, gas compressor and many oil wells nearby. The site lies by a tarred road and traffic is relatively low. Cultivated plants included plantain, cassava and maize.

Site 2 lies between latitude 5°C, 25’ 31.1 and longitude 6°C 08’ 4N. It is a farmland in which cassava and plantain are cultivated. It lies by a tarred road. There are few inhabited houses. The site is opposite a secondary school and is about 5.30 km away from site 1. Traffic is relatively low and petroleum activities are completely absent.

Collection of Samples

Soil

Four random composite soil samples were collected from 20 cm depth into clean polythene bags and kept in a cooler.

Cassava Tubers and Plantain Fruits

Three cassava tubers were uprooted manually while three plantain fruits were plucked from three parent plants at both sites. All samples were kept in a cooler and carried to laboratory where they were preserved in refrigerator at a temperature of less than 4°C until the analysis were carried out.

Soil Sample Preparation

Soil samples were homogenized with a clean glass rod and oven-dried at 85°C to constant weight. Any lump present was broken up with a clean glass rod in order to expose the inside for drying and

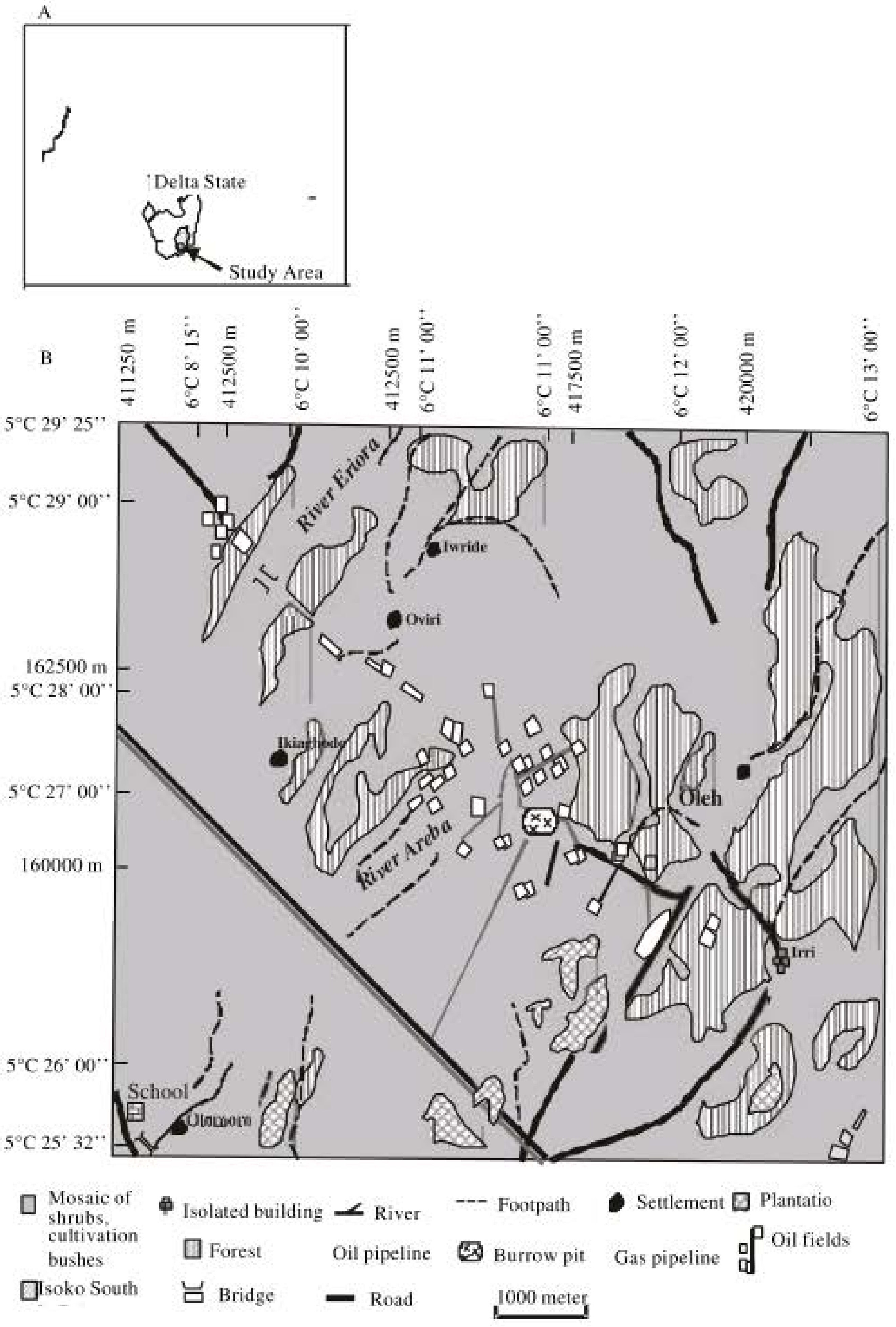

Fig. 1: (A) Map of Nigeria showing Delta State; (B) Map of the study area showing River Areba

all plant materials were removed. The oven dried soil sample was thoroughly ground into powdery form and sieved through 650 µm stainless sieve.

Extraction and Analysis of Heavy Metals

Soil

Ten grams of the sieved dry soil was weighed into acid-washed 250 mL polythene extraction bottles and 100 mL of extraction solution (0.05 M HCL and 0.0125 M HNO_3) was added and shaken for 1 h on a mechanical shaker. The solution was filtered through Whatman No 42 filter paper. Blank samples were prepared using the same procedure with deionised water instead of soil solution.

Analysis of Cd, Zn, Cu, Pb, Mn, Co, Ni, Cr and V was carried out with Unican 929 atomic absorption spectrophotometer fitted with solar software. Mercury and As were analyzed by Cold Vapour Technique (Goldwater, 1971).

Extraction and Analysis of Total Petroleum Hydrocarbons

Five grams of the soil was weighed into a clean 50 mL glass vial with a teflon cap. One gram of anhydrous sodium sulphate was added to remove moisture and the mixture was thoroughly mixed with a clean spatula. Twenty milliliter of tetrachloroethylene was added to the mixture, corked and properly shaken to ensure thorough mixture. The cork was removed and the mixture was placed in a water bath sonicator and sonicated for 30 min. The mixture was filtered through a glass wool. Additional 10 mL of tetrachloroethylene was added and the process was repeated as above to extract any minute oil left. One gram of deactivated florosil was added to remove all polar compounds (that might interfer with TPH determination) and filtered through a 0.45 µm solvent resistant membrane filter to remove all particulate matter. Tetrachloroethylene was scanned as a blank. The filtered solution was analyzed using Fourier Transformed Infrared (FTIR) Spectrophotomer fitted with Winfirst software and values were expressed in mg kg^{-1}. Tetrachloroethylene was scanned as a blank.

Extraction and Analysis of Heavy Metals in Plantain Fruits and Cassava Tubers

Plantain and Cassava

The plantain and cassava samples were brought out of refrigerator and kept in clean polythene bags and allowed to attain room temperature. The epicarps of plantain fruits and piliferous layers of cassava tubers were carefully removed. The epicarps and mesocarps of plantain, piliferous layers and cortex of cassava were cut into pieces and oven dried at 85°C to constant weight. The dried samples were ground into powdery form and labeled.

One gram of each ground sample was weighed into 100 mL beaker. Five milliliter concentrated nitric acid and 2 mL perchloric acid were added and heated in a fume cupboard to almost dryness. Then, 10 mL 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 instead of plantain or cassava sample. The filtrate of each sample was aspirated into the flame of AAS along with standard solution.

RESULTS

The Total Petroleum Hydrocarbons (TPH) value at site 1 was 5251.99 mg kg^{-1} compared to the below detection level' in Site 2. All heavy metals showed higher values in Site 1. Cadmium (Cd), Ni, As and Hg were below detection levels in both sites while in Site 2, Cd, Pb, Ni, Cr V, As and Hg were also below detection levels. All heavy metals detected recorded higher values in site 1 soil than site 2 soil (Table 1).

The order of abundance of heavy metals in petroleum impacted soil was Fe>Zn>Mn>Cu>Co>V>Pb while in non-petroleum soil it was Fe>Zn>Mn>Cu>Co.

Heavy metals below detection levels both in epicarp and endocarp were Cd, Cr, V, As and Hg. In both sites, Zn was not detected in the mesocarp while Ni was not detected in the epicarp but bioaccumulated in the mesocarp. Higher values were recorded in epicarp than in endocarp in samples of both sites. In both samples, Fe was the most abundant heavy metal both in epicarp and endocarp (Table 2).

Table 3 shows the values of heavy metals in cassava. Cadmium, Cr, V, As and Hg were below detection levels in samples from both sites. The values of other heavy metals were higher in the piliferous layer than cortex except Zn, Pb and Ni that were higher in the cortex than piliferous layer. In Site 1, Cu had equal value in the piliferous layer and cortex.

The concentrations of all the metals, except iron were higher in the mesocarp and epicarp of plantain fruits from the contaminated site than the levels found in fruits from control site. Cassava tubers from the contaminated site also had higher concentrations of heavy metals in the piliferous layer and cortex, except zinc which was slightly higher in the piliferous layer of tubers from the control site (Fig. 2a-d).

Table 1: Concentrations of TPH and heavy metals (mg kg^{-1}) in soil

Chemical parameters	Site 1: (Petroleum activities)	Site 2: (Non-petroleum activities)
TPH	5251.99	BD
Cd	BD	BD
Zn	3.02	2.74
Cu	1.94	1.05
Pb	0.79	BD
Fe	90.45	62.732
Mn	40.02	1.95
Co	0.96	0.20
Ni	BD	BD
Cr	0.76	BD
V	0.86	BD
As	BD	BD
Hg	BD	BD

Table 2: Accumulation of heavy metals in epicarp and mesocarp of plantain fruits

	Site 1: (Petroleum activities)		Site 2: (Non-petroleum activities)	
Heavy metal	Epicarp	Mesocarp	Epicarp	Mesocarp
Cd	BD	BD	BD	BD
Zn	3.39	BD	0.48	BD
Cu	0.795	0.38	0.145	0.155
Pb	2.44	0.48	1.17	BD
Fe	13.635	4.865	12.965	2.145
Mn	0.915	0.68	0.76	0.16
Co	0.53	0.215	0.185	0.11
Ni	0.19	0.29	BD	0.12
Cr	BD	BD	BD	BD
V	BD	BD	BD	BD
As	BD	BD	BD	BD
Hg	BD	BD	BD	BD

Table 3: Accumulation of heavy metals in piliferous layer and cortex of cassava tubers

	Compressor station 1		Grammar school station 2	
Heavy metal	Piliferous layer	Cortex	Piliferous layer	Cortex
Cd	BD	BD	BD	BD
Zn	2.11	5.599	4.385	1.405
Cu	0.225	0.225	0.99	0.11
Pb	0.57	1.75	0.02	0.58
Fe	56.60	3.95	29.495	2.91
Mn	1.745	1.395	1.19	0.175
Co	0.33	0.205	0.12	0.10
Ni	BD	0.195	0.155	0.36
Cr	BD	BD	BD	BD
V	BD	BD	BD	BD
As	BD	BD	BD	BD
Hg	BD	BD	BD	BD

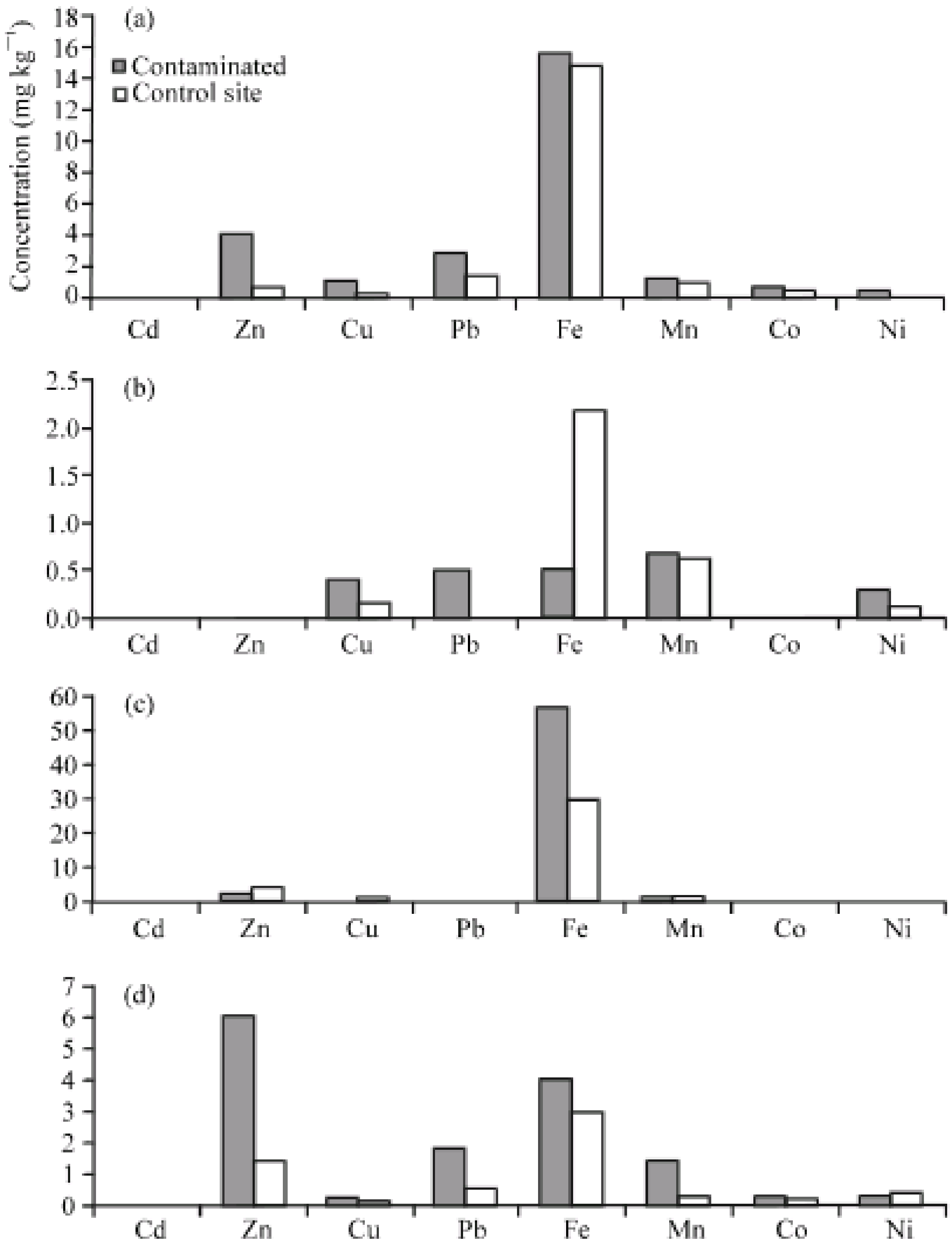

Fig. 2: Comparison of heavy metal accumulation in the mesocarp and epicarp of Plantain fruits and the piliferous layer and cortex of Cassava tubers; (a) Mesocarp, (b) Epicarp, (c) Piliferous and (d) Cortex

DISCUSSION

Heavy metals have been found in food crops and have a potential health hazards to man through the dietary pathway in Nigeria (Obiajunwa *et al.*, 2001). The Total Petroleum Hydrocarbons (TPH) at Site 1 (area of petroleum activities) was 5251.99 mg kg^{-1} while the below detection level was recorded for site 2 (an area of non-petroleum activities). This high value could be attributed to the operation of petroleum activities. Flow stations, gas compressor, giant electric generators, flaring of gas and numerous oil wells are associated with site 1, an abandoned dry burrow pit probably receiving wastes arising from petroleum activities. Rain water runoff could also have carried spilled crude oil and petroleum effluents to the burrow pit during the rainy season. The absence of petroleum hydrocarbons in site 2 (Grammar School Area) which is 5.30 km away from site 1 is a confirmation of petroleum activities being responsible for the value recorded at site 1. Pollution of the groundwater with petroleum hydrocarbons and heavy metals is a possibility since the soil of Olomoro is mainly composed of sand (Allen, 1965). The soil also lacks clay layer above the aquifer (Egwebe, 2003).

Petroleum renders the soil infertile, burns vegetation and kills useful soil organisms (Idodo-Umeh, 2004). The bioaccumulations of heavy metals in plantain fruits and cassava tubers were generally higher at site 1, than at site 2. This is expected since any area near petroleum activities has higher level of pollutants including heavy metals (Woodward and Riley, 1983). Uptake of heavy metals is increased in plants that are grown in areas with increased soil concentrations of heavy metals (LeCoultre, 2001). Heavy metal concentrations were generally higher in the epicarps of plantain than in the mesocarps at both sites 1 and 2 except Ni in site 1 and Cu in site 2. This phenomenon could be explained in two ways. It seems, the epicarp is a storage site or is the route through which metals enter the mesocarp since it is exposed to the atmosphere. The atmosphere is a major source of metal pollution (Förstner and Wittman, 1981; National Water and Soil Conservation, 1985). Cr, V, As and Hg were below detection levels in both plantain fruits and cassava tubers, indicating non-absorption and contamination from anthropogenic source.

In cassava, the values of heavy metal bioaccumulated both in piliferous layer and mesocarp were higher at site 1 than at site 2 except Ni that recorded higher values at site 2, suggesting that absorption and bioaccumulation depend upon availability of metals. Metals tend to bioaccumulate in animals and plants (Melville and Burchett, 2002). Anthropogenic origin of petroleum wastes, crude oil and continuous gas flaring in site 1 could have possibly enriched the soil with heavy metals than site 2.

Heavy metal uptake from soil is generally increased in plants that are grown in areas with increased heavy metal concentrations (LeCoultre, 2001). Anthropogenic sources of heavy contaminants such as burning of fossil fuel, oil spills and use of fertilizers are likely the cause of higher heavy metals contaminants in soil (Woolson, 1973; Boon and Soltanpour, 1992; Manahan, 1994; Ademoroti, 1996; Cobb *et al*., 2000; LeCoultre, 2001). Many investigators have reported that some common garden vegetables accumulate high levels of heavy metals from soil (Garcia *et al.*, 1979; Xiong, 1998; Cobb *et al*., 2000; LeCoultre, 2001). Species of some *Brassica* (cabbage) are hyperaccumulators of heavy metals in the edible tissues of the plant (Xiong, 1998) and thus creating a pathway for heavy metal accumulation for people who consume the vegetables and fruits grown in heavy metal contaminated soil (LeCoultre, 2001).

The values of Zn (3.39), Pb (1.17-2 .44) in the epicarp of plantain fruits and Zn (4.385-5.955) in the cortex and piliferous layer respectively and Pb (1.75) in the cortex of cassava were higher than the values recorded in soils, indicating hyperaccumulation. Therefore, plantain fruits and cassava tubers can be used as bioindicators of soil pollution.

The levels of heavy metals in farm soil are generally not analyzed before planting and therefore consumption of contaminated fruits, seeds or tubers is common (LeCoultre, 2001). Heavy metal concentrations in tree fruits are very low even when grown on contaminated soils (ISHS, 2005). However, the levels of Fe (4.865 mg kg^{-1}) and Mn (0.65 mg kg^{-1}) in mesocarp of plantain fruits and Fe (3.92 mg kg^{-1}) and Mn (1.395 mg kg^{-1}) in the cortex of cassava grown in the soils impacted with petroleum activities call for serious concern as these heavy metals exceeded WHO (1984) maximum acceptable limits for food. Although the value of Pb (1.75 mg kg^{-1}) in the cortex of cassava in site 1 (petroleum impacted soil) was below WHO limit (2 mg kg^{-1}) for food, threat to Pb poison is likely.

Garri which is a product of cassava is consumed daily by Nigerians in large quantities. Therefore, Pb concentrations could be cumulative. Pb can easily cross the placenta and damage the foetal brain and may also cause 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 (Casarett and Doull, 1996). The populations most affected by consumption of contaminated farm products are pregnant women and young children (Boon and Soltanpour, 1992; LeCoultre, 2001). Neurological disorders, central nervous system destruction and cancers of various body organs are some of the reported effects of heavy metal disorders (Luckey and Venugopal, 1978; Förstner and Wittmann, 1981; Manahann, 1994; Casarett and Doull, 1996; Van Vuren and Nussey, 1999). Low birth weight and severe mental retardation of newborn children have been reported in some cases where pregnant mothers ingested toxic amounts of heavy metals (Mahaffey *et al.*, 1981). Soils contaminated with Pb have been reported to decrease the growth and yield of plants (Balba *et al.*, 1991).

CONCLUSION

This study is a pioneer work on heavy metal accumulation by edible food crops in this part of the country ravaged by oil pollution activities. All heavy metals showed higher values in petroleum impacted soil than non-impacted soil. The heavy metal concentrations in cassava tubers and plantain fruits grown in petroleum impacted soil were significantly higher than the levels recorded in the same crops grown in non-impacted soils. The levels of Fe and Mn in mesocarp of plantain fruits and Fe and Mn in the cortex of cassava grown in the soils impacted with petroleum activities call for serious health concern as these heavy metals exceeded WHO (1984) maximum acceptable limits for food. The reported hyperaccumulation of heavy metals in plantain fruits and cassava tubers indicates the potential of these plants as bioindicators of soil pollution. Further studies on the socio-economic and health status of the neighbouring communities will throw more light on the overall impact of petroleum activities.

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