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***Journal of Scientific and Engineering Research*, 2017, 4(8):54-61**

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Correlation between Extractable Heavy Metals (Ni, V, Cd, and Pb) in Soil and *Colocasia Spp* (Cocoyam corm) from Farm Lands in Ibeno Coastal Area, Niger Delta, Nigeria

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Abstract Understanding the concentrations of some toxic metals in soil and food crops is important in assessing the extent of contamination of arable land and food crops especially in industrialized Niger Delta Region, Nigeria. This will reduce multiplier effect on human and farm animals. Correlation between extractable heavy metals in soil and *colocasia spp* corm from farmlands in Ibeno Coastal Area was investigated. Soil and cocoyam corm from farm lands in five communities were sampled and analyzed to determine the concentrations of the heavy metals between January to March 2017 using atomic absorption spectrophotometer Unicam 939 model. Soil pH and electrical conductivity were also investigated. The mean concentrations in mg kg^{-1} of the heavy metals in soil and *Colocasia spp* corm were (January) soil Ni(22.49), V(14.96), Pb(2.33), Cd(0.28), *Colocasia spp* corm Ni(1.19), V(0.37), Pb(0.11), Cd(0.94); (February) soil Ni(2.75), V(1.56), Pb(27.12), Cd(0.09), *Colocasia spp* corm Ni(0.69), V(0.83), Pb(0.12), Cd(0.08) and (March) soil Ni(2.42), V(1.61), Pb(8.99), Cd(0.40) *Colocasia spp* corm Ni(0.34), V(0.33), Pb(0.07), Cd(0.04) The mean concentrations of Pb(27.12) and (101.30 mg kg^{-1}), in soil of station -1(Mkpanak); V(31.30 mg kg^{-1}) at station 5 (Usiak Ifia) Cd(0. 094 mg kg^{-1}) in cocoyam corm were high when compared to WHO standards and signaled a threat of possible bio accumulation. The observed correlation coefficients were: Ni(0.316), V(0.305), Pb(0.768) and Cd(0.305) respectively. The pollution implications of these heavy metals together with their associated health hazards on humans, farm animals and economic crops have been discussed based on the results, international standards, controls and available related literatures.

Keywords cocoyam; correlation; heavy metal; pollution; concentrations

Introduction

Evaluation of arable lands especially those close to high industrial activities for contaminants is essential for agricultural sustainability and reduction in potential health risk. Heavy metal pollution in urban environment is a global phenomenon caused due to variety of anthropogenic activities [1]. Heavy metals abound in our environment and are much more prevalent in petroleum oil processing areas of the world. Many of these heavy metals are toxic at certain concentration in man. Contamination of foods by heavy metals has become an inevitable challenge these days. Air, soil, and water pollution are contributing to the presence of harmful elements, such as cadmium, lead, and mercury in foodstuff [2]. Analysis of heavy metals concentrations in soils and identifying the sources are essential to implement control measures to reduce heavy metal inputs to soils. Oil spills are known to have long effect on soil [3].

Contamination of foods by heavy metals has become an inevitable challenge these days. Air, soil, and water pollution are contributing to the presence of harmful elements, such as cadmium, lead, and mercury in foodstuff. Pollution of the ecosystem by toxic metals during man's activities poses serious concern because heavy metals are not biodegradable and are persistent in the ecosystem. Once metals are introduced and contaminate the environment, they will remain for a very long time. Metals do not degrade easily like carbon based organic molecules. It is very difficult to eliminate heavy metals from contaminated environment [4-5]. The amount of heavy metals in the environment can be changed because of many industrial processes such as smelting, burning of fossil fuels, petroleum prospecting and mining. These activities produce heavy metals which if not properly controlled end up in the environment.

Apparently, most of the terrestrial ecosystems and shoreline in the oil producing communities are important agricultural lands and are under continuous cultivation. After heavy spills of crude oil, soils are usually barren of plant growth for several years. In forest, spilled oil usually runs into low-lying areas with organic soils and natural re-vegetation of the soil generally slow. Depending on the amount of oil in the soil, the soils may remain completely barren for many years. Oil spillage and other industrial activities may therefore have far reaching implication on the agricultural productivity of the area and multiplier effect on the socio-economic well being of people. It is on this ground that this research work was designed to determine the concentrations of Ni, V, Pb and Cd in soil and cocoyam and establish a relationship between the amount of the heavy metals in soil and *collocasia spp* in planting period under review.

Materials and methods

Study area

Ibeno Local Government Area has a coastal area of over 1,200 square kilometers. It is situated on the eastern flanks of Niger Delta which in turn is part of gulf of Guinea. It is located at the south end of Akwa Ibom State with latitude 7^{o}54’ and 4^{o}34’ North of the equator and longitude 7^{o}54’ and 8^{o}02’ east of the Greenwich Meridian.

The communities on the west bank of Qua Iboe River do not have access to the hinterland except by boat through the river and creeks. Qua Iboe River estuary which lies within the study area coordinates, has Douglas Creek emptying into it. This creek is about 900m long and 8m deep. It is the point where petroleum exploration and production (E and P) waste from the Exxon Mobil Qua Iboe Terminal (QIT) tank farm are transferred to the lower Qua Iboe River Estuary and adjourning creeks through two 24 cm diameter pipes. The Exxon Mobil oily sludge dumpsite is located adjacent to this creek and the flare stack, where gas is flared continuously is also situated. Some communities in Ibeno Local Government Area are located at the bank of Qua Iboe River while others are located on the Atlantic Littoral, Mkpanak, Upenekang, Iwu-achang, are located on the east bank of Qua Iboe River, Okoritip and Ikot Inwang are located on the west bank while Iwokpom-Opolom, Itak Abasi, Akete, Okoritak are located on the Atlantic Coast line. Qua Iboe River estuary situates in close proximity to the Exxon Mobil oil effluent treatment and discharge plant. The wastes are discharged into the Atlantic Ocean but may recede into the estuary due to tidal motion [8].

Cocoyams are herbaceous perennial plants belonging to the family Araceae and are grown primarily for their edible corm. It is cultivated as food crops belong to either the genus *Colocasia* or *Xanthosoma*. Cocoyams are generally comprised of a large spherical corm (swollen underground storage stem), from which a few large leaves emerge. The petioles of the leaves stand erect and can reach lengths in excess of 1 m (3.3 ft). The leaf blades are large and heart-shaped and can reach 50 cm (15.8 in) in length. The corm produces lateral buds which give rise to tubers or corms and suckers or stolons. Cocoyams commonly reach in excess of 1 m in height and although they are perennials, they are often grown as annuals, harvested after one season. *Colocasia* species originates from Central and South America. All parts of the plant are edible. *Colocasia* is grown for its corm which is consumed after boiling, frying or roasting. The corms can be dried and used to make flour or sliced and fried to make chips. The soft variety is used mainly as a thickener in some Nigerian soup recipe. The leaves of the plant are also edible and are usually consumed as a vegetable after cooking in dishes such as stews. *Colocasia spp* produce tubers much like potato and are boiled, baked, steamed or fried prior to consumption. Young leaves are eaten as a vegetable. The fresh tender leaves and young corm are used in preparing ekpang nkukwo a popular delicacy in the study area. *Colocasia spp* grow best in fertile soil and will tolerate a pH range of 4.2–7.5. They can be grown in wetland areas in paddies using a similar system to that of rice. *Colocasia* species are usually vegetatively propagated using suckers [6].

Sampling procedure

Five sampling stations: Mpanak (station 1), Iwo Opom (station 2), Iwokwang (station 3), Ubenekang (station 4) and Usiak lfia (Station 5) as shown in the map of the study area were chosen for the research Fig. 1 were selected. The sampling took on January, February and March 2017. This coincided with the planting season in other to alert the local farmers of safe areas for planting. Five soil and *Colocasia spp* samples were collected at each station and mixed to form one composite sample for that station. The *Colocasia spp* samples were collected before the soil samples. At each sampling station, all material and organic detritus were removed from the surface soil; the corm of the plant was harvested with a hoe. A hand soil auger (nickel-plated carbon steel) was used to gather soil samples by taking 5 auger borings to the point of plant roots at random grid at each sampling station. The cocyam corm and soil samples were put into clean polythene bags labeled appropriately and taken to the laboratory for pretreatment and analysis. Control soil and cocyam corm samples were collected at Iba Oku, Uyo Local Government, Akwa Iborn State.

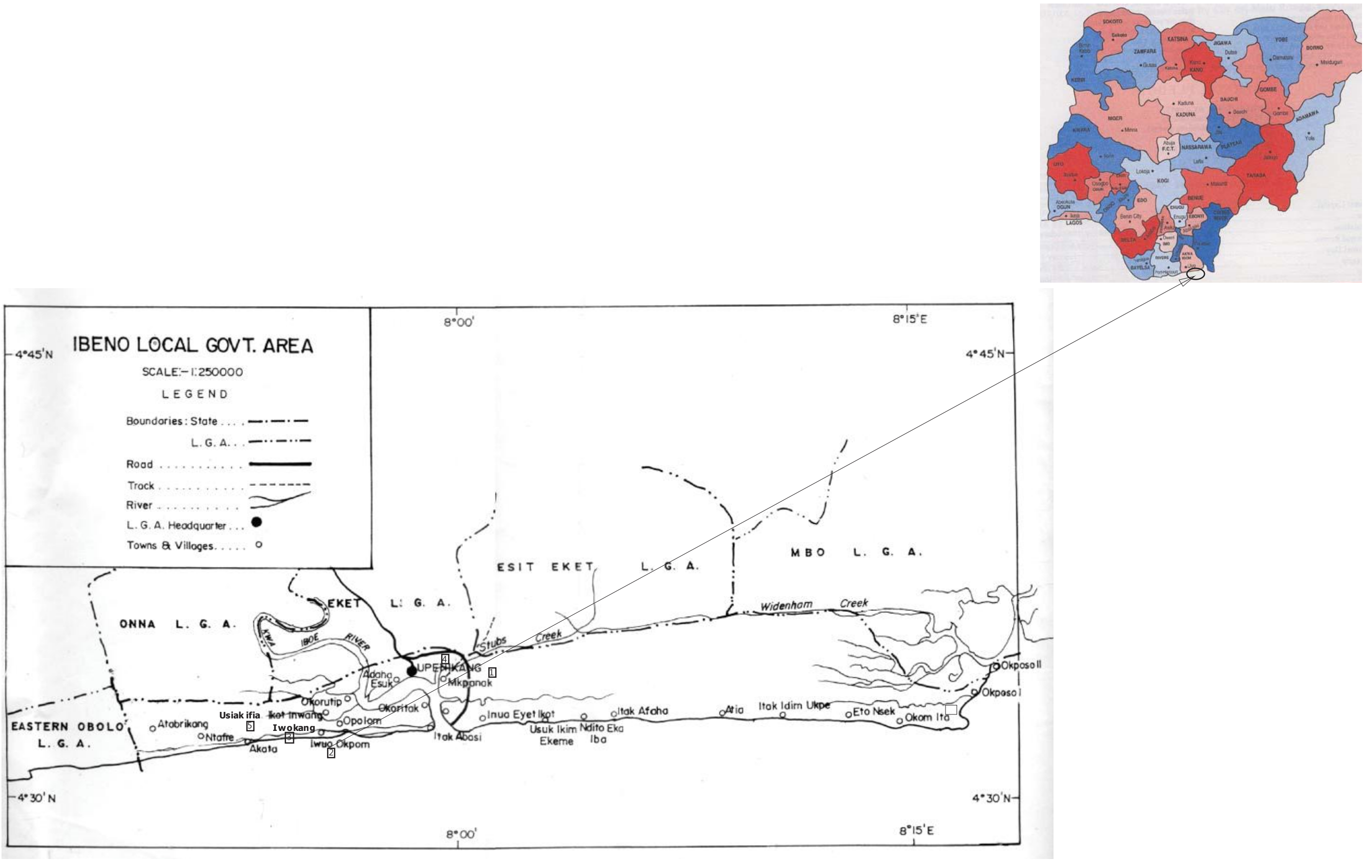

Figure 1: Map of the study area showing sampling locations adapted from Department of Survey and Geo-informatics, Ministry of Lands and Housing, Akwa Ibom State, Nigeria

Analytical procedure

The soil samples were air dried and mechanically ground using mortar and pestle, sieved and 2 mm mesh size obtained for further analysis. The soil samples (1.0 g) were weighed into Kjeldahl flasks. Aqua regia (15 ml) was added, swirled to mix the samples and kept overnight. The flasks were heated on a hot plate to 50 ^oC for 30 minutes; temperature was later adjusted to 120 ^oC and heated continuously for 2 hours. The samples were cooled, and 0.2 M HNO_3 (10 ml) was added to the mixtures. The resulting mixtures were filtered with a Whatman (no. 541) filter paper. The flasks and filter papers were washed with small aliquots of 0.2 M HNO_3. Filtrates were transferred into 50 ml standard flasks and made up to the mark with 0.2 M HNO_3. A blank sample was prepared using the same methods but excluding the sample. The corms of the cocoyam samples were washed under running water to remove adhered soil particles, rinsed with de-ionized water to wash off dirt. The samples were sun dried to remove moisture. It was then dried in an oven to a constant weight at 105 ^oC, pulverized to fine powder using mechanical grinder and sieved and a 2 mm mesh size. The ground sieved samples were put into labeled polyethylene bags and kept in desiccators. 2.0 g of oven-dried ground sieved sample was weighed into a 50 ml Kjeldahl flask. Concentrated $HClO_4$ (1 ml), concentrated HNO_3 (5 ml) and concentrated H_2SO_4 (0.5 ml) were added. The mixture was swirled gently and digested at moderate heat first, and the temperature increased slowly. Digestion lasted for about 15 minutes after the appearance of white fumes. The digest was left to cool. 10 ml of de-ionized water was added. The mixture was filtered into 50 ml volumetric flask and made up to the mark with de-ionized water. Blank sample was prepared by repeating the same procedure but omitting the plant sample. The concentrations of Ni, V, Pb, and Pb were determined using flame Atomic Absorption Spectrophotometer (Unicam solar, model 969). A calibration graph was plotted for each element using measured absorbance and the corresponding concentration. The calibration curve was then used to determine the concentrations of the metals. [10].

Statistical analysis

Correlation coefficients (r) between extractible heavy metals in soil and *Colocasia spp* corm were evaluated by Pearson's Product Moment Correlation Coefficient using Statistical Package for Social Science (SPSS) 2010.

Results

The concentrations of the aqua-regia extractable heavy metals in mg kg^{-1} in soil and *Colocasia spp corm* from Qua Iboe costal Area between the months of January to March 2017 are presented in Tables 1- 3. The results of the statistical analysis for correlation coefficient (r) between concentrations of heavy metals in soil and *Colocassia spp* revealed *Ni* (0.316), V (0.305), Pb (0.768) and Cd (0.305) respectively.

Table 1: Concentrations of heavy metals in soil and *Colocasia spp corm* in mg kg^{-1} for January 2016

Heavy	station 1		station 2		station 3		station 4		station 5		control		mean	
metal	S_1	P_I	S_2	P_2	S_3	P_3	S_4	P_4	S_5	P_5	S_c	P_c	S	P
Ni	3.95	1.20	4.92	1.28	4.73	1.48	4.68	0.88	49.20	1.10	0.60	0.15	28.12	1.19
V	4.28	0.70	2.28	1.08	2.93	0.45	4.33	1.13	31.30	0.78	0.09	0.02	9.03	0.83
Pb	0.45	0.03	0.38	0.03	0.78	0.10	7.15	0.10	2.88	0.33	0.03	0.03	2.33	0.11
Cd	0.03	0.03	0.08	0.03	0.18	0.03	0.13	0.03	0.05	0.45	0.08	0.03	0.28	0.094

P = plant sample, S = soil sample. ** = strong positive significant

Table 2: Concentrations of heavy metals in soil and *Colocasia spp* corm in mg kg^{-1} for February 2016

Heavy	station 1		station 2		station 3		station 4		station 5		control		mean	
metal	S_1	P_I	S_2	P_2	S_3	P_3	S_4	P_4	S_5	P_5	S_c	P_c	S	P
Ni	2.48	0.45	1.85	0.85	3.20	0.70	3.85	0.28	2.38	1.15	0.40	0.05	2.75	0.69
V	0.85	0.35	1.28	0.20	2.95	0.35	1.18	0.18	1.55	0.78	0.70	0.15	1.56	0.83
Pb	101.30	0.98	1.23	0.43	0.67	0.05	32	0.73	0.38	0.05	0.07	0.02	27.12	0.12
Cd	0.35	0.10	0.20	0.13	0.23	0.03	0.30	0.05	0.30	0.10	0.07	0.08	0.09	0.08

Table 3: Concentrations of heavy metals in soil and *Colocasia spp* corm in mg kg^{-1} for March 2016

Heavy	station 1		station 2		station 3		station 4		station 5		control		mean	
metal	S_1	P_I	S_2	P_2	S_3	P_3	S_4	P_4	S_5	P_5	S_c	P_c	S	P
Ni	1.58	0.18	3.20	0.70	4.95	0.08	0.43	0.23	1.95	0.38	2.58	0.15	2.42	0.34
V	0.73	0.13	2.95	0.35	3.42	0.63	0.30	0.35	0.66	0.18	0.38	0.13	1.61	0.33
Pd	0.63	0.08	0.61	0.05	10.98	0.05	31.48	0.08	1.29	0.10	0.20	0.03	8.99	0.07
Cd	1.15	0.03	0.23	0.03	0.20	0.03	0.18	0.05	0.23	0.08	0.075	0.03	0.40	0.04

Discussion

The mean concentrations in mg kg^{-1} of the heavy metals in soil and *Colocasia spp* corm were: January soil N (22.49), (14.46), Pb(2.33), Cd(0.28), *Colocasia spp* corm Ni(1.19), V(0.03), Pb(0.11), Cd(0.94); February soil Ni(2.75), V(1.56), Pb(0.11), Cd(0.09), *Colocasia spp* corm Ni(0.69), V(0.83), Pb(0.12), Cd(0.08) and March soil Ni(2.42), V(1.61), Pb(8.99), Cd(0.40) *Colocasia spp* corm Ni(0.34), V(0.33), Pb(0.07), Cd(0.04). All the investigated heavy metals were detected in all the samples throughout the period of study.

The highest mean concentration of Ni (22.49 mg kg^{-1}) in soil was recorded in the month of January. An abnormally high concentration of Ni (49.20 mg kg^{-1}) was noticed in soil samples at Usiak Ifia (Station 5) Table 1. Also, the highest mean concentration of Ni (1.19 mg kg^{-1}) in *Colocasia spp* corm was recorded in January Table 1, higher WHO standard of 1.037 mg kg^{-1}. The mean concentrations of Ni in soil was higher than the background concentration but within normal range of (2-750) mg kg^{-1} as recommended by Federal ministry of Environment, Nigeria and World Health Organization (WHO). There was a generally decrease in concentrations of Ni (22.49 > 2.75 > 2.42) in soil and *Colocasia spp* corm (1.19 > 0.69 > 0.34) for January, February and March respectively. This might be due to dilution of soil water by rain water as wet season sets in. The high level of nickel could be due to leaching from garbage, solid wastes dump, industrial processes and oil spillage due to extensive crude oil exploration as Ni is the major metallic component in crude oil. (Ekeanyanwu et al. 2010) [13] in "Trace Metals Distribution in Some Common Tuber Crops and Leafy Vegetables Grown in the Niger Delta Region of Nigeria" reported a mean concentration of (0.19 and 0.13) mg kg^{-1} in *Discorea alata and Manihot esculenta* respectively. In a study by Orish et al (2012) [4], concentration of Ni ranged from 0.00-3.13 mg kg^{-1} in rice (Oryza sativa). Sunflowers plant, oats and grass-Bahiagrass, grown in soils with different levels of nickel (16.5 till 38.4 mg kg $^{-1}$) the quantities of the element found in the aerial parts of plants were: 0.11 to 10.74 mg kg^{-1} (Sunflower), 0.73 to 52.70 mg kg^{-1} (black oats) and 2.83 to 11.88 mg kg^{-1} (Grass-Bahiagrass). Small amount of nickel are needed bythe human body to produce red blood cells, however in excessive amounts Ni can become mildly toxic. Short-term overexposure to nickel is not known to cause any health problem, but long term exposure can cause decreased body weight, heart and liver damage and skin irritation [6]**.** It occurs naturally more in plants than in animal flesh. It activates some enzyme systems in trace amount but its toxicity at higher levels is more prominent. Some patients develop vesicular type of hand eczema following the ingestion of nickel in diet [6]. Although rare, chronic urticaria, a type 1 hypersensitivity response, has been attributed to dietary nickel

The rank profiles in mean concentrations of V in mg kg^{-1} in soil and *Colocasia spp* corm samples (14.96 > 1.61 > 1.56) and (0.37 > 0.33 > 0.12) for January, February and March respectively Tables 1-3. The highest mean concentration of V (14.96 mg kg^{-1}) and (0.37 mg kg^{-1}) for soil and *Colocasia spp* corm samples respectively were recorded in January Table 1. The values were significantly higher than the amount obtained in the background soil and plant samples Tables 1-3. Station 5 (Usiak Ifia) recorded the highest individual concentration of V(31.30 mg kg^{-1}) in soil compared to other sampling stations. The amount of heavy metal in soil may influence the concentration in plant. In related study by (Iwegbue et al. 2006) [17] in the study area, (24.05±17.25) mg kg^{-1} V in soil was recorded. Also, (Osuji and Adesiyan, 2005) [14] in "Extractable hydrocarbons, nickel and vanadium contents of Ogbodo-Isiokpo oil spill polluted soils in Niger Delta, Nigeria" reported a range of (0.19 to 0.70) mg kg^{-1} V. Such levels of Ni and V may result to enhanced absorption by plants, which may bring about possible bioaccumulation in such plants and the animals that depend on them for survival and all of these may lead to toxic reactions along the food chain. Absorption and accumulation of heavy metals in plant tissues depend upon many factors. These include temperature, moisture, organic matter, pH and nutrient availability [9]. A research by (Onyeike et al. 2004) [19] in Ogoni land, Rivers State, Nigeria revealed higher concentrations of V, Ni and Pb in soil of the oil rich area. V is essential for green algae and can stimulate higher plants in small amount, but can be fatal at concentration of 10.0 mg $kg^{-1.}$ The concentration of V (31.30 mg kg^{-1}) at station 5 (Usiak Ifia) and mean concentration of 14.96 mg kg^{-1} signals threat to the environment.

The level of lead in soil and *Colocasia spp* corm were in descending order of (27.17 > 2.33 > 8.99) mg kg^{-1} and (0.12 > 0.11> 0.07) mg kg^{-1} respectively. The concentrations of lead in soil of the different sampling locations were within the normal range of (20-10,000) mg kg^{-1} as specified by (Alloway 1999) [20]. Notwithstanding, the concentration of 101.30 mg kg^{-1} of Pb recorded in station 1(Mkpanak) present risk of potential pollution in the environment. The elevated level of lead in soil of the study area could be attributed to low solubility, relatively freedom from microbial degradation. In addition, huge amount of lead - load domestic and industrial wastes dumped in the area could account for this. The average concentration 0.10 mg $kg^{-1}$of Pb in *Colocassia spp* was low compared to the standard stipulated by WHO standard of 0.01 mg kg^{-1}. The larger ionic redii of Pb^{2+} (1.20 Å) might account for decrease in absorption of Pb by *Colocasia spp* corm [10]. Nwadinigwe *et. al* (2015) recorded mean concentrations of 0.02 mg kg^{-1} and 0.090 mg kg^{-1} of Pb in soil and *Telfairia occidentalis* samples in the study area.[23] Similarly, Nwadingwe *et. al* (2014) recorded a mean concentration of 0.029 mg kg^{-1} and 0.26 mg kg^{-1} of Pb in soil for dry and wet season respectively in the study area [24]

The order in distribution of concentration of Cd in mg kg^{-1} in soil and *Colocasia spp* corm were in descending order of (0.40 > 0.28 > 0.09) and (0.12 > 0.08 > 0.04) respectively. The mean concentrations of Cd (0.40, 0.28 and 0.117) mg kg^{-1} in *colocasis spp* corm exceeded WHO limit of 0.1 mg kg^{-1} in root and tuber crops. The range of Cd in soil was within the normal range of (0.01-2.0) mg kg^{-1}. The small ionic size of Cd^{2+} may be the principal factor responsible for increased absorption of Pb by *Colocasia spp* corm [10]. Aisien et al. 2010 [11], reported that the accumulation of Cd and Zn in leaves and roots of water hyacinths increased with increase in pH. The elevated level of Cd compared to background sample could be attributed to anthropogenic sources such as spent batteries, sewage sludge, paints, plastic and metal plating. The distributions of the investigated heavy metals in the soil and plant samples were highly variable. Cadmium is one of the major pollutants produced in the industrial area. It is easily absorbed and spread to the whole paddy plant and its bioavailable in the soil. In related study by Ekeanyanwu et al. (2010) [13] in the study area, 0.33 mg kg^{-1} and 0.89 mg kg^{-1} were recorded in *Discorea alata* and *Manihot esculenta r*espectively. Cadmium is a non-essential element in foods and natural waters and it accumulates principally in the kidneys and liver. Cadmium may be the unknown factor responsible for cases of hypertension in the human being. Toxic elements accumulate in the soils and induce a potential contamination on food chain, and endanger the ecosystem safety and human health [15].

The statistical analysis for correlation coefficient (r) between mean concentration of heavy metals in soil and cocoyam corm revealed a very strong positive significant relationship of r = 0.774** at significant level of 0.001 between Pb in soil and Pb in *Colocasia spp* . It also indicated a weak positive insignificant relationship of r = 0.316 and 0.305 for Ni and V content in soil and that *Colocasia spp* respectively. There was no significant relationship between Cd in soil and Cd in plant as shown by the correlation coefficient of -0.211. The trend of uptake (absorption) of Pb, Ni, V, and Cd by *Colocasia spp* was Pd > Ni > V > Cd with 0.774 > 0.316 > 0.305 > -0.211. The strong positive significant r implies that, the concentrations of the heavy metals in soil is proportional to the amount in cocoyam, the metallic pollutant was bound to the plant in the same period, and discharged from the same pollution source. Depending on the concentrations of the metals in the soil and other factors including nature of soil, the plant species, climate, pH, and temperature *Colocasia spp* has high ability to absorb Pb from the soil of the study area and it can be used as phytoremediator of Pb pollutant in the soil of the study area. Heavy metals, such as cadmium, lead, chromium and mercury, are important environmental pollutants, particularly in areas with high anthropogenic pressure. Their presence in the atmosphere, soil and water, even in traces can cause serious problems to all organisms, and heavy metal bioaccumulation in the food chain especially can be highly dangerous to human health [22]. In a related study "Study of Phytoremediation Potential of Fluted Pumpkin (*Telfairia occidentalis*) for Soil contaminated with heavy metals" [12]. Also Aisien et al (2010) [11] observed that Water hyacinth may be used in environment technology in constructed wetlands as it has been shown to be a good hyperaccumulator of Zn, Pb and Cd. Similarly, Naima et al 2010 [13] stated that *Eucalyptus* spp., and *Prosopis juliflora* L. proved to be good indicators of lead pollution and due to their diverse distribution in different parts of the world their leaves can be used as bioindicators of lead pollution. The plant accumulate the Cu and Cr metals more in the roots than in the shoots, while Pb and Co metals were accumulated more in the shoots than in the roots.

Conclusion

Understanding the concentrations of some toxic metals in soil and common food crops is important for establishing baseline concentrations from which anthropogenic effects can be evaluate. The results and statistical data obtained from this work indicated that:

- farmers should be discourage from cultivating in stations 1(Mkpanak) and station 5 (Usiak Ifiak) because of high concentrations of Pb and V.
- the concentrations of heavy metals pollutant in soil can increase the amounts in plant. These may bring about possible bio-accumulation with resultant toxic reaction in food chain among populations of livestock and humans that depends on the plants for food,
- *Colocasia spp* has high ability to absorb Pb and can be used as excellent phytoremediator of Pb pollutant in the soil of the study area.

Acknowledgments
The authors wish to thank staff of post graduate laboratory, Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka for their technical assistance, provision of equipment and glassware necessary for this work.

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