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Research Article

Assessment of Heavy Metals in Cassava Mill Effluents Contaminated Soil in a Rural Community in the Niger Delta Region of Nigeria

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Abstract

This study assessed the level of some selected heavy metals in cassava mill effluents contaminated soil from Ndemili community in the Niger Delta region of Nigeria. Triplicate soil samples were collected using soil augar at 0 - 20 cm depth from 6 locations including one control. Sampling was carried out bimonthly (from November 2016 to September 2017) covering the two predominant seasons - wet and dry. The samples were dried, digested and analyzed using flame atomic absorption spectrophotometer (FAAS). Result for both spatial and bimonthly distribution of heavy metals for copper 1.10 - 6.83 mg/kg, zinc 14.32 - 46.15 mg/kg, manganese 18.42 - 47.49 mg/kg, iron 1303.29 - 4934.04 mg/kg, lead 1.33 - 9.42 mg/kg, cadmium < 0.001 - 0.24 mg/kg, chromium 0.19 - 3.41 mg/kg, nickel 1.57 - 3.76 mg/kg and cobalt < 0.008 - 9.71 mg/kg. Analysis of variance showed that there was significant variation ($P < 0.05$) among the various locations, months and interaction of locations and months apart from iron and chromium in the bimonthly distribution. Positive significant correlation ($P < 0.05$) also exists among most of the heavy metals, indicating that contamination is of similar origin apart from cadmium that showed negative correlation with cobalt. The study showed that cassava mill effluents are having impact on soil receiving the effluent with regard to heavy metals concentration.

Keywords: *Cassava; Environmental Management; Small-Scale; Soil Quality*

Introduction

The soil is a unique habitat for lives. According to Gu., *et al*. [1], Gasiorek., *et al*. [2], Hou., *et al*. [3], soil is the foremost constituent of the environment. The soil also plays social, ecological and economic role to lives. Since soil is an important part of the ecosystem, it directly and/ or indirectly affects environmental quality [2,4,5]. Several human activities also take place in the soil. As such, it's a fundamental assets needed for human existence. In addition, soil is also the platform through which structures are erected and plant/vegetation is cultivated. Papozotas., *et al*. [6] reported that soil is an integral part of landscape due to its diverse and unique characteristics that results from the transformation of natural regolith. According to Kolwan., *et al*. [7], Ibe., *et al*. [8], soil is basically formed during weathering processes. During soil formation weathering, geologic materials and microbial interactions are necessary.

The soil is the major recipient of different wastes stream mainly from agricultural and industrial activities [9,10]. For instance, during food processing, the effluents generated are discharged into the soil which my drain to nearby pit, drainage system and/or surface water. Izah., *et al*. [11] reported that effluents resulting from oil palm processing end up in the soil, and are capable of altering the soil properties. According to Okwute and Isu [12], Awotoye., *et al*. [13], Izah., *et al*. [11], soil contaminated with palm oil mill effluents typically becomes bare, dark brown with humus, damp, odiferous and contains debris from the processing palm fruit into palm oil. Cassava is another food processing outfit that generates several wastes stream. In a developing country like Nigeria, the effluents are hardly treated.

Typically, Nigeria is the largest producer of cassava in the world [14,15]. During processing, three major streams of waste are generated including solid (peels, cassava cake), liquid (whey or cassava mill effluents) and air emission (gaseous emissions) [14]. The liquid waste popularly known as cassava mill effluents is generated in the grating and dewatering zone.

Cassava mill effluents alter the receiving soil microbial characteristics with regard to microbial diversity and density [8,16-23], physicochemical properties including cation and anions exchange, soil particle size, bulk density and porosity etc [17,20,23-28]. The potential of cassava mill effluents to impact on soil characteristics could be associated to the fact that it contains cyanide which is highly lethal, fairly mobile in soil and damages microorganisms [17,29]. Soil contaminated by cassava mill effluents is highly acidic and can cause acidification [26]. Cassava mill effluents contaminated soil leads to reduction in plant growth [30]. Furthermore, high concentration of heavy metals especially non-essential metals has the tendency to affect soil native micro-biota [31]. The concentration of heavy metals from cassava mill effluents often exceeds the permissible limit recommended by Federal Environmental Protection Agency (FEPA) for all category of effluent to be discharged into the environment (i.e. soil and surface water).

Like the microbial and physicochemical characteristics of the soil, heavy metals concentration in cassava mill effluents has been reported in several locations in Nigeria. For instance, Osakwe [24] reported heavy metals in cassava mill effluent contaminated soil in Abraka and its environs, Delta state. Nwakaudu., *et al.* [25] reported heavy metal in cassava mill effluent contaminated soil (from Rivers, Imo and Abia state) on maize growth. Igbinosa and Igiehon [21], Igbinosa [32] reported heavy metals in cassava mill effluents contaminated soil in Oluku, Isihor and Ehor in Edo South region of Edo State. Therefore, this present study assessed the heavy metal concentration from cassava mill effluents contaminated soil in a rural community (Ndemili) in the Niger Delta region of Nigeria.

Materials and Methods

Study Area

Ndemili Umusadege, Utagba-Uno is one of the communities in Ndokwa west local government area of Delta state. Typically, Delta state is blessed with abundant surface and groundwater resources with a high average annual precipitation of about 1900 mm [32]. Delta state is one of the states in the Niger Delta that has the three major structural basin from the oldest to the youngest formations including Akata (which comprises of about 10% sandstone and shale which is also believed to be over pressured carbonaceous and under-compacted, and it ranged from Eocene to Recent), Agbada (which is a parallic sequence of alternating shale and deltanic sandstone with a variable age ranging from Eocene in the north to Pliocene/Pleistocene in the south, and recent in the delta surface with hydrocarbon potentials), and Benin Formations (which overlies the Agbada formation comprises of about 10% shale/clays and over 90% sands which consist of gravel, coarse and fine grain which are spatially distributed and is Oligocene to Pleistocene in age [33-35]. Most of the surface rock in the state consists of the Ogwashi-Uku formation the surface equivalent of the Agbada Formation. This formation is mostly found in the Delta North. The state is boarded by Rivers, Imo, Anambra, Edo and Bayelsa states [33]. Typically, Benin formation covers west and northwest of Asaba town [36], Abraka [33-35], Sapele [37], Warri [38], Ughelli and Agbor [33]. The formation is masked by the younger Holocene deposits of the Sombreiro-Warri Deltaic Plain, mangrove and freshwater swamp wetlands [33]. Hence, Ndemili which is close to the Agbor and Abraka and may be within Benin Formation. Ndemili lies between N06º01' and E006º17' [33]. The aquifers of the study area is unconfined where clays of < 1 meter provides semi- confined conditions [33].

Farming is a major source of livelihood to resident of the area. Some notable food crops cultivated in the area include cassava, yam, maize, oil palm etc. The area has an important river known as Umu. The region has similar climatic condition peculiar to other Niger Delta region and is characterized by two distinct seasons viz: wet season (April to October - 7 months) and dry season (November to March of the following year- 5 months). In the region, the rainfall pattern appears to be shifting from the known conventional period. The relative humidity and temperature of the area is 50 -95% and 28 ±8 ºC respectively all year round.

Sample Collection

Triplicate soil samples were collected bimonthly from cassava mill effluents contaminated soil at a depth of 0 - 20cm from November 2016 to September 2017. Sampling was carried out from six different locations including one control using soil augar. The soil samples were collected using Ziploc bags and labeled appropriately.

Sample Preparation

In the laboratory, the samples were air dried in a clean, well-ventilated room temperature prior to analysis. The dried samples was grounded and homogenized, and sieved by passing through a 2 mm mesh size sieve to remove debris and gravels larger than 2 mm in diameter. The portions of the pulverized soil were transferred into their respective reaction vessels using a sterile stainless steel spoon spatula for heavy metal determinations.

Five (5) g of sieved sample was weighed into a 250 ml beaker, and an empty beaker was stood in the analysis set up to represent the reagent/glass ware blank. 100 ml of distilled water was added. Then after, 1.0 ml and 10ml of concentrated HNO_3 (sp. gr 1.42) and concentrated HCl (sp. gr 1.19) were added respectively. Then, the beakers were covered with ribbed watch glasses and heated at 95°C on a hot plate. Heating stopped when the content of the beaker solution remain about 10 to 15 ml. The mixture was allowed to cool to room temperature. The content was filtered and quantitatively transferred into volumetric flask and was diluted distilled water to 50 ml mark of the volumetric flask.

Soil Heavy Metal Analysis- Instrumentation and condition

Aqua/Regia Digestion (ASTM D 3974 - 99) method was adopted for heavy metal determination. The flame atomic absorption spectrometry (FAAS) (GBC Avanta PM A6600) was calibrated with prepared working solutions from stock solutions (AccuStandards, 1,000 mg/l) for each of the respective metals to be analyzed. The soil extracts were aspirated into the flame atomizer via the capillary tube attached to the nebulizer unit of the FAAS (air-acetylene flame was applied at flow rates of 2 l/min for the fuel and 10 l/min for the oxidant when copper, cadmium, chromium, manganese, zinc, lead, nickel and cobalt was analyzed); the overall system had to convert the liquid into aerosol by selecting the correct droplet size (rejecting the oversized droplets) and transporting the gaseous sample to the flame atomizer on the burner head (air-acetylene burner). Ground state atoms are formed by desolvation (solvent removal and chemical bond breakage to form free atoms) by the chemical flame (air-acetylene flame) and the particles absorb the light beam from a light source (Hollow cathode lamp), while the population of ground state atoms in the flame is directly proportional to the concentration of element of interest. The wavelength at which the various metals were detected was 213.9 nm, 324.70 nm, 232.0 nm, 248.3 nm, 279.5 nm, 357.90 nm, 228.8 nm, 217.00 nm and 240.70 nm for zinc, copper, nickel, iron, manganese, chromium, cadmium, lead and cobalt respectively.

Quality control

The accuracy of the analytical procedure employed for the study was checked calibrating equipment with known solution and analysis of metals of known concentration for 6 - 10 times prior to sample analysis. The limit of detection and limit of quantification were evaluated. The limit of detection for each of the heavy metal were 0.002 mg/kg (copper), 0.001 mg/kg (zinc), 0.008 mg/kg (cobalt), 0.002 mg/kg (nickel), 0.09 mg/kg (iron), 0.006 mg/kg (chromium), 0.001 mg/kg (cadmium), 0.002 mg/kg (lead) and 0.004 mg/kg (manganese). The limit of quantification were 5.00 mg/kg (copper), 1.50 mg/kg (zinc), 9.0 mg/kg (cobalt), 8.0 mg/kg (nickel), 80.0 mg/kg (iron), 15.0 mg/kg (chromium), 1.80 mg/kg (cadmium), 20.0 mg/kg (lead) and 4.0 mg/kg (manganese). The linearity curve were straight line, R and $R^2 = 1.000$ for each of the heavy metals under study.

Median and Geometric means computation

In environmental studies, data is commonly compared with the control. In as much as the activity is releasing heavy metals into the environment. Studies have also suggested that impacts environment i.e. soil could be compared with pre-industry (data generated before the commencement of an activity in a location). But this type of data is not readily available in some sector including small scale cassava processing. Therefore, the natural background data is used as reference value. The use of geometric mean as background value for assessing environmental risk have been considered by Thambavani and Uma Mageswari [39], Bhutiani., *et al*. [40]. Also, the use of median value has also been recommended by Monakhov., *et al*. [41], Bhutiani., *et al*. [40]. Therefore, in this study, the median and geometric mean was calculated and used as background median mean (BMM) and background geometric mean (BGM). In the non-detected heavy metals, 50% of the mean detected value was considered to be the value [40] before the calculation of the median and geometric means. The background reference values were calculated from the data in the 5 cassava mills under study.

Statistical analysis

The data were subjected to univariate analysis. The data were expressed as Mean ± standard deviation. Two-way analysis of variance was carried out at $P = 0.05$, and Waller-Duncan multiple range test statistics was used to determine the source of the observed variation using SPSS software 20. Spearman rho correlation matrix was used to show relationship among the various metals. Paleontological statistics software package by Hammer., *et al*. [42] was used for the cluster analysis and geometric mean computation. In the cluster analysis, similarity measure was carried out with Bray Curtis test at single linkage algorithm.

Results and Discussion

The spatial and seasonal distribution of heavy metal parameters of cassava mill effluents contaminated soil from a small scale cassava processing are presented table 1 and 2 respectively. While the Spearman's rho correlation coefficient (r) matrices for the heavy metal parameters and the p-value (significant level) of the statistics carried out are presented in table 3 and 4 respectively. The overall arithmetic, geometric and median mean for each of the heavy metals based on seasons (wet and dry) are presented in figures 1-9.

Copper

The concentration of copper ranged from 1.10 - 6.83 mg/kg for spatial distribution. There was significant difference ($P < 0.05$) among the various locations. The control location (LF) was significantly lower compared to other locations (Table 1). Furthermore, the seasonal distribution ranged from 3.36 - 5.94 mg/kg. Basically, there was significant variation ($P < 0.05$) between two season of study. Wet season period (November, January and March) showed no significant variation ($P > 0.05$). Like, wet season, the dry season period (May, July and September) showed no significant difference ($P > 0.05$) (Table 2). Based on interaction, there was significant difference ($P < 0.05$) between the seasons and spatial distribution (Table 3). Copper shows positive relationship with iron ($r = 0.192$, $p < 0.05$), lead ($r = 0.645$, $P < 0.01$), cadmium ($r = 0.268$, $P < 0.01$), chromium ($r = 0.268$, $P < 0.01$), nickel ($r = 0.325$, $p < 0.05$) and cobalt ($r = 0.311$, $P < 0.01$) (Table 4). On the overall, the concentration of copper in LB and LD in the dry season exceeded 6 mg/kg (Figure 1). The significant variation is copper suggests the effect of season, and anthropogenic activities in the soil locations receiving cassava mill effluents. During the wet season, the effect of runoff of waste water could account for lower concentration. Based on spatial distribution, variation in human activities in the mill could also account for difference in copper concentration among the various locations. Control has lower copper concentration suggesting the impact of cassava mill effluents in the mills. The concentration of copper in the contaminated soil in this study is generally higher than the values reported by other authors. For instance, in soil receiving cassava mill effluents copper values of 0.112 mg/kg and 0.12 mg/kg at the edge of the discharge point and control respectively [20], 0.149 - 0.158 mg/kg at cassava mill effluent contaminated soil and control respectively [25], 0.146 - 0.643 mg/kg and 0.235 mg/kg at discharge point and control respectively [24], 1.69 - 2.90 mg/kg and 1.09 - 2.12 mg/kg at cassava mill effluents contaminated soil and control respectively [21]. Variation in the findings of this study with previous works could be due difference in geological formation as well as prevailing anthropogenic activities in the mills.

Parameters	Locations					
	LA	LB	LC	LD	LE	LF
Cu, mg/kg	4.96 ± 1.23b	6.83 ± 2.16c	3.99 ± 0.60b	6.88 ± 3.71c	3.97 ± 0.99b	1.10 ± 0.58a
Zn, mg/kg	14.32 ± 4.95a	43.87 ± 7.68cd	39.08 ± 5.93bc	42.87 ± 4.91cd	46.15 ± 5.22d	37.33 ± 6.79b
Mn, mg/kg	18.42 ± 1.97a	37.39 ± 18.63bc	36.63 ± 4.53bc	43.43 ± 4.21cd	47.49 ± 9.55d	29.62 ± 10.52b
Fe, mg/kg	2223.82 ± 853.55b	2230.21 ± 443.44b	4934.04 ± 823.65d	4709.33 ± 1588.28d	3417.52 ± 194.24c	1303.29 ± 147.88a
Pb, mg/kg	4.96 ± 5.20b	9.42 ± 2.06c	3.03 ± 2.49a	1.44 ± 1.55a	2.01 ± 1.13b	1.49 ± 1.13a
Cd, mg/kg	< 0.001 ± 0.00a	0.24 ± 0.25b	< 0.001 ± 0.00a	< 0.001 ± 0.00a	0.22 ± 0.26b	< 0.001 ± 0.00a
Cr, mg/kg	3.01 ± 0.99c	0.19 ± 0.29a	1.85 ± 0.46b	1.37 ± 0.29b	3.41 ± 1.24c	0.19 ± 0.21a
Ni, mg/kg	2.55 ± 1.78bc	2.41 ± 0.76abc	3.76 ± 1.29d	2.79 ± 1.50c	1.57 ± 0.65a	1.83 ± 0.71ab
Co, mg/kg	1.72 ± 2.45a	5.16 ± 5.37b	5.64 ± 5.85b	5.43 ± 6.11b	4.23 ± 4.32b	4.69 ± 4.91b

Table 1: *Spatial distribution of heavy metals concentration in cassava mill effluent contaminated soil.*

Data is expressed as mean ± standard deviation; Different letters across the row indicate significant variation (P < 0.05) according to Waller-Duncan test statistics

Parameters	Locations					
	November	January	March	May	July	September
Cu, mg/kg	5.63 ± 2.98b	5.55 ± 2.92b	5.94 ± 3.83b	3.61 ± 1.58a	3.64 ± 1.45a	3.36 ± 1.40a
Zn, mg/kg	36.47 ± 13.19ab	37.05 ± 13.25ab	40.29 ± 15.61b	37.87 ± 11.08ab	38.70 ± 10.37b	33.24 ± 9.31a
Mn, mg/kg	35.35 ± 11.90a	36.09 ± 14.41a	36.69 ± 14.78a	38.83 ± 17.27a	33.83 ± 12.34a	32.21 ± 10.70a
Fe, mg/kg	3198.83 ± 1951.15a	3022.05 ± 2040.07a	3341.02 ± 2162.60a	3186.49 ± 986.77a	3120.62 ± 956.12a	2949.17 ± 991.99a
Pb, mg/kg	4.73 ± 3.72c	5.53 ± 3.50c	5.98 ± 4.22c	3.06 ± 3.65b	1.74 ± 3.14ab	1.30 ± 2.25a
Cd, mg/kg	< 0.001 ± 0.00a	< 0.001 ± 0.00a	< 0.001 ± 0.00a	0.16 ± 0.23b	0.18 ± 0.27b	0.12 ± 0.19b
Cr, mg/kg	1.80 ± 1.15a	1.63 ± 1.30a	1.90 ± 1.37a	1.80 ± 1.84a	1.51 ± 1.45a	1.39 ± 1.48a
Ni, mg/kg	2.40 ± 1.05ab	3.03 ± 1.07b	3.06 ± 1.30b	2.48 ± 1.45ab	2.06 ± 1.51a	1.88 ± 1.51a
Co, mg/kg	7.72 ± 3.71b	9.71 ± 2.53c	9.35 ± 3.44b	< 0.001 ± 0.00a	< 0.001 ± 0.00a	0.08 ± 0.12a

Table 2: *Bimonthly variation of heavy metals concentration in cassava mill effluent contaminated soil.*

Data is expressed as mean ± standard deviation; Different letters across the row indicate significant variation (P < 0.05) according to Waller-Duncan test statistics

Parameters	Model (interaction)	Bimonthly distribution	Spatial distribution
Cu, mg/kg	0.000	0.000	0.000
Zn, mg/kg	0.000	0.011	0.000
Mn, mg/kg	0.000	0.442	0.000
Fe, mg/kg	0.000	0.786	0.000
Pb, mg/kg	0.000	0.000	0.000
Cd, mg/kg	0.000	0.000	0.000
Cr, mg/kg	0.000	0.223	0.000
Ni, mg/kg	0.000	0.009	0.000
Co, mg/kg	0.000	0.000	0.000

Table 3: *P-Values for the statistical analysis of heavy metals from cassava mills effluent contaminated soil.*

Parameters	Cu	Zn	Mn	Fe	Pb	Cd	Cr	Ni	Co
Cu	1								
Zn	0.044	1							
Mn	-0.018	0.778**	1						
Fe	0.192*	0.351**	0.407**	1					
Pb	0.645**	0.139	0.002	-0.185	1				
Cd	0.230*	0.371**	0.357**	-0.045	0.232*	1			
Cr	0.268**	-0.142	-0.054	0.321**	0.001	0.019	1		
Ni	0.325**	0.078	0.115	0.184	0.401**	-0.159	-0.01	1	
Co	0.311**	0.282**	0.113	0.138	0.402**	-0.366**	0.065	0.204*	1

Table 4: *Spearman's rho (r) correlation matrix of heavy metals in cassava mill effluents contaminated soil.*

**: Correlation is significant at the 0.05 level (2-tailed).*

***: Correlation is significant at the 0.01 level (2-tailed).*

N = 108, n = 18(3)

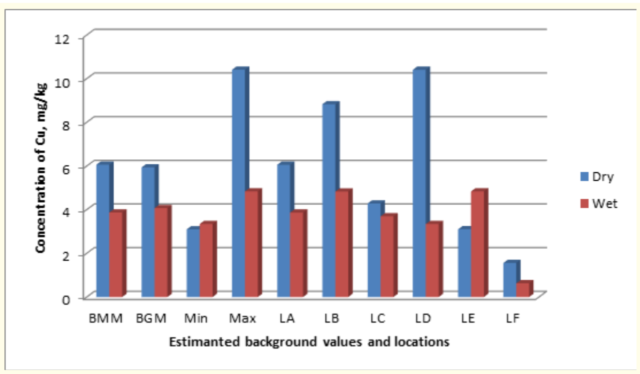

Figure 1: *Environmental background and distribution of copper in cassava mill effluent contaminated soil.*

Zinc

The level of zinc ranged from 14.32 - 46.15 mg/kg for spatial distribution. There was significant difference ($P < 0.05$) among the various locations. The control location (LF) was significantly higher than LA (Table 1). The seasonal distribution ranged from 33.24 - 40.29 mg/kg (Table 2). Basically, there was significant variation ($P < 0.05$) between the two seasons of study. The significant variation ($P < 0.05$) occurred in the month of March for dry season and September for wet season. Based on interaction, there was significant difference ($P < 0.05$) between the seasons and spatial distribution (Table 3). Zinc showed positive significant relationship with manganese ($r = 0.778$, $P < 0.01$), iron ($r = 0.351$, $P < 0.01$), cadmium ($r = 0.371$, $P < 0.01$) and cobalt ($r = 0.282$, $P < 0.01$) (Table 4). On the overall, the highest and least level of zinc in location LC, LD, LE and LF for dry season and LA and LB in the wet season (Figure 2). The result showed that no significant variation ($P > 0.05$) in the enrichment of zinc from the cassava mill effluents into the soil for most of the locations. Zinc may have entered the environment resulting from processing materials such as graters and basin made with zinc in addition to cassava mill effluent that contain heavy metals. The trend of control being significantly higher than some cassava mill effluents contaminated soil is comparable to finding of an author that reported similar trend [21]. For instance, in soil receiving cassava mill effluents zinc values of 1.41 mg/kg and 1.37mg/kg was reported at the edge of the discharge point of cassava mill effluents and control respectively [20], 0.618 -

1.684 mg/kg and 0.506 mg/kg at discharge point and control respectively [24], 1.43 - 1.89 mg/kg and 1.33 - 1.78 mg/kg at contaminated soil and control respectively [21], and comparable to values reported by an author with a value in the range of 25.40 - 32.24 mg/kg and 14.67-17.84 mg/kg at cassava mill effluents contaminated soil and control respectively [25]. Again the difference that exists could be due to variation in soil geology.

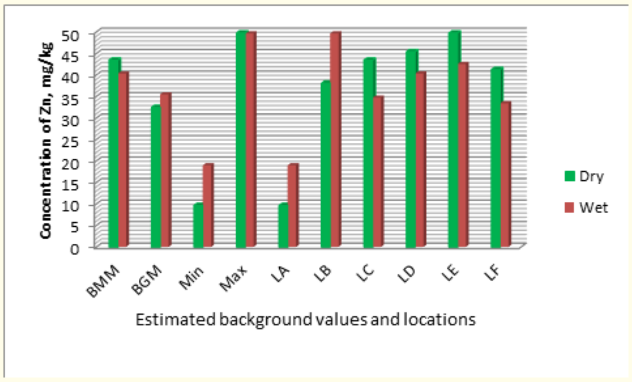

Figure 2: *Environmental background and distribution of zinc in cassava mill effluent contaminated soil.*

Manganese

The level of manganese ranged from 18.42 - 47.49 mg/kg for spatial distribution. There was significant difference ($P < 0.05$) among the various locations. The control location (LF) was significantly higher than LA (Table 1). The seasonal distribution ranged from 32.21 - 38.83 mg/kg (Table 2). There was no significant variation ($P > 0.05$) between two season (viz: November, January and March - wet season and May, July and September - dry season) of study. Significant variation ($P < 0.05$) exists in the interaction of seasons and spatial distribution (Table 3). Manganese showed positive significant relationship with iron ($r = 0.407$, $P < 0.01$) and cadmium ($r = 0.357$, $p < 0.01$) (Table 4). Generally, manganese level was highest in wet season for LB and dry season for LE (Figure 3). The significant difference ($P < 0.05$) among the various locations suggests difference in heavy metals load of cassava mill effluents deposited in the soil and other anthropogenic activities in each site. Lack of significant variation among the various seasons suggests that manganese may have leached into the soil through cassava mill effluents is uniform manner in the study area. Like zinc, manganese concentration were significantly higher in the in the control LF compared to LA in line with the findings of previous work [21]. The concentration of manganese in the contaminated soil in this study is apparently higher than the values reported by other authors. For instance, in soil receiving cassava mill effluents manganese values of 1.729 - 3.420 mg/kg and 0.314 mg/kg at cassava mill effluents discharge point and control respectively [24], 0.05 - 0.69 mg/kg and 0.01 - 0.61 mg/kg at cassava mill effluents contaminated soil and control respectively [21]. Again, the difference that exists between this study and other previous works could be associated to variation in the geology of the soil as well as other human activities peculiar to each area.

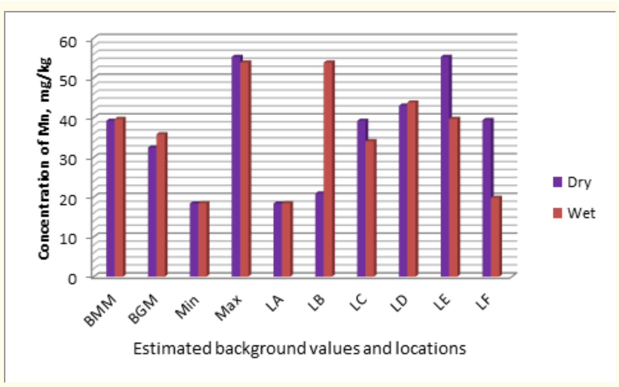

Figure 3: *Environmental background and distribution of manganese in cassava mill effluents contaminated soil.*

Iron

The level of iron ranged from 1303.29 - 4934.04 mg/kg for spatial distribution. There was significant difference (P < 0.05) among the various locations. The control location (LF) was significantly lower than every other location (Table 1). Furthermore, the seasonal distribution ranged from 2949.17 - 3341.02 mg/kg, being not significantly different (P > 0.05) among both seasons viz: wet season - November, January and March, and dry season - May, July and September. In addition, Significant variation (P < 0.05) exists in the interaction of seasons and spatial distribution (Table 3). Iron showed positive significant relationship with chromium (r = 0.321, P < 0.01) (Table 4). Generally, iron concentration was highest in LC and LD for both seasons (Figure 4). Least concentration was observed in the control (LF). This suggests the effect of iron resulting from the cassava mill effluents on the soil quality. The high iron concentration reported in this study compared to other heavy metals may be associated to the geology of the area [43]. Lack of significant difference (P > 0.05) among both seasons of study could be due continuous processing of cassava in the area throughout the year. High iron concentration among other heavy metals followed the trend reported by other authors [21,24]. For instance, in soil receiving cassava mill effluents, iron values was 84.88 - 139.28 mg/kg and 84.88 mg/kg at discharge point and control respectively [24], 4.58 - 12.0 mg/kg and 4.33 - 12.60 mg/kg at contaminated soil and control respectively [21], 0.118 - 0.147 mg/kg and 0.034 - 0.064 mg/kg at cassava mill effluents contaminated soil and control respectively [25]. Again, the variation that occurred in the findings of this study when compared to previous works is probably due to the geology of the soil as well as prevailing anthropogenic activities in the area.

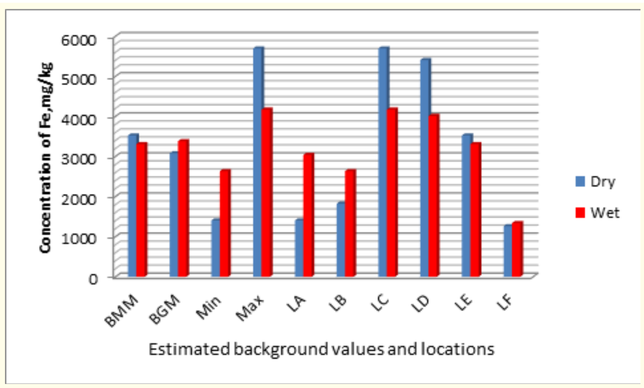

Figure 4: *Environmental background and distribution of iron in cassava mill effluent contaminated soil.*

Lead

Lead concentration for spatial distribution ranged from 1.44 - 9.42mg/kg. There was significant difference (P < 0.05) among the various locations. The control (CF) and other locations LC and LD were significantly lesser compared to other locations (Table 1). The seasonal distribution ranged from 1.30 - 5.98 mg/kg (Table 2). There was no significant variation (P > 0.05) between two season (viz November, January and March - wet season, and May, July and September - dry season) of study. Furthermore, significant difference (P < 0.05) also exist in the wet season between May and September (Table 2). Significant variation (P < 0.05) exists in the interaction of seasons and spatial distribution (Table 3). Lead showed positive significant relationship with cadmium (r = 0.232, P < 0.05), cobalt (r = 0.402, P < 0.01) and chromium (r = 0.401, p < 0.01) (Table 4). On the overall, LB in both seasons (wet and dry season) had the highest lead concentration (Figure 5). The significant difference (P < 0.05) among the various locations could be due to degree of anthropogenic activities and geological formation of the soil. Based on season, lower concentration in the wet season could be due to runoff resulting from dilution after precipitation. The concentration of lead in the contaminated soil in this study is apparently higher than the values reported by other authors. For instance, in soil receiving cassava mill effluents, lead values of 0.108 mg/kg and 0.097 mg/kg have been reported at the edge of the discharge point and control respectively [20], 0.106 - 0.636 mg/kg and 0.009 - 0.042 mg/kg at contaminated soil and control respectively [25]. Furthermore, higher lead concentration in this present study could be due to anthropogenic activities in the area as well as geological formation. High concentration of lead in soil could lower soil fertility [21].

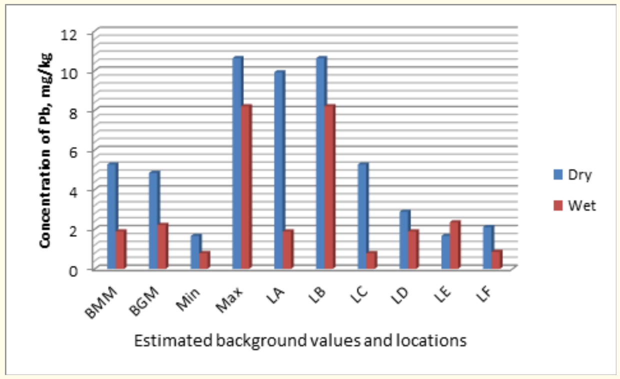

Figure 5: *Environmental background and distribution of lead in cassava mill effluents contaminated soil.*

Cadmium

Cadmium concentration for spatial distribution ranged from < 0.001 - 0.24 mg/kg. There was significant difference ($P < 0.05$) among the various locations. Significant variation is mostly from LB and LE (Table 1). The seasonal distribution ranged from < 0.001 - 0.18 mg/kg (Table 2). Typically, there was significant variation ($P < 0.05$) between both seasons (viz November, January and March - wet season and May, July and September - dry season) of study. The concentration of cadmium in the wet season was significantly higher (Table 2). Significant variation ($P < 0.05$) exists in the interaction of seasons and spatial distribution (Table 3). Cadmium showed negative significant relationship with cobalt ($r = - 0.366$, $P < 0.05$) (Table 4). On the overall, the cadmium concentration in wet season was highest especially in LB and LE (Figure 6). The higher concentration in the wet season could be due to runoff resulting rainfall. The significant difference ($P < 0.05$) among the various locations could be associated to level of human activities in each of the mills. The concentration of cadmium in the contaminated soil in this study had some similarity with previous works. For instance, in soil receiving cassava mill effluents, cadmium values of 0.012 mg/kg and 0.012 mg/kg at the edge of the discharge point and control respectively [20], 0.006 - 0.04 mg/kg and 0.002 mg/kg have been reported at discharge point and control respectively [24]. The similarity of cadmium level (low concentration) in this present study compared to other work could be due to the fact that cadmium is highly toxic non-essential element. As such, their concentration in the soil is by contamination resulting from anthropogenic activities.

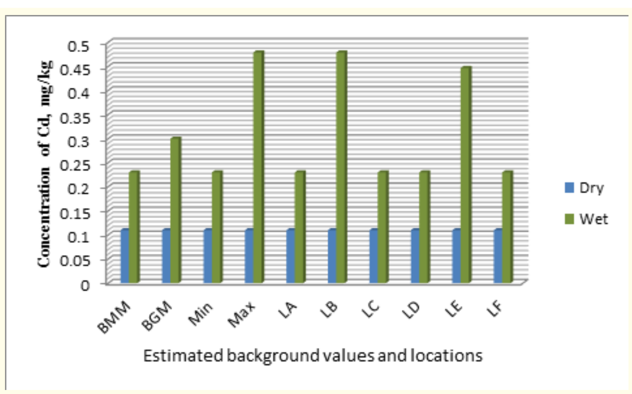

Figure 6: *Environmental background and distribution of cadmium in cassava mill effluent contaminated soil.*

Chromium

Chromium concentration for spatial distribution ranged from 0.19 - 3.41 mg/kg. There was significant difference (P < 0.05) among the various locations. No significant variation (P > 0.05) between LB and LF, LC and LD, LA and LE (Table 1). The seasonal distribution ranged from 1.39 - 1.90 mg/kg (Table 2). Typically, there was significant variation (P < 0.05) between both seasons (viz November, January and March - wet season and May, July and September - dry season) of study (Table 2). Significant variation (P < 0.05) exists in the interaction of seasons and spatial distribution (Table 3). On the overall, LE in both seasons (wet and dry) had the highest concentration of chromium (Figure 7). The significant difference (P < 0.05) that occurred in the spatial distribution could be due to variation in human activities in each of the mills. The lower concentration of LF (control) suggests the effect of chromium due to cassava processing apart from LB which had same value with LF. Lack of significant variation based on seasons could be due to similarity in human activities all year round. The concentration of chromium in the contaminated soil in this study is apparently higher than the values reported by other authors. For instance, in soil receiving cassava mill effluents, chromium values of 0.03 mg/kg and 0.01 mg/kg have been reported at the edge of the discharge point and control respectively [20], 0.002 - 0.022 mg/kg and 0.016 mg/kg at discharge point and control respectively [24]. Furthermore, the difference that exists between the findings of this study and previous works could be associated to geology of the soil.

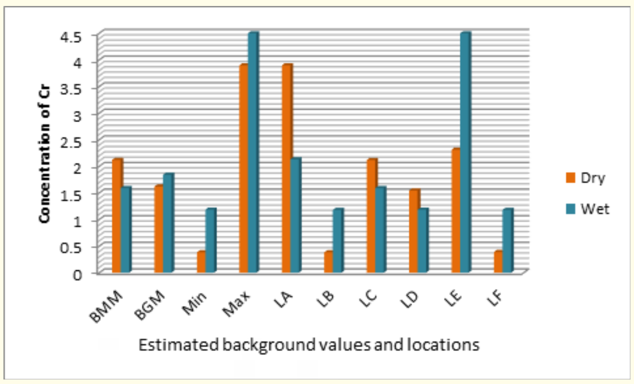

Figure 7: *Environmental background and distribution of Chromium in cassava mill effluent contaminated soil.*

Nickel

Nickel level for spatial distribution ranged from 1.57 - 3.76 mg/kg. There was significant difference (P < 0.05) among the various locations. No significant variation (P > 0.05) between LE and LF, LA, LB and LF, LA, LB and LD (Table 1). The seasonal distribution ranged from 1.88 - 3.06 mg/kg (Table 2). Typically, there was significant variation (P < 0.05) between both seasons of study (Table 2). Significant variation (P < 0.05) exists in the interaction of seasons and spatial distribution (Table 3). Nickel showed positive significant relationship with cobalt (r = 0.204, P < 0.01) (Table 4). On the overall, LC and LD had highest nickel concentration in wet and dry season respectively (Figure 8). The significant difference (P < 0.05) that occurred in the spatial distribution could be due variation in human activities in the mills. Runoff resulting from rainfall may have accounted for the seasonal influence.

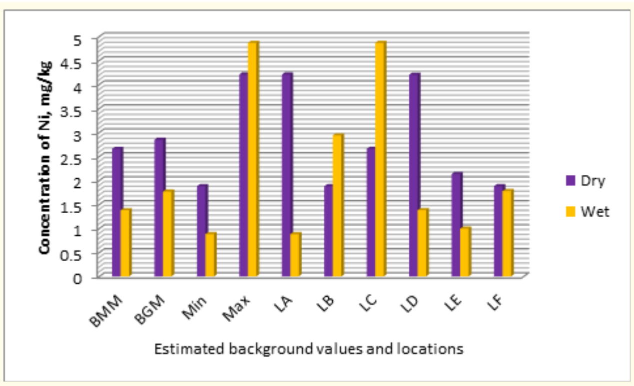

Figure 8: *Environmental background and distribution of Nickel in cassava mill effluents contaminated soil.*

Cobalt

In the spatial distribution cobalt concentration ranged from 1.72 - 5.64 mg/kg. There was no significant difference (P > 0.05) among the various locations apart from LA (Table 1). Furthermore, seasonal distribution of cobalt ranged from < 0.001 - 9.71 mg/kg (Table 2). There was significant variation (P < 0.05) between both seasons (viz November, January and March - wet season and May, July and September - dry season) of study (Table 2). Significant variation (P < 0.05) exists in the interaction of seasons and spatial distribution (Table 3). The concentration of nickel in the dry season was significantly higher compared to wet season. In addition, the overall concentration based on wet and dry season showed that dry season samples were far higher in all the location compared to the wet season (Figure 9). The significant variation (P < 0.05) that exist in the spatial distribution could be due difference in anthropogenic activities in each of the mill (dewatering location). Lower concentration of cobalt during the wet season could be due to dilution effect resulting from runoff after precipitation.

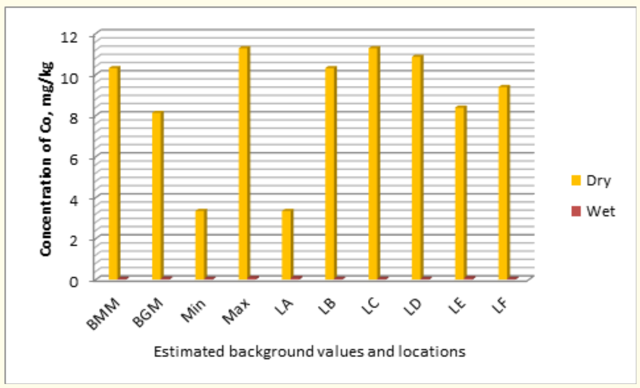

Figure 9: *Environmental background and distribution of cobalt in cassava mill effluent contaminated soil.*

Based on Table 4, the high significant relationship between copper and other metals under study apart from zinc and manganese suggests that most of the heavy metals in the soil samples are coming from similar origin. According to Rodriguez., *et al*. [44], Hirschfeld [45], Jiang., *et al*. [46], heavy metals originating from similar source tend to have significant relationship. Jiang., *et al*. [46] further reported that positive relationship among heavy metals suggest common sources, mutual dependence and identical behavior during transport, while negative correlations is an indication of difference in sources and mutually independent.

Cluster analysis was calculated according to seasons and is presented in figure 10 and 11 for dry and wet season respectively. This was carried out to divide the heavy metal pollutant and to determine their possible sources [47]. The close distance cluster is an indication of significant relationship, while distance cluster showed the degree of association among the heavy metals [47,48]. The level of all heavy metals under study has been reported to be influenced by anthropogenic activities in the environment [43].

The occurrence of these heavy metals in the environment could be from anthropogenic sources such as cassava mill effluents. Furthermore, cassava mill effluents is also known to contain heavy metals such as cadmium, copper, manganese, lead, zinc, iron, chromium [30,49-51] leading to increased iron, cadmium, copper, manganese, chromium, chromium, zinc and lead concentration in the soil receiving the effluents [20,21,24,25].

Typically, soil contaminated with cassava mill effluents lead to alteration in the soil parameters [23]. The finding of this study showed that there is some level of heavy metals (viz: copper, zinc, manganese, iron, lead, cadmium, chromium and nickel) enrichment. This trend is comparable to the findings of Igbinosa and Igiehon [21], who reported cassava mill effluent increases the concentration of heavy metals (zinc, manganese and copper) in the soil. These tend to be affected by seasons probably due to dilution effects resulting from rainfall in wet season. Furthermore, the occurrence of heavy metals in cassava mill effluent contaminated soil could also be due to wear and tear resulting different machine part used for grating the cassava as well as emission from the exhaust of the engine [21,24].

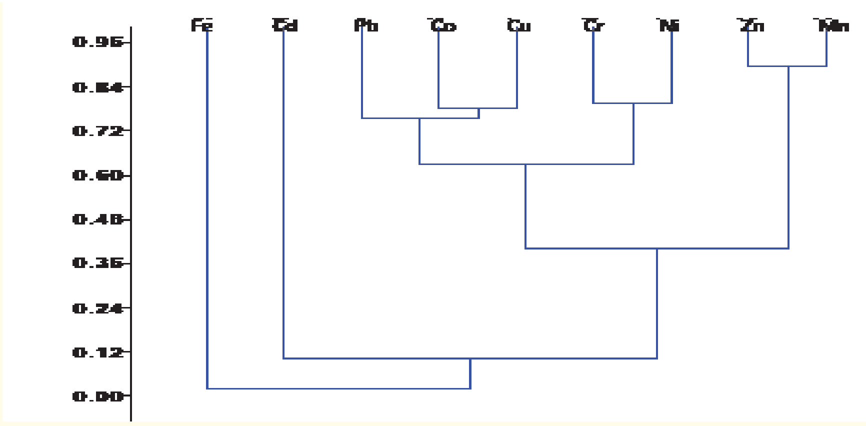

Figure 10: *Dendrograms of produced cluster analysis of heavy metal in soil receiving cassava mill effluents during dry season.*

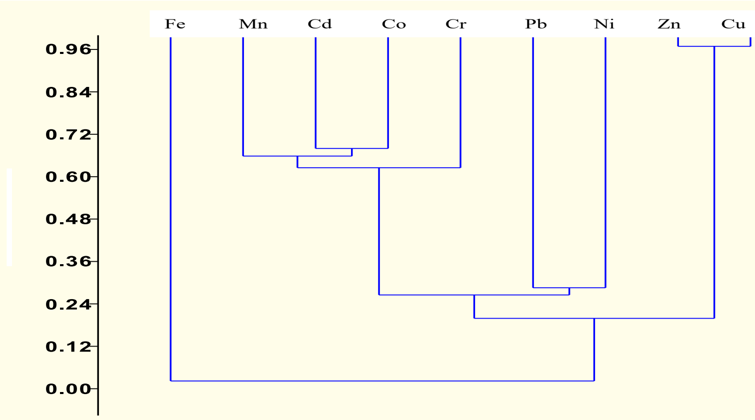

Figure 11: *Dendrograms of produced cluster analysis of heavy metal in soil receiving cassava mill effluents during wet season.*

Conclusion

Nigeria is the world leading producer of cassava. During processing of cassava tuber into gari, larges volume of effluents is discharged into the and are discharged soil which percolated and/ or drains to nearby pit, drainage system or surface water. Cassava mill effluents are toxic to the environment and some of its associated biota. This study evaluated the concentration of some selected heavy metals in cassava mill effluents contaminated soil in a rural community in the Niger Delta. Results showed that heavy metals such as chromium, manganese, iron, zinc, cobalt, copper, nickel and mostly found in cassava mill effluent contaminated soil and to lesser extent cadmium and lead. Correlation analysis suggests that most of the heavy metals are from similar origin. The study also showed seasons and prevailing human activities affect the distribution of heavy metals in cassava mill effluent contaminated soil.

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