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MULTIVARIATE ANALYSIS OF THE IMPACT OF ORGANIC AND INORGANIC MANURES ON THE TRACE METALS LOAD OF AGRICULTURAL SOIL IN SOUTHERN NIGERIA

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ABSTRACT

Organic and inorganic manures used by farmers for the improvement of plant yield have the potential of elevating the levels of metals in soil significantly. This study investigated the impact of the applications of inorganic fertilizers and untreated wastes from fish pond, livestock farms and dumpsites (organic manure) on the level of trace metal accumulation in agricultural soils in Southern Nigeria. Analysis of the contamination Factor (CF) and Degree of Contamination (C_{deg}) indicated high level of soil contamination by the metals determined. The mean contamination factor for trace metals determined followed the order: As > Ni > Cu > Fe > Cd > Pb > Zn. The results also showed that the Cdeg value for all the amended locations was in the Very High Degree of contamination class. The Cdeg in amended soils varied between 92.10 in Uruan and 128.33 in Ibeno. The Principal Component Analysis (PCA) revealed three major factors responsible for the availability of trace metals in the amended soils. These factors have Eigen values > 1 with a significant 95.06% of the total variance. Hierarchical cluster Analysis (HCA) of sources showed that the use of organic and inorganic manures contributed more to the trace metals level in agricultural soils. These findings have shown that the accumulation of toxic metals; As, Cd, Pb, Zn, Cu, and Ni in agricultural soils could be attributed to the applications of untreated organic and inorganic manures as supplements however; geogenic factor was the major source of Fe in the amended soil. Hence, the use of untreated wastes on agricultural farms to improve crop yield should be discouraged while the application of inorganic fertilizers should be minimized.

INTRODUCTION

Metals are natural components of the soil but mostly below their recommended limits. Metals such as Cu, Fe, Zn, Mn, and Co at very low concentrations are known to play essential roles in biological metabolism but at higher concentrations they become toxic to biological systems (Nguyen *et al*., 2005). Studies have shown that the application of untreated wastes from animal farms, inorganic fertilizers, untreated wastewater, and sewage to soil could result in buildup of metals (Orisakwe *et al*., 2017). Inorganic fertilizers have the potential of contaminating the soil environment with Cd, Hg, and Pb significantly. However; these metals have no known physiological function but are very toxic even at very low concentrations. Composts, municipal sewage sludge and animal wastes from poultry, cattle, and pig farms are commonly applied to agricultural farms as fertilizers, however studies have shown their application to soil may eventually results in accumulation of metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Tl, and Sb (Basta *et al*., 2005). Wastes from dumpsites are known to contain high levels of Fe, Pb, Cr, As, Zn, Cd, Cu, and Hg hence may contaminate the soil when applied as a source of manure (USEPA, 1996). A related study has shown that wastes from fish ponds contain very high levels of Mn, Fe, Zn, Cr, Ni, Pb, and Cd which can contaminate the soil when applied as manures (Onuoha, 2017). Plants have the potential to accumulate very high levels of metals from contaminated soil (Al-Jassir *et al*., 2005). Bioaccumulation and biomagnification of metals along the food chain reduces crop yield and quality and may result in significant negative impact on human and economic losses to the society. Thus, it necessary to assess agricultural farms exposed to untreated wastes and inorganic fertilizers to know the extent of metal accumulation due to the application.

Multivariate statistical approach involving correlation analysis (CA), principal component analysis (PCA), agglomerative hierarchical cluster analysis (AHCA) and multivariate analysis of co-variance (MANCOVA) have previously been used to evaluate interrelationships between large numbers of variables. These approaches have earlier been reported as successful and therefore reliable in studies on fertility parameters of humic soil cultivated with coffee, trace metal contamination of sediments (Benson *et al.,* 2014), soil fertility parameters around nuclear power plant, determination of soil pedo-environmental indicators and soil fertility relationships for predicting environmental persistence of pollutants. It has also been reported that multivariate analysis approach identifies the impact of natural and anthropogenic factors on environmental problems (Samara *et al*., 1994). This research utilized the principal component analysis and hierarchical cluster analysis for the assessment of pollution status of the studied soils. The study was undertaken to examine effectively the impact of untreated waste materials and inorganic fertilizers on the accumulation of trace metals in the study soils.

MATERIALS AND METHOD

Study Area

Cultivated farms located in Ibeno, Itu, Nsit Ubium, Oron, Uruan, and Uyo LGAs of Akwa Ibom State, Nigeria were investigated during dry season months of December 2017 and February 2018. Akwa Ibom State is located in South South region of Nigeria (Fig. 1). The study area lies between latitude 4°32′N and 5°33′N) and longitudes 7°25′E and 8°25′E.

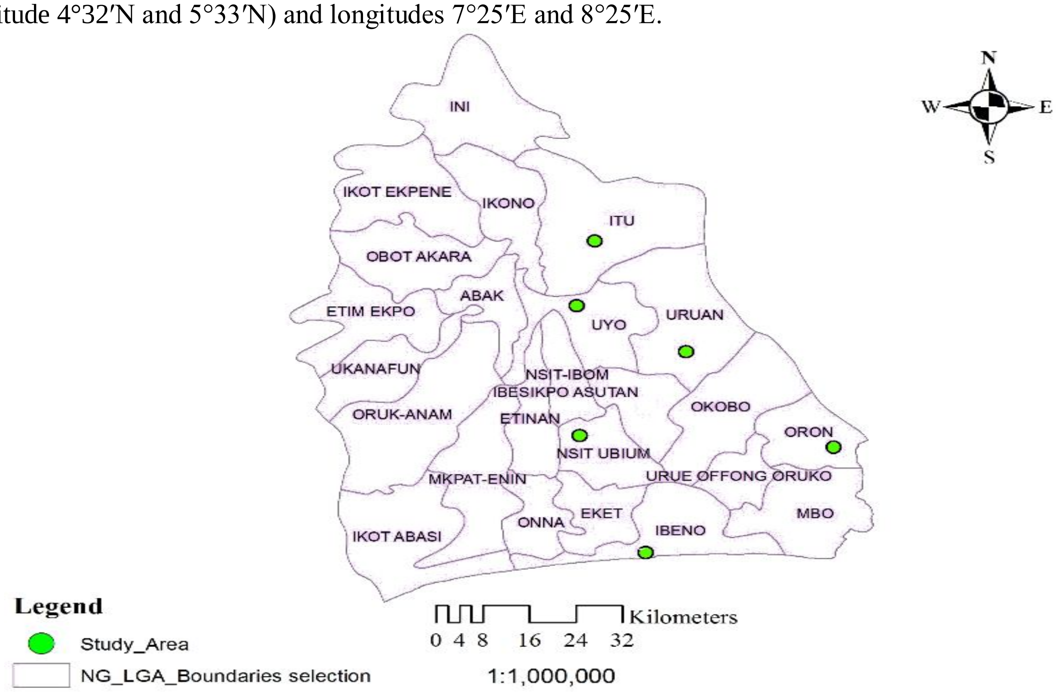

Figure 1: Map of Akwa Ibom State showing the sample locations.

Using soil auger top soil (0 -15cm) samples of farm soils amended with livestock farms, fish ponds, abattoirs, dumpsites organic and inorganic fertilizers were obtained from the farms. Un-amended (Control) soil samples were also obtained from farm soil within the study area. At each location, soil samples were collected from three different points into pre-cleaned polyethylene bags, the samples were air-dried for three days, ground, sieved and later homogenized to into composite samples. A total of eighteen composite samples plus the control sample were analyzed.

Elemental Analysis of Soil Samples

Precisely 0.5 g the samples were separately mixed with Aqua Regia and digested on a hot plate following standard procedures. The levels of As, Cd, Cu, Fe, Ni, Pb, and Zn were determined in the filtrates obtained using Agilent 710 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

Determination Pollution Status of trace metals in soils

The Contamination Factor (CF) and Degree of Contamination (C_{deg}) models were employed to assess the extent of soil contamination by trace metals (Mmolawa *et al*., 2011).

Contamination Factor:

Contamination factor of the trace metals in the investigated soils was calculated using equation 1.

$$CF = \frac{Cm}{Bm} \quad (1)$$

Where: CF = Contamination factor; Cm = Concentration of the metal in studied sample; Bm = Background concentration of the metal obtained in the study (Control). According to Pekey *et al.* (2004) contamination factor is classified into four classes namely: CF < 1 = low contamination; $1 \leq CF \leq 3$, moderate contamination; $3 \leq CF \leq 6$, considerable contamination, and CF > 6 very high contamination.

Degree of Contamination:

Degree of Contamination (C_{deg}) signifies the summation of all the contamination factors of trace metals for a particular location.

$$Cdeg = \Sigma\left(\frac{Cm}{Bm}\right) \quad (2)$$

Where: Cm = Concentration of the metal in the studied soil; Bm = Background concentration of the metal obtained in the Control. The four classes of Cdeg are: Cdeg < 8 = low degree of contamination, 8 < Cdeg < 16 = moderate degree of contamination, 16 < Cdeg < 32 = considerable degree of contamination and 32 < Cdeg = very high degree of contamination (Pekey *et al*., 2004).

Statistical Analysis

Data was first subjected to Pearson bivariate correlation to establish data appropriateness for multivariate statistics. Over-correlated data were removed and principal component analysis (PCA) performed on remaining data. Principal Component Analysis and Cluster Analysis of trace metals determined in soil were done using IBM SPSS statistics 20.

RESULTS AND DISCUSSION

Trace metals Load and Distribution in Test Soils:

Results for the distribution of trace metals (Table 1) obtained exhibited a high degree of variability among the metals and between sample locations. Levels of As in test soils varied between 0.714 to 1.279 $mgkg^{-1}$with a mean of 1.014±0.191 $mgkg^{-1}$. The range recorded is higher than 0.55 – 0.66 $mgkg^{-1}$ obtained by Opaluwa *et al.* (2012) but lower than 1.15 – 3.14µg/g reported by Yahaya *et al.* (2010) in contaminated soils. As level was remarkably high in samples from Ibeno. The mean (1.014±0.191 $mgkg^{-1}$) obtained was higher than 0.013 $mgkg^{-1}$ recorded for the un-amended (Control) soil. This may be ascribed to the activities of petroleum industry within the area and the application of livestock wastes on the soil (Orisakwe *et al.*, 2017). The applications of inorganic/organic manures to the studied soils may also have contributed significantly to the quantity of As in agricultural soil. Nevertheless, the value is lower than the 20.00 mg/kg limit recommended for unpolluted soil by FAO/WHO (2001). Study has shown that As may not be regarded as a pollutant in the amended soils despite it's highly toxic potential. However, its availability should be closely monitored to avoid bioaccumulation and the associated implications along the food chain.

The range and mean of 1.556 – 2.817mgkg^{-1}and 2.220±0.516 mgkg^{-1}respectively were recorded for Cd in amended soils. The range is higher than 1.06 – 1.35 mgkg^{-1} reported by Ebong *et al* (2018) for soil but lower than 17.22–34.81mg kg^{-1} reported by Paul *et al*. (2015). The highest level of Cd was obtained in soil from Uruan.

Table 1: Total concentration (mgkg^{-1}) of Trace metals in soil

LOCATION	As	Cd	Cu	Fe	Ni	Pb	Zn
IBB	1.279	2.368	43.563	2146.623	29.572	16.640	18.351
ITT	1.085	1.724	46.742	2671.158	51.671	19.846	25.756
NSU	1.104	1.556	44.384	2361.472	37.285	16.903	20.145
ORN	0.957	2.131	47.530	2395.415	34.216	21.539	23.472
URN	0.714	2.817	49.743	2234.207	41.827	26.352	20.116
UYY	0.945	2.726	54.281	2853.062	40.073	18.604	26.250
MIN	0.714	1.556	43.563	2146.623	29.572	16.640	18.351
MAX	1.279	2.817	54.281	2853.062	51.671	26.352	26.250
MEAN	1.014	2.220	47.707	2443.656	39.107	19.981	22.348
SD	0.191	0.516	3.913	268.533	7.541	3.621	3.284
CONTROL	0.013	0.558	6.572	361.350	3.632	5.836	8.583

Key:
IBB: Ibeno; ITT: Itu; NSU: Nsit Ubium; ORN: Oron; URN: Uruan; UYY: Uyo;
MIN = Minimum; MAX = Maximum; SD = Standard Deviation

The elevated level of Cd in Uruan could be attributed to the application inorganic (NPK) fertilizer (Benson *et al.*, 2014). The mean level of Cd (2.220±0.516 mgkg^{-1}) recorded was higher than 0.558mgkg^{-1}recorded for control site. Hence, the inorganic and organic substances applied to the amended soils might have contributed to the Cd level of soil in the area. Though the mean recorded was lower than 3.00mgkg^{-1} limit recommended by FAO/WHO (2001) for unpolluted soil, the application of inorganic and organic substances should be controlled to avoid Cd toxicity and the associated health problems on those exposed to it (Onuoha, 2017). Presently, the Cd has not reached the nuisance level in the studied soils but as a highly toxic metal its availability should be monitored closely. Results also indicate that Cu levels in soils varied between 43.563 and 54.281mgkg^{-1}with a mean of 47.707±3.913mgkg^{-1}. This range is lower than 8.41–148.73mgkg^{-1}reported by Song *et al.* (2015) but higher than 41.84 – 46.23mgkg^{-1}by Ebong *et al.* (2018) in contaminated soils. The highest Cu level was recorded for soils obtained from Uyo and this could be attributed to the impact of untreated wastes from dumpsites and fish ponds on the soil quality. The mean, 47.707±3.913mgkg^{-1} reported for Cu was higher than 6.572mgkg^{-1}recorded for the Control. The applications of untreated wastes materials and inorganic fertilizers to soils might have contributed significant amounts of Cu to the studied soil (Basta *et al.*, 2005). Nevertheless, the mean obtained was lower than 100.00mgkg^{-1}recommended for unpolluted soil by FAO/WHO (2001). Though at this level, Cu could be considered a pollutant, however because of its essential status, the negative impact may not be pronounced but bioaccumulation over time may occur and should be avoided.

The treated soils were rich in Fe levels. The levels ranged between 2146.623mgkg^{-1}in Ibeno and 2853.062mgkg^{-1}obtained in Uyo. This range is lower than 14,821.87 – 69,641.05 mgkg^{-1} obtained by Oni and Hassan (2016) but higher than 46.70 – 1340.00 mgkg^{-1}reported by Sha‟Atoa *et al.* (2012) in contaminated soils elsewhere. The high level of Fe in Uyo soil could be attributed to the impact of untreated wastes from dumpsite and fish ponds (Basta *et al.*, 2005). The mean level of Fe (2443.6 ±2.68 mgkg^{-1}) obtained is higher than the level (361.350mgkg^{-1}) recorded for the Control. Consequently, the untreated waste products and inorganic fertilizers applied to the soils might have impacted on the Fe content significantly. Though, Fe is naturally very high in soils within Nigeria, the mean level obtained in this study is higher than 425.00mgkg^{-1}stipulated for unpolluted soil by FAO/WHO (2001). Thus, the level of Fe obtained at the various locations might lead to soil toxicity and the attendant implications. However, as an essential metal it may not have significant negative impact along the food chain as it is commonly used for enzymatic activities in biological cells (Nguyen *et al.*, 2005).

Range and mean values of 29.572 – 51.671mgkg^{-1}and 39.107±7.541mgkg^{-1} respectively were recorded for Ni in amended soils. The range obtained is higher than 5.15–12.10 μgg^{-1}reported by Umoren *et al*. (2007) but lower than 5.00 – 140.50 mgkg^{-1} reported by Ajiboso *et al*. (2003) in contaminated soils. The highest level of Ni was at Itu and it may be ascribed to the application of untreated abattoir wastes on the environment (Orisakwe *et al*., 2017). The mean value of 39.107±7.541mgkg^{-1} recorded for Ni in amended soils was higher than 3.632mgkg^{-1} obtained from the Control. This is an indication of anthropogenic addition of Ni by untreated wastes and inorganic fertilizers applied to the soils. However, the mean is less than 50.00mgkg^{-1} limit recommended by FAO/WHO (2001) for unpolluted soil. This implies that the levels of Ni in studied soils may have little or no impact along the food chain. Nevertheless, the application of untreated wastes on soil should be discouraged to avoid the bioaccumulation of toxic levels and the associated problems over time.

The levels of Pb in amended soils varied between 16.640 and 26.352mgkg^{-1}with a mean of 19.981±3.621mgkg^{-1}. This range is lower than 259.1 – 735.7µgg^{-1} reported by Udousoro *et al.* (2010) but higher than 0.24 – 2.15 mgkg^{-}1 obtained by Amadi and Nwankwoala (2013) in contaminated soils. The highest level of Pb was recorded in Uruan and may be associated with the application of inorganic fertilizers in the area (Benson *et al*., 2014). The mean value of 19.981±3.621mgkg^{-1} recorded for amended soils was higher than the level (5.835mgkg^{-1}) obtained from the Control sample; an indication of anthropogenic inputs. Though, the mean is below recommended limit of 50.00mgkg^{-1}for unpolluted soil (FAO/WHO, 2001). Nonetheless, the artificial addition of Pb to the environment should be discouraged considering the high toxicity Pb. On the other hand, the range and mean of Zn recorded for the amended soils were 18.351–26.250mgkg^{-1}and 22.348±3.284mgkg^{-1} respectively. The range obtained is lower than 156.32 – 92.50 μgg–^{1} reported by Umoren *et al*. (2007) but higher than 9.70 - 18.50µgg^{-1} obtained by Idris *et al*. (2015) in contaminated soils. The highest Zn level was obtained in samples from Uyo and this may be attributed to the impact of untreated waste materials from dumpsite and fish pond used as amendments. The mean value of 22.348±3.284mgkg^{-1} detected in the amended soils was relatively higher than 8.583mgkg^{-1} recorded for Control soil. However, it is much lower than 300.00mgkg^{-1}limit recommended by FAO/WHO (2001) for unpolluted soil. The findings have shown that the level of Zn obtained may not impact negatively on the food chain but useful for the proper functioning of biological cells. Nevertheless, the application of untreated waste products on soil should be minimized to forestall Zn toxicity and its attendants' effects along the food chain.

Pollution Indices of Trace Metals and Degree of Contamination of Study Locations:
Results for the degree of pollution of trace metals are shown in Table 2 while the degree of contamination of the different locations studied are indicated in Figure 2.

Contamination factors (CF) of trace metals in studied soils showed that the CF values for As varied between 54.92 and 98.39 thus; As belongs to the very high contamination class. Contamination factors for Cd ranged from 2.79 to 5.05 and hence belongs to the considerable contamination class. The results also indicate that contamination factors for Cu, Fe, and Ni are in the very high contamination class while, Pb and Zn belong to the considerable contamination class. The mean contamination factors for trace metals determined is in the order: As > Ni > Cu > Fe > Cd > Pb > Zn. Consequently, As was the metal with highest of level of contamination while Zn had the least potential to impact the fertility of the soil.

Table 2: Contamination factor of trace metals in studied soils.

LOCATION	As	Cd	Cu	Fe	Ni	Pb	Zn
IBB	98.39	4.24	6.63	5.94	8.14	2.85	2.14
ITT	83.46	3.09	7.11	7.39	14.23	3.40	3.00
NSU	84.92	2.79	6.75	6.54	10.27	2.90	2.35
ORN	73.62	3.82	7.23	6.63	9.42	3.69	2.74
URN	54.92	5.05	7.57	6.18	11.52	4.52	2.34
UYY	72.69	4.89	8.26	7.90	11.03	3.19	3.06
MIN	54.92	2.79	6.63	5.94	8.14	2.85	2.14
MAX	98.39	5.05	8.26	7.90	14.23	4.52	3.06
MEAN	78.00	3.98	7.26	6.76	10.77	3.43	2.61

Degree of contamination of the studied soils varied between the trace metals and study locations (Fig, 2). The Cdeg in amended soils varied between 92.10 in Uruan and 128.33 in Ibeno. The result has shown that the Cdeg in all the studied locations was high and belong to the very high degree of contamination class (Pekey *et al*.,2004)). Consequently, all the studied locations were heavily contaminated by the trace metals determined.

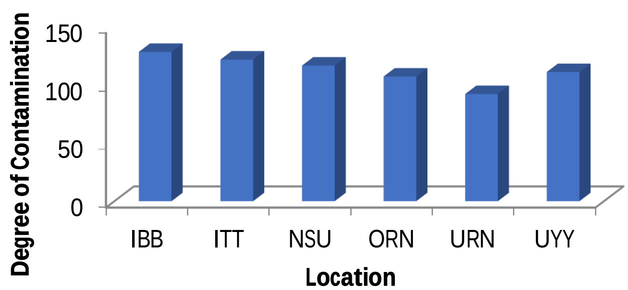

Fig.2: Degree of contamination of the studied locations.

Source and Affinity of Metals in Soils

Multivariate analysis using the Principal Component Analysis (PCA) was used to identify the factors responsible for the accumulation of trace metals determined in treated soils while the Hierarchical Cluster Analysis (HCA) (Wu and Kuo, 2012) was employed to establish the relationships between the metals and study locations.

The PCA in Table 3 indicates three major factors responsible for the availability of trace metals in the amended soils. These factors have Eigen values greater than one with a significant 95.06% of the total variance (Table 3). Factor One contributed 48.75% of the total variance with significant positive loadings on Cu, Zn, Fe, Ni, Pb, and Cd but a strong negative loading on As (Table 4). This represents the negative impact of untreated wastes on the quality of the soils. The second factor (Factor Two) contributed 31.32% of the total variance with strong positive loading on As, Zn, and Fe but significant negative loadings on Pb and Cd (Table 3). This represents both the negative impact of natural and anthropogenic inputs on the soil quality. The third factor (Factor Three) contributed 14.99% of the total variance with a significant negative loading on Ni and a strong positive loading on Cd (Table 3). This represents the negative impact of inorganic fertilizers on the quality of the amended soils. Similar observations have earlier been reported Mugoša *et al*., (2016).

Table 3: Total variance explained for trace metals determined in the studied locations.

Component	Initial Eigen values			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.412	48.749	48.749	3.412	48.749	48.749	2.843	40.617	40.617
2	2.192	31.316	80.065	2.192	31.316	80.065	2.203	31.478	72.095
3	1.050	14.993	95.058	1.050	14.993	95.058	1.607	22.963	95.058
4	.227	3.249	98.307						
5	.118	1.693	100.000						
6	1.034E-016	1.478E-015	100.000						
7	-9.154E-017	-1.308E-015	100.000						

Table 4. Matrix of the major principal components.

	Component 1	Component 2	Component 3
Cu	.914	-.075	.382
As	-.765	.548	.225
Zn	.749	.609	.072
Fe	.699	.679	.216
Ni	.625	.406	-.590
Pb	.575	-.671	-.438
Cd	.468	-.663	.511

The pair-wise associations among trace metals in soils are illustrated in Figure 3. The figure indicates two major clusters namely: The one linking As, Cd, Pb, Zn, Cu, and Ni; the second cluster links Fe alone. This shows the common source and similarities among the metals in cluster one (Yang *et al.*, 2011). The possible source common to these metals could be the untreated wastes and inorganic fertilizers applied to the soils. The HCA has also shown that the major source of Fe in soils is different from others (untreated wastes and inorganic fertilizers) and possibly the geogenic factor.

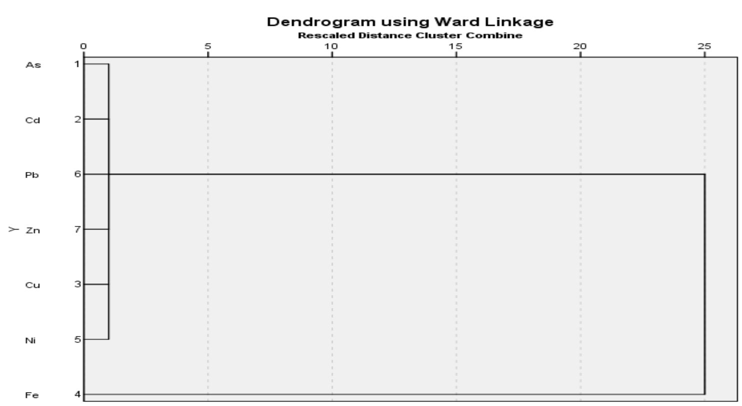

Fig. 3: Hierarchical clusters formed among trace metals determined.

The site to site relationships shown in Figure 4 indicate three major clusters namely: Cluster one linking Nsit Ubium and Oron; the second cluster links Ibeno and Uruan while the third cluster connects Itu and Uyo. The figure reveals the similarities in the type of metal contaminants available at the locations in each cluster.

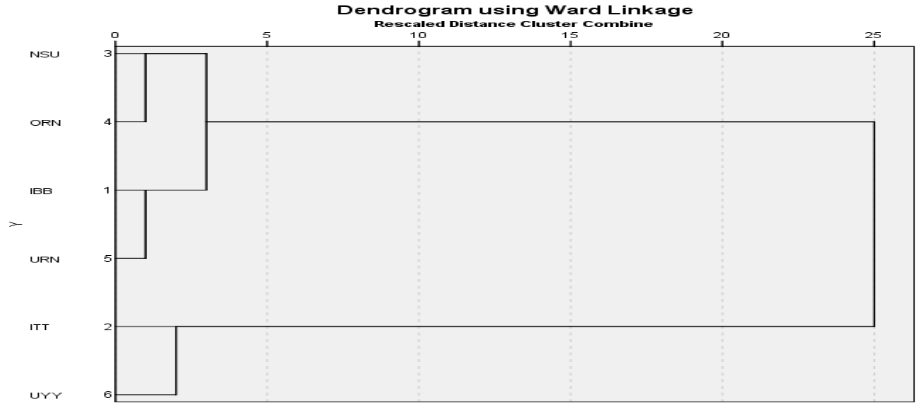

Fig. 4: Hierarchical clusters formed among studied locations.

CONCLUSION AND RECOMMENDATION

The results of this research have revealed the negative impact of untreated wastes and inorganic fertilizers used for the improvement of plant yield on the quality of soils in the Niger Delta region of Nigeria. The accumulation of toxic metals; As, Cd, Pb, Zn, Cu, and Ni in agricultural soils has been traced mainly to the use of untreated wastes and inorganic fertilizers as supplements although geogenic factor is the main determinant of Fe in the amended soil. The three factors identified by Principal Component Analysis are associated with this common agricultural practice. A practice if not properly managed may result in a devastating condition along the food chain over time. Hence, the use of untreated wastes on agricultural farms should be discouraged and the application of inorganic fertilizers should be minimized.

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