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Application of Chemometric Analysis on Agricultural Soil in Maitumbi, Minna for Heavy Metals Source Identification

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Abstract
Environmental pollution with toxic substances in most developing nations in recent time is of great concern because of its negative effect on soil ecosystems and its threat to food security. This study aimed at assessing the sources of heavy metals pollution in agricultural soils using chemometric analysis. Soil samples were collected and analysed for Pb, Cu, Cd, Fe, Zn, Cr, Mn, & Ni contents using Atomic Absorption Spectrophotometer and chemometrics analysis was applied on the results obtained. The mean concentrations of Pb, Cu, Cd, Fe, Zn, Mn, & Ni in the soils were 2.18, 11.73, 5.70, 26.89, 3.50, 2.19 and 1.58 mg/kg respectively. The Varimax Factors (VFs) generated showed that the soil pollution could be attributed to three sources. The first varimax factor with an eigenvalue of 2.312 accounts for 33.0% of the total variance and has high negative loading on Zn (-0.601), Mn (0.609) and Fe (0.626). This factor suggested pharmaceutical effluent as a probable source of these heavy metals in the soil. The second VF has an eigenvalue of 1.862 which explains 26.6% of the total variance and has high positive loading on Pb (0.666) and Cd (0.743). The loadings on this component indicated urban runoff as the likely source of these metals in soil. The third principal component has an eigenvalue of 1.247 which accounts for 17.8% of the total variance and has high positive loading on Cu (0.754). The loading on this component attributed source of the metal to agricultural practice. The study showed that chemometrics is a good tool for pollution source identification, which could give a guide on amelioration scheme to be adopted.

Keywords: Pollution sources, Pharmaceutical effluent, heavy metals, Minna

1.0 INTRODUCTION

Environmental pollution with toxic substances in most developing nations in recent time is of great concern because of its negative effect on soil ecosystems and its threat to food security (Kamaruddin et al., 2013). Though, some of the pollutants could be due to natural geochemistry, anthropogenic sources are to a large extent, major contributors. Of all the pollutants, focus is mostly on heavy metals in area of intense industry and agriculture (Bhargava *et al.*, 2012). This is because while some of these metals (Ni, Cd and Cu) are relevant in industrial processes, some others (Pb) are generated during the process. The issue of these metals becomes topical because of their toxicity, persistence, bioaccumulation and resultant uptake by plant (Aruleba and Ajayi, 2012).

Agriculture, which is supposed to be the backbone of the economy of any country blessed with fertile soil, has been adversely affected by upsurge in the indiscriminate release of these metals into lands and fresh water systems. Consequently, a number of diseases and disorders have been associated with the consumption of these metals which include reduction in mental and central nervous function, lowering energy levels, and causing damage to blood composition, lungs, kidneys, liver, and other vital organs in the body (Adeoye et al., 2015). Since a diverse natural and anthropogenic sources (which include parent materials, forest fires, vehicle exhaust particles, weathered street surface particles, industrial power plants emission, coal combustion, auto repair shops and chemical plants) has been noted for these metals, identification of a probable definite source contributing to agricultural soil pollution of a particular site will be helpful in mitigating their effects on soil, crop and ultimately man who consumed them through food chain (Ahaneku and Sadiq, 2014).

Chemometric is a useful mathematical and statistical tool for extracting information from large amounts of data, containing multiple parameters measured in many samples collected at different points and periods, whose interpretation is far from simple (Yang et al., 2012; Felipe-Sotelo, 2007). The analysis helps to extract meaningful information from multivariate data arrays, finding relationships between groups of variables and identifying the main pollution sources affecting the sampling points (Felipe-Sotelo, 2007). Some of the chemometrics analysis includes Pearson's Correlation Coefficient Analysis, Principal Component Analysis and Cluster analysis (CA) .This method has been employed by a number of researchers to identify the sources of trace element in soils (Mat Ripin et al., 2014; Xiaoping and Linna, 2011). Earlier study done on agricultural soils in Maitumbi industrial layout indicated that the soils are rich in heavy metals contents (Adeoye et al., 2015). This study thus aimed at determining the pollution sources of the metal.

2.0 MATERIALS AND METHODS

2.1 Description of Study Area

The study was conducted on agricultural land in Maitumbi industrial layout, Minna, Niger State. The site was on the latitude 9° 38' N and longitude 6° 34' E (Fig. 3.1). The study involved sampling of soil contaminated with Industrial effluent from Dana Pharmaceutical Company. The company provides employment for a large number of people thereby leading to an economic development of the community. However, the company discharges its poorly treated or untreated effluents to the surrounding through a point source leading to environmental degradation. Soils in the study site which serve as the recipient of the effluents are also used for agricultural purposes as Maize are planted on it during the rainy season.

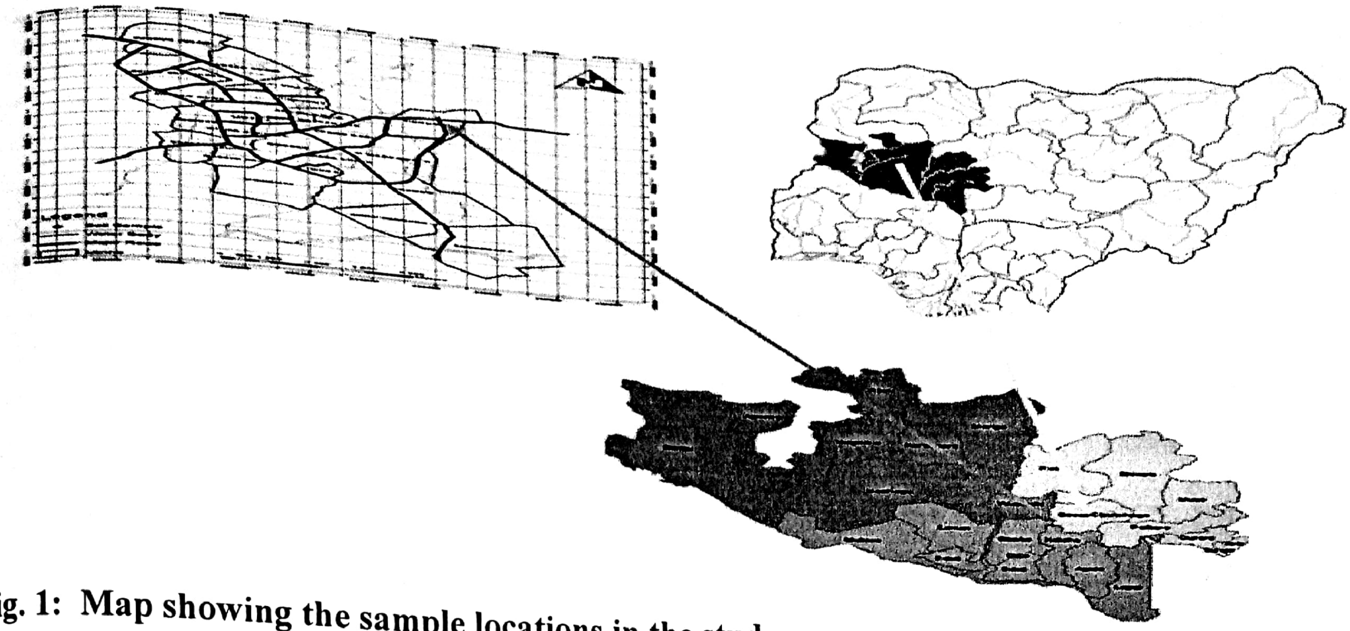

Fig. 1: Map showing the sample locations in the study area

2.1 Soil Sampling and analysis

Soil samples were randomly collected from the study area during the dry and rainy season at a depth of 0-20cm from five points using a stainless steel soil auger. The Samples were collected into polythene bags, properly tied and labeled as A, B, C, D, and E respectively. The Samples were air dried to constant weight for 7days, crushed using mortar and pestle, and sieved through a 0. 2mm stainless sieve mesh and stored in a dried clean polythene bags before taking to the lab for the analysis.

The samples were digested using nitric acid-perchloric acid digestion (Animashaun et al, 2015). Some 0.5 g of the finely ground soil samples were weighed using a digital weighing balance and placed in a 50 ml beaker. Some 20 ml of a mixture of nitric acid and perchloric acid in 1:1 molar ratio was poured into the soil in the beaker and the content was placed on a hot plate and heated gently at low temperature until dense white fumes of $HClO_3$ appears. The digested soil sample was allowed to cool before it was filtered into a 50 ml standard volumetric flask which was made up to mark with deionised water and the samples were placed in storage containers and taken for analysis.The digested samples were analysed for heavy metals (Zn, Pb, Cd, Fe, Ni, Mn, and Cu) using Atomic Absorption Spectrophotometer (AAS).

2.2 Chemometrics Analysis

The results obtained from AAS were employed for the pollution source apportionment of the soil using Correlation Analysis, Factor Analysis (using Principal Component method of extraction) and Cluster analysis (CA). These were all performed using Minitab 17 software.

2.3 Correlation Analysis

Correlation coefficient is defined as a summary value of a large set of data representing the degree of linear association between two measured variables (Taylor, 1990). Its purpose is to measure the closeness of the linear relationship between the defined variable. In this study, Pearson‘s correlation analysis was performed to determine the relationships among the heavy metals (Mat Ripin, 2014).

2.4 Principal Component Factor Analysis

Factor Analysis was performed for data reduction using principal component method of extraction. Principal Component Analysis (PCA) is one of the most powerful techniques commonly used in explaining the variance of a large set of inter-correlated variables and reducing it into smaller set of uncorrelated artificial variables called principal components (PCs) (Shrestha & Kazama 2007). PC is a linear combination of the original variables, which provides information on the most meaningful parameters (Jiwens *et al.*, 2013). It is appealing to note that while PCA summarises the entire data set with asmaller number of PC, there is a minimum loss of original information (Adamu & Ado, 2012). The extracted PCs were further subjected to varimax rotation to produce varimax factor, thus reducing the dimensionality of the data and identifying most significant new variables for easy interpretation of data (Ul-Saufie et al., 2011).

The magnitude of the variance capture by the PCs reduces with the number of axis, while the first PC captures the greatest variance, the second greatest variance is on the second PC and so on (Ul-Saufie et al., 2011). In order to know the number of PCs to retain for rotation, scree test is performed. This is to avoid undesirable effects of over extraction and under extraction of retained factors on the results. The scree (which is a plot of eigenvalues scores) also formed basis for selection of number of factors. Factors with eigenvalues greater than one were extracted, while factors with eigenvalues less than one were not. Aside the eigenvalue, communalities of the retained components is also considered as it shows whether or not that the variance of each of the variables in the components has been described to an acceptable level (Nazire et. al, 1999).

2.5 Cluster analysis (CA)

Cluster analysis (CA) is a way of grouping cases of data based on the similarity of responses to several variables. It helps to identify groups whose observations or variables share common characteristics .There are two types of measure, namely similarity coefficients and dissimilarity coefficients. The result of cluster is often presented in a graphical representation n of a matrix of distances which is perhaps the easiest to understand – a dendrogram, where the objects are joined together in a hierarchical fashion from the most similar, to the most different. Cluster analysis (CA) was performed to classify heavy metals as a function of their different sources or basis of similarities in their sources (Mat-Ripin, 2014).

3.0 Results and Discussion

3.1 Heavy Metals content of the analysed soil

Heavy metals concentrations of agricultural soils in Maitumbi industrial layout were assessed from five sampling points using AAS. The results showed that the levels of seven (7) heavy metals (Zn, Ni, Pb, Cu, Mn, Cd and Fe) assessed were Zn varied from 2.84 to 4.01 mgkg^{-1}, Ni varied from 0.84 to 2.24 mgkg^{-1}, Pb varied from 1.08 to 3.52 mgkg^{-1}, Cu varied from 8.91 to 14.02 mgkg^{-1}, Mn varied from 0.88 to 3.00 mgkg^{-1}, Cd varied from 1.42 to 7.52 mgkg^{-1} and Fe varied from 18.58 to 33.60 mgkg^{-1}. Though some of the analysed metals are within the established limits, some others (Pb, Cd) are above the limits (Table 1). The mean concentration of Pb and Cd were 2.18 and 5.70 mgkg^{-1} while the established limits by FAO/WHO are 0.2 and 0.3 mgkg^{-1} respectively. The accumulation of Cd in the body usually affects kidney and liver (Hubbs, 2000). Also, lead (Pb) is a problematic element that can cause mental lapses even at low concentration (Hubbs, 2000). This also agrees with the finding of Adeoye et al. (2013) who opined that the concentrations of Pb and Cd of agricultural soils in Maitumbi industrial layout are above the WHO standard.

Table 1. Descriptive statistics of the soil heavy metal (mg/kg)

	Zn	Ni	Pb	Cu	Mn	Cd	Fe
Minimum	2.84	0.84	1.08	8.91	0.88	2.55	18.58
Maximum	4.01	2.24	3.52	14.02	3.00	7.52	33.60
Mean	3.50	1.58	2.18	11.73	2.19	5.70	26.89
S.D	0.48	0.53	0.69	1.44	0.76	1.42	5.47
FAO/WHO	-	2	0.2	20	-	0.30	30

S.D= Standard deviation

3.2 Correlation Coefficient Analysis

The result of the correlation coefficients between heavy metals concentrations showed that some of the metals are strongly correlated with each other (Table 2). Zn has a strong positive correlation with Mn and Fe. There also existed a strong correlation between Cd and Pb. Though, some other metals are also correlated, their correlation is weak. Existence of strong correlation among some metals could suggest a probable common source of pollution (Mat-Ripin, 2014).

Table 2 Correlation coefficient matrix (r) between metals

	Zn	Ni	Pb	Cu	Mn	Cd	Fe
Zn	1						
Ni	-0.438	1					
Pb	0.448	0.360	1				
Cu	-0.574*	0.537*	0.371	1			
Mn	0.925**	-0.296	-0.169	-0.483	1		
Cd	0.312	0.470	0.897**	-0.331	-0.421	1	
Fe	0.816**	-0.350	-0.454	-0.515*	0.518*	-0.514	1

Correlation is significant at the 0.05 level (2tails)

$\geq$ 0.5 indicates strong relationship between the metals

$<$ 0.5 indicates weak relationship between the metal

* Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level

3.3 Principal component Factor Analysis (PCA)

Principal component Factor Analysis was used in identifying the sources of heavy metal in soil being a good technique for source apportionment (Mat-Ripin, 2014). Though, seven principal components (PCs) described the data perfectly (Fig. 1), four PCs with total variance of 89.0% were first considered with PCA, but considering eigenvalue and communalities to know if each of the heavy metals is well represented, only three (with total variance of 77.4.0%) were retained after varimax rotation (Anonymous, 2003) in Factor Analysis. This is because only the first three components have eigenvalues that is greater than one and they were also favoured by their communalities, VF1 with an eigenvalue of 2.312 accounts for 33.0% of the total variance and has negative loadings on Zn (-0.601), Mn (-0.609) and Fe (-0.626) as shown in Table 3. The loadings on VF1 suggest that the agricultural soil of the study area was being contaminated by the industrial activities (Prestes *et al.*, 2006). These heavy metals probably get into the soil through the pharmaceutical effluent discharged. A number of researches have confirmed that pharmaceutical effluents are often rich in Zn and Fe and Mn ((Fakayode and Owolabi, 2013; Adeoye et al. 2015; Ramola and Singh, 2013). The negative sign with each of these three metals indicates a negative correlation with other metals loading on the same component.

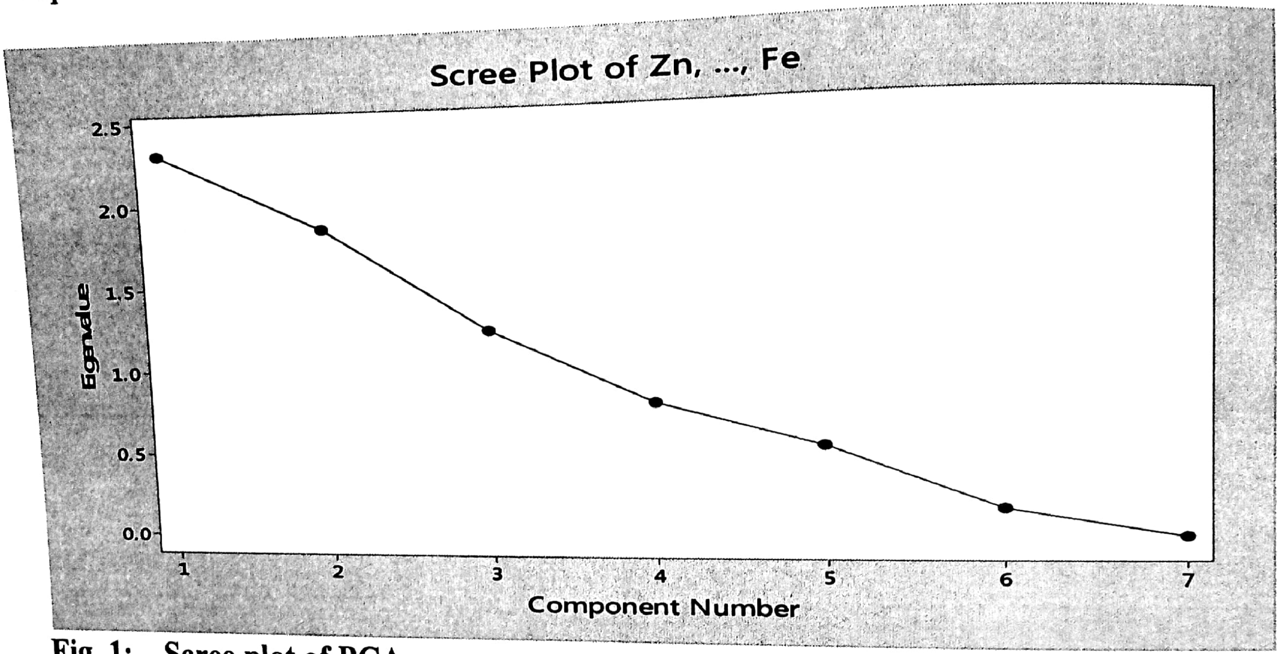

Fig. 1: Scree plot of PCA

VF2 with an eigenvalue of 1.862 explains 26.6% of the total variance which has high positive loading on Pb (0.666) and Cd (0.743). The loadings on this component suggest runoff as probable source. The runoff of traffic and industrial emissions from road, auto repair shops and pharmaceutical industries are often rich in these metals. This assertion is supported by the report of Ogunleye and Izuagie (2013) that claimed non-presence of the two metals in five different industrial effluents assessed. Though, Ramola and Singh (2013) claimed the presence of Pb in pharmaceutical effluent, Anyakora et al. (2011) however reported presence of Pb only in one out of nine pharmaceutical companies effluents at the third batch effluent samples taken. This indicated that it could be due to soils the effluents were in contact with. Our submission is in line with Gobel *et al.* (2007) and Iwegbue et al. (2012) research works which identified Pb as toxic heavy metal in runoff and Cd as an emission from traffic. Higher values reported for Pb in Iyaka *et al.* (2012) work and Ahaneku and Sadiq work (2014) on Maitumbi agricultural soils also showed that the sources of these metals could be attributed to runoff rather than the effluent from the company.

VF3 has an eigenvalue of 1.247 which accounts for 17.8% of the total variance and has high positive loading on Cu (0.754). Though, presence of Cu could be attributed to different anthropogenic sources, loading on different component suggested another major source other than industry. The presence of Cu in the soil could be as a result of agricultural practices (Schulte & Kelling, 1999). High level of Cu in soil could be as a result of repeated use of copper-containing fungicide, application of some copper-containing organic and inorganic fertilizers and the use of sheep manure also increase copper content of soil (Schulte & Kelling, 1999).

Table 3 Rotated Component matrix for heavy metals

Variable	VF1	VF2	VF3	Communialities
Zn	**-0.601**	0.389	-0.046	0.764
Ni	0.301	0.278	0.219	0.824
Pb	0.171	**0.666**	-0.410	0.640
Cu	0.193	-0.187	**0.754**	0.826
Mn	**-0.606**	0.024	-0.047	0.712
Cd	0.131	**0.743**	0.286	0.578
Fe	**-0.626**	0.038	-0.352	6.53
Eigenvalue	2.312	1.862	1.247	
Variance%	33.00	26.6	17.8	
Cumulative%	33.0	59.6	77.4	

VF= Varimax Factor

3.4 Cluster Analysis (CA)

Cluster analysis was further carried out to confirm the results obtained by PCA and probably provides additional information on the grouping of the metals done with factor analysis (Chen *et al*, 2008; Mat-Ripin 2014). Though, all the metals seem to be linked together, the mode of clustering of certain ones points to a common source. Four clusters were extracted for the classification of the major groups of metals that indicate different sources of heavy metals pollution (Fig. 2). Aside Nickel which appear on cluster 2, all other clusters have the same metals as group by the varimax factor. Nickel was not considered in factor analysis because of its eigenvalue (0.809), which is less than one, though, it has a loading of 0.824.

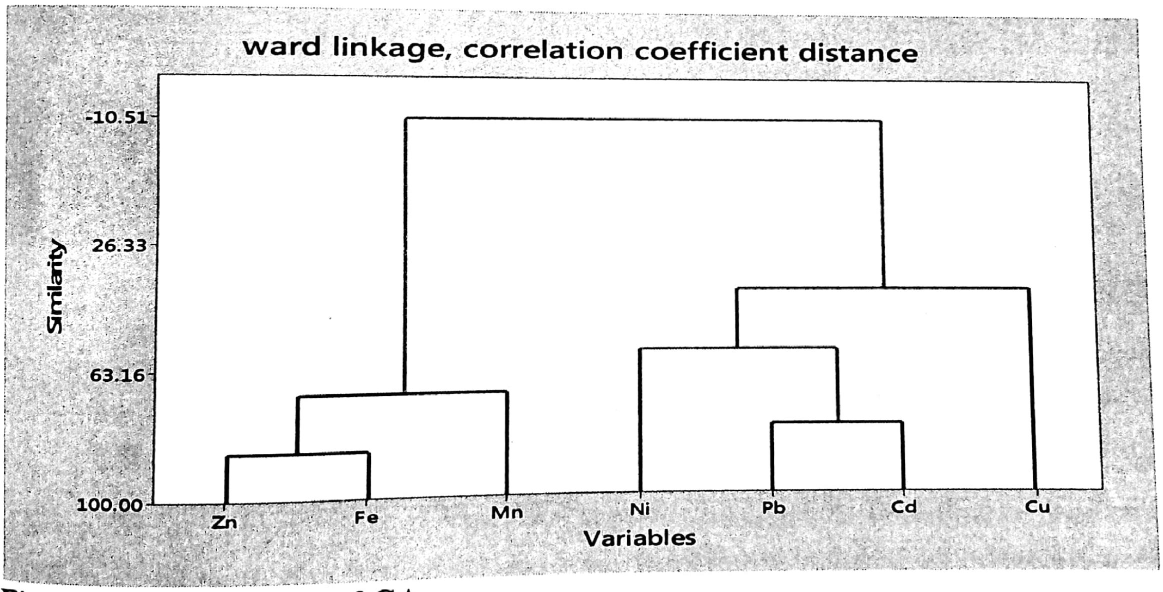

Fig. 2 Dendogram plot of CA.

It could be inferred from the appearance of Ni has a sub-cluster to the main cluster to which Pb and Cd were attached that it has a relatively similar source (Mat-Ripin et al., 2014). Though, Ni could have a natural source, the dendogram showed that its probable source may be due to aerial deposition resulting from wind-blown dust of combustion of coal, diesel and fuel oil, the incineration of waste and sewage, and tobacco smoking (Cempel, and Nikel, 2006; Adah et al., 2013)

4.0 CONCLUSION

The sources of heavy metals contents in Agricultural soil around a pharmaceutical industry Maitumbi was assessed using chemometrics analysis. Though, the sources of the metal pollution are diverse, they are mainly anthropogenic. The results of the Principal Component Factor Analysis PCA/FA and Cluster Analysis CA identified sources of pollution as industrial effluent discharge, runoff of industrial and traffic emission, agricultural practice of agro-chemical and manure usage and aerial deposition.

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