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Distribution and Variation of Heavy Metals and Soil Properties around a Mega Cement Factory in Gboko, Benue State, Nigeria

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ABSTRACT

Fifteen soil samples were collected from Gboko local government area of Benue state around the Dangote cement factory in Yandev. The samples were obtained at random distances round the factory and were analyzed by atomic absorption spectrophotometer(AAS) for Zn, Cu Pb, Cr and Cd. Physicochemical parameters believed to affect the mobility of metals in soil of the study area were examined to include; pH, LOI and CEC. The relatively high concentrations of zinc, copper and lead in the soil samples of the investigated area were related to anthropogenic sources such as cement industry, agriculture activities and traffic emissions. It was found that zinc, copper and lead have the highest level in areas close to the cement factory as seen in sites 1, 2, and 3 while the concentration of cadmium remained low. This study indicates that the metal pollution is caused by perculiar point source within the factory vicinity .Principal component analysis showed that anthropogenic activities seem to be the responsible source of pollution for metals in the soils with the varimax rotation indicating only two important components as Component 1 accounted for 69.14% of the total variance, while having high loadings on the elements Cr, Cd and Pb. ANOVA and pearson's correlation analysis done at $P < 0.05$ showed a significance in metal variation among sites with the exception of the non-metallic properties as confirmed by the dendrogram.

Keywords: *Metals; Cement; Soil; Statistical analysis*

1. INTRODUCTION

The occurrence of heavy metals in soil can be of geogenic or natural and anthropogenic origins. The anthropogenic sources include cement production, mining, smelting, fossil fuel combustion and various industrial activities. Cement production is an important emission source of heavy metals such as Cd, Cr, Cu, Pb and Zn (Al-Khashman and Shawabkeh, 2006). These heavy metals are deposited into soil at various distances depending on wind velocity and particle size (CPCB, 2007) through cement dusts and stack fumes. The majority of heavy metals in cement dust originate from raw materials. Soil has been recognized as the major sink for anthropogenic heavy metal deposition through various pathways (Harrison et al., 1981). The contamination of soil by heavy metals can be problematic on several levels because they do not degrade biologically (Emmanuel et al., 2009) and this always result in several soil disfunctions leading to concerns about the environmental quality. Metal contaminated soil poses risks to humans and animals through ingestion of plants that have bio-accumulated toxic metals from contaminated soil (Turner, 2009). The host community of yandev in gboko area of benue state depend on the vast arable land sorrounding the dangote cement factory for their agricultural activities which include growing of crops and vegetables like tomatoes, pepper, soybean, groundnuts, yams, potatoes etc. . One of the major challenges to human health and environmental quality is contamination of the environment by potential toxic elements depending on pollutant type, pathway of attack and vulnerability of the exposed population. and this is of major concern to the environmental scientists. Benue state houses large agricultural activities hence the acronym "food basket of Nigeria" yandev community in gboko local government area hosts the Dangote cement factory producing over three

million tones of cement per annum, emmiting huge dust in the process, these has necessitated the concern to ascertain the level of contamination caused by these dust if any and possible remediation if rates are alarming.

Environmental pollution related to industrialization and urbanization is inevitable unless proper measures are taken. (Muhammad and Muhammad 2001) air pollution has become a serious problem of recent, soil constitutes part of a vital environmental, ecological and agricultural resources that have to be protected from further degradation as an adequate supply of healthy food needed for the world's increasing population(. Alloway, B.J.et al, 1990.) Heavy metals can affect both the yield of crops and their composition. Thus determination of the elemental status of a cultivated land has to be made in order to identify yield-limiting factors and deficiencies of essential micronutrients of plants grown on polluted soils. These metals are important since they are capable of decreasing crop production due to the risk of bioaccumulation and biomagnifications in the food chain. There's also the risk of superficial and groundwater contamination therefore knowledge of the basic chemistry of these metals in soil as well as the environmental and health risk they pose in soil is necessary in understanding their speciation and bioavailability (USEPA Report 1996.) The fate and transport of a heavy metal in soil depends significantly on the chemical form and speciation of the metal. Once in the soil, heavy metals are adsorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bioavailability, mobility, and toxicity (Shiowatana *et al.*, 2001) Atmospheric emissions

from industrial establishments are one of the major sources of environmental pollution. One type of industry that causes particle pollution is the cement industry (Zerrouqi, *et al* 2008). The main inputs of cement activity on the environment are the broadcasts of dust and gases. Cement dust spreads along large areas through wind rain etc. and are accumulated in and on soils, plants and animals and can affect human health badly (In: Isikli *et al*, 2006, “) Heavy metals are among the most relevant substances emitted. during the process of cement manufacture. The influence of cement dust as a major cause of heavy metal contamination in plants and soils has been observed by several researchers. Among the metals especially known to have toxic effect in environmental studies are arsenic cadmium, lead, mercury and thallium, Aluminium, beryllium, chromium, copper, manganese, nickel and zinc, among others, have been identified in the emission

from cement plant. (Schumacher 2002). Bioavailability of metals released from deposits is very complex and dependent on many interrelated chemical, biological and environmental processes. These processes may vary overtime and among micro - organisms, plants and animals. Field and laboratory studies of particular sites using soil, plants and selective chemical extraction methods may enhance understanding of this concept which is of environmental concern

2. MATERIALS AND METHODS

2.1. Study Area

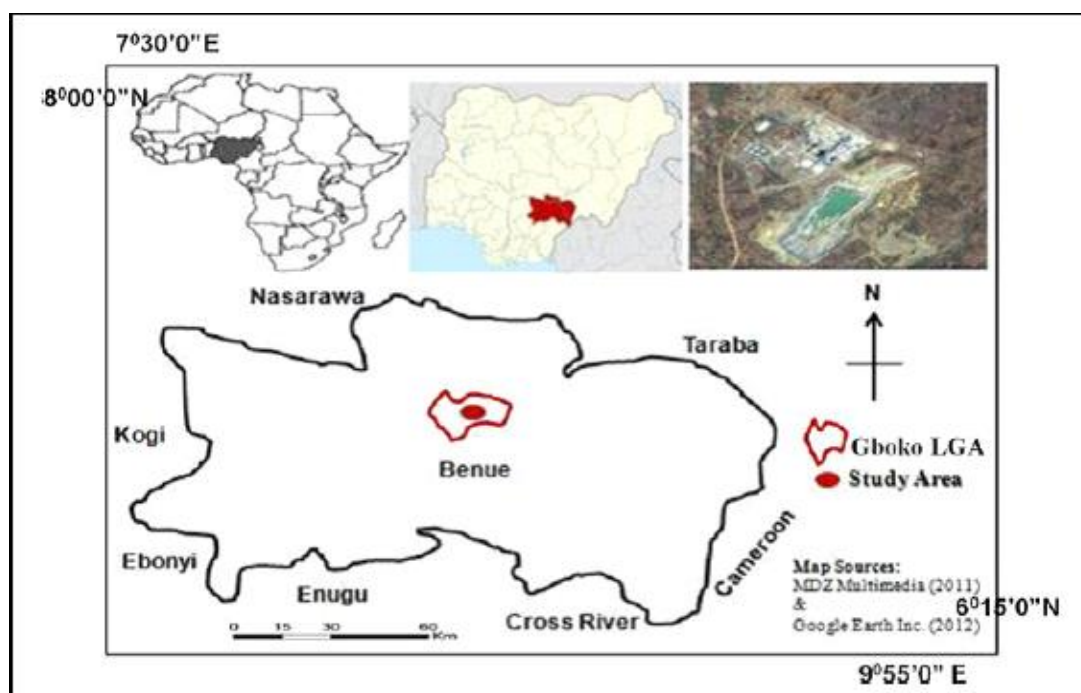


Figure 1. Map of study area





Figure 2. Aerial view of of study area

Dangote Cement Plc is located at Yandev, near Gboko town, in Gboko Local Government Area (LGA) of Benue State in Nigeria's north-central region. Gboko LGA is located between Latitudes $07^{\circ} 08' 16''$ and $07^{\circ} 31' 58''$, and Longitudes $08^{\circ} 37' 46''$ and $09^{\circ} 10' 31''$. The central location of the factory is at $7^{\circ} 24' 42.45''N$ and $8^{\circ} 58' 31.28''E$, at about 532 feet above mean sea level (Figure 1). The study area is located within a sub-humid tropical region with mean annual temperature ranging from $23^{\circ}C$ to $34^{\circ}C$, and with mean annual precipitation of 1,370mm. The average wind speed over the study area is about 1.50 m/s, while the average ambient air temperature is about $30^{\circ}C$ (Nigeria Meteorological Agency 2012)

2.2. Sample Collection

Samples were collected from fifteen(15) selected locations at 10-15cm depth well mapped using GPS instrument around the vicinity of the cement plant. The soil was collected with the aid of a stainless steel spoon. A washed shovel was used to dig to the 10cm-15cm depth before sample was collected. Control samples were collected from two (2) locations; the collected samples were stored in the polyethylene bag and well labelled properly at room temperature for not more than 24 hr from starting analytical procedures. Particle size distribution was determined by hydrometer method. Soil chemistry properties were determined following standard procedures (Madrid et al., 2002). The pH was determined in water with a 1:2.5 soil to solution ratio, Loss on Ignition was measured by a standard procedure (Krogstand, 1992) slightly modified though in accordance with ISO10694. CEC was measured according to ISO 13536 using $BaCl_2$ buffered at $pH = 8.1$. three soil samples from each sampling location were randomly collected and air-dried in the laboratory for three days. The samples for physicochemical analysis were removed from the representative sample before sieving. Soil samples were grounded and homogenized with a mortar and pestle and passed through a 10-mesh (2 mm) sieve to achieve uniform particle size. a total of fifteen(15) samples were

collected on the same day and homogenized to get a representative sample of five(5). Atomic absorption spectrophotometer(AAS) was used for elemental analysis of sample.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Parameters

The physical and chemical characteristics of soil samples: pH, cation exchange capacity (CEC) and loss on ignition (LOI) are given in Table 1. the soil in the study area is predominantly tropical ferruginous. It is generally well drained, low in organic matter, bases and cation exchange capacity. Also, hydromorphic soils are found along the major streams and river courses. These soils are generally suitable for cropping. The soil pH ranging in narrow interval (6.10 - 8.19), for the soils and (6.1) for the control, indicating that the soils are originally acidic except for the activities of cement which suggests neutral to sub-alkaline conditions for the soil samples. The cation exchange capacity (CEC) range from 13.6-17.4 meq/100g

Table 1. Mean, standard deviation and ranges for the descriptive parameters of the five (5) soil samples

Parameters	N	Range	Min	Max	Mean	Std. dev
Zn	5	112.25	11.26	123.46	76.69	48.73
Cu	5	88.58	14.06	102.64	79.85	37.18
Pb	5	101.45	0.10	82.12	47.87	35.15
Cr	5	49.41	6.89	55.43	35.75	17.91
Cd	5	7.29	0.94	8.01	6.06	3.02
pH	5	2.09	6.10	8.19	7.07	0.79
LOI	5	10.09	8.15	18.23	12.35	3.73
CEC	5	4.10	13.60	17.40	15.52	1.51

3.2 Metal distribution

Table 2. Mean metal content(mg/g) in soil with location

Samples	Co-ordinates	Zn	Cu	Pb	Cr	Cd
Site 1	4 96' 72" 8 18' 81"	98.32	87.55	82.12	55.43	8.01
Site 2	4 97' 00" 8 19' 85"	111.013	102.64	77.81	43.112	7.201
Site 3	4 99' 06" 8 18' 39"	123.45	96.74	54.78	34.87	6.54
Site 4	4 97' 65" 8 19' 44"	39.43	98.23	24.54	38.46	7.81
control	4 94' 93" 8 23' 65"	11.26	14.064	0.104	6.89	0.74
	Mean	92.69	79.85	63.27	35.75	6.06
	Std Dev.	43.07	34.41	36.14	16.77	2.79

Descriptive statistics for metals are presented in Table 1 above. metal concentrations in the soils of the study area are said to be low. These metals originating mainly from industrial activities are distributed in soil by the atmosphere with distance depending on the size of particles. metal concentration in soil can vary greatly according to the strength and direction of wind, type of soil, composition and cation exchange capacity(CEC) and pH. Usually pH influences the CEC of soil composition, which in turn affects the heavy metal mobility and distribution in the soil samples. zinc concentrations in the soil were in the range of (11.26-123.45 mg /g) giving the results of the concentration at 15 points cumulated into five(5) points .The mean concentration of zinc was found to be (76.69 mg/g), while the highest value was 123.45mg/g in the soil samples, this concentration was found in site3 located 50m away from the plant but close to a motorable road. Zinc particles may also be derived from industrial sources, whereas the abrasion of tires of motor vehicles may be a second source of emission (Beckwith et al., 1985; Garty et al., 1996; Carreras and Pignata, 2002; Al-Khashman, 2004). The high levels of zinc in the soil are associated mainly with the emission sources of the cement industry and traffic emissions in the investigated area. while the lowest zinc concentration (39.43mg/g) was found in site 4 Which is across the road from the factory site. Fairly average

values were obtained from site2 and site3. And Compared to mean soil concentrations, the mean values of zinc in the analyzed soils are much lower than those of SEPAC standard limit which is 300mg/kg these zinc values are relatively low

as can be seen in figure 3. Where K represents the standard SEPAC limit.

Agricultural soils receive metals mainly from fertilizers, manure, pesticides, wastewater and other scattered diffuse pollution sources such as; industries, traffic emissions, incineration (Wong et al., 1996) The highest copper concentration was found to be 102.64mg/g at site2 while concentration of 87.55mg/g found in site1 are considered to be the lowest though only site2 exceeds the standard permissible limit, all other sites are also considered to be relatively high in copper concentrations. The mean concentration was found to be at 79.85mg/g. Lead is mostly gotten from burning fossil fuels, the mean concentration was found to be 47.87 mg/g in site3 with the highest concentration at site1 to be 82.12 mg/g owing to the fact that site1 is only 20m from the plant with heavy vehicular traffic close by. This could also be due to the fact that process and production of cement industry require a substantial amount of energy supplied by burning fossil fuel and traffic activity in the plant (Banat et al., 2005; Carreras and Pignata, 2002). The mean concentration considered to be quite low compared to

standard limits. The lowest chromium concentration was recorded in the reference soil as 6.89mg/g while site1 had the highest concentration of 55.43mg/g probably due to its closeness to the cement plant at about 5m and the quarry activities located in this site. The mean concentration was found to be 35.75mg/g. way lower than the acceptable limit; also in the cement industry the linings for the rotaries contain chromium, which could be liberated by wear and friction to be the source of chromium in the soil samples (Banat et al., 2005).

Generally, cadmium is found to be lower in concentration compared to the other metals in soil. Cadmium is emitted into the atmosphere from natural sources, mainly basaltic rocks and from anthropogenic sources, followed by waste incineration and by other sources, including the production of batteries, fossil fuel combustion and generation of dust by industrial processes such as cement manufacturing

(Yamagata, 1970). Cadmium concentration range from 0.74-8.03mg/g with the mean concentration of cadmium found to be 6.06mg/g while its highest concentration was found at site1 to be 8.03mg/g this could be due to the quarry activities in this site. According to Ellis and Revitt (1982) zinc and cadmium may be derived from the mechanical abrasion of vehicles and also associated with tire wear.

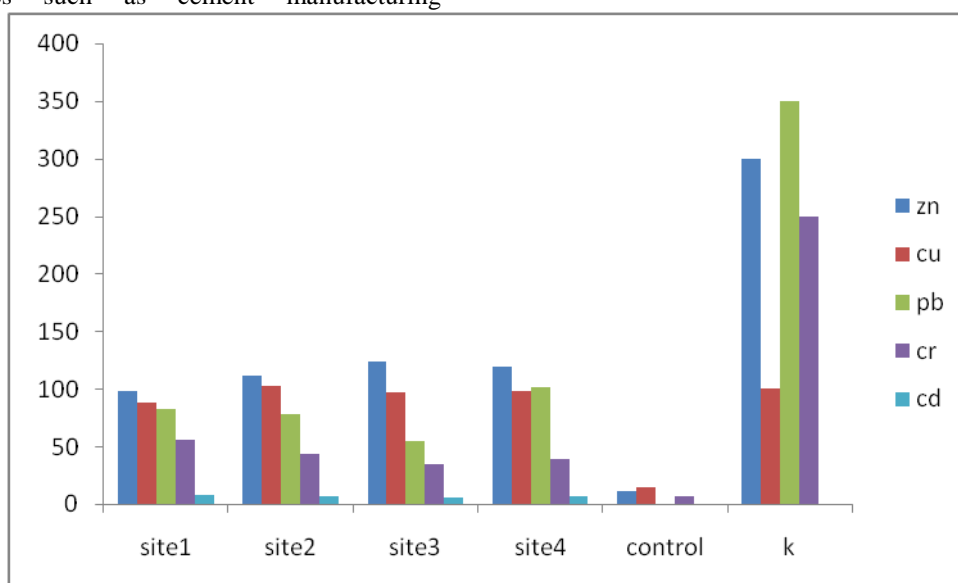


Figure 3. Mean of metals in sites with comparison to (SEPAC) standard

3.3 Statistical data analysis

Statistical analyses were performed with SPSS for windows 7.0. Data were log-transformed prior Principle Component Analysis (PCA) to reduce the influence of high data and varying unit (Moller et al., 2005). Principal Component Analysis was conducted using factor extraction with an Eigenvalue larger than one (1) after varimax rotation. Concentrations of metal were compared using One-Way

analysis of variance (ANOVA) to compute the statistical significance of the mean. If the difference for each metals concentration were significant at $P < 0.05$ (Chen et al., 1997).

The results of the ANOVA showed significant differences in the metals across the sites, these could be due to the positioning of sample site with respect to wind direction and industrial activity in that part of the factory nearer the site.

Table 3.: Statistical variation (ANOVA) between metals and soil samples

parameters	Sum of squares between groups	Degree of freedom	Mean square between groups	Sum of squares within groups	Degree of freedom	Mean square between groups
Zn	0.275	1	0.275	0.531	3	0.177
Cu	0.201	1	0.201	0.359	3	0.1201
Pb	2.143	1	2.143	4.487	3	1.496
Cr	0.220	1	0.220	0.299	3	0.100
Cd	0.274	1	0.274	0.528	3	0.176
PH	0.000	1	0.000	0.009	3	0.003
LOI%	0.003	1	0.003	0.062	3	0.021
CEC	0.001	1	0.001	0.007	3	0.002

Significant at P<0.05

SUMMARY

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	14221.43	4	3555.357	7.583921	0.001261	3.006917
Columns	18883.95	4	4720.988	10.07033	0.000287	3.006917
Error	7500.83	16	468.8019			
Total	40606.21	24				

Pearson's correlation coefficient can be used to measure the degree of correlation between the logarithms of the metal data (Garcia and Millan, 1998). The correlation coefficient are shown in the Table 5. The results show a general strong correlation among the metals with Zn and Cd positively and strongly correlated ($R^2=0.997$) supporting Ellis and Revitt (1982) that they may have come from the same source. PH and LOI are also strongly correlated indicating the influence of pH on CEC which may also affect metal mobility. while Cu and Cd correlated ($R^2=0.998$). Generally Cu had relatively strong correlation with most metals as is seen in Cu and Zn ($R^2=0.999$), Cu and Pb ($R^2=0.998$). Copper associated with particulate matter is emitted into the air naturally from windblown dust, volcanoes, and anthropogenic sources, the largest of which are industrial activities(Romo-Kröger et al. 1994).

Table 5 Correlation matrix between metals in urban samples

Zn	Cu	Pb	Cr	Cd	PH
LOI	CEC				
Zn	1				
Cu	0.999	1			
Pb	0.998	0.998	1		
Cr	0.989	0.996	0.995	1	
Cd	0.997	0.998	0.901	0.996	1
PH	0.904	0.902	0.914	0.875	0.906
LOI	0.352	0.359	0.392	0.616	0.460
CEC	0.818	0.242	0.887	0.852	0.884

By using extraction method of principal component analysis to get associations of metals in factors that would give some information about the distribution and source of metal

pollution. Principal component analysis was performed by computing the eigenvalues. The rotation of principal component was carried out. The factor loadings obtained by

component analysis matrix for various metals are presented in (Table 5). The loadings having a greater than 0.70 are marked bold in the table 6. with Component 1 accounting for 69.14% of the total variance, while having high loadings on the elements Cr, Cd and Pb indicates the influence of local anthropogenic activities of quarrying, vehicular traffic and cement dust etc. on soil samples. On the other hand, component 2 explains that about 30.86% of the variance, was composed by soil characteristics of PH and LOI% This factor had high loadings of natural and anthropogenic sources. (Moller et al., 2005; Biasioli et al., 2005). Results of the statistical analysis and distribution of the pollutant metals suggested that cement emissions represents the most important pollutant source for the investigated area. The scree

plot shows the two most important components in relation to the others.

Table 6. Component Matrix

Factors	Component 1	Component 2
Cr	.987	-.161
Zn	-.985	.171
Cd	.984	-.180
CEC	-.948	.318
Pb	.819	-.574
Cu	-.771	-.637
PH	.327	.945
LOI	.590	.807
Eigen value	5.531	2.469
% variance	69.14	30.86
% cummulative	69.14	100.00

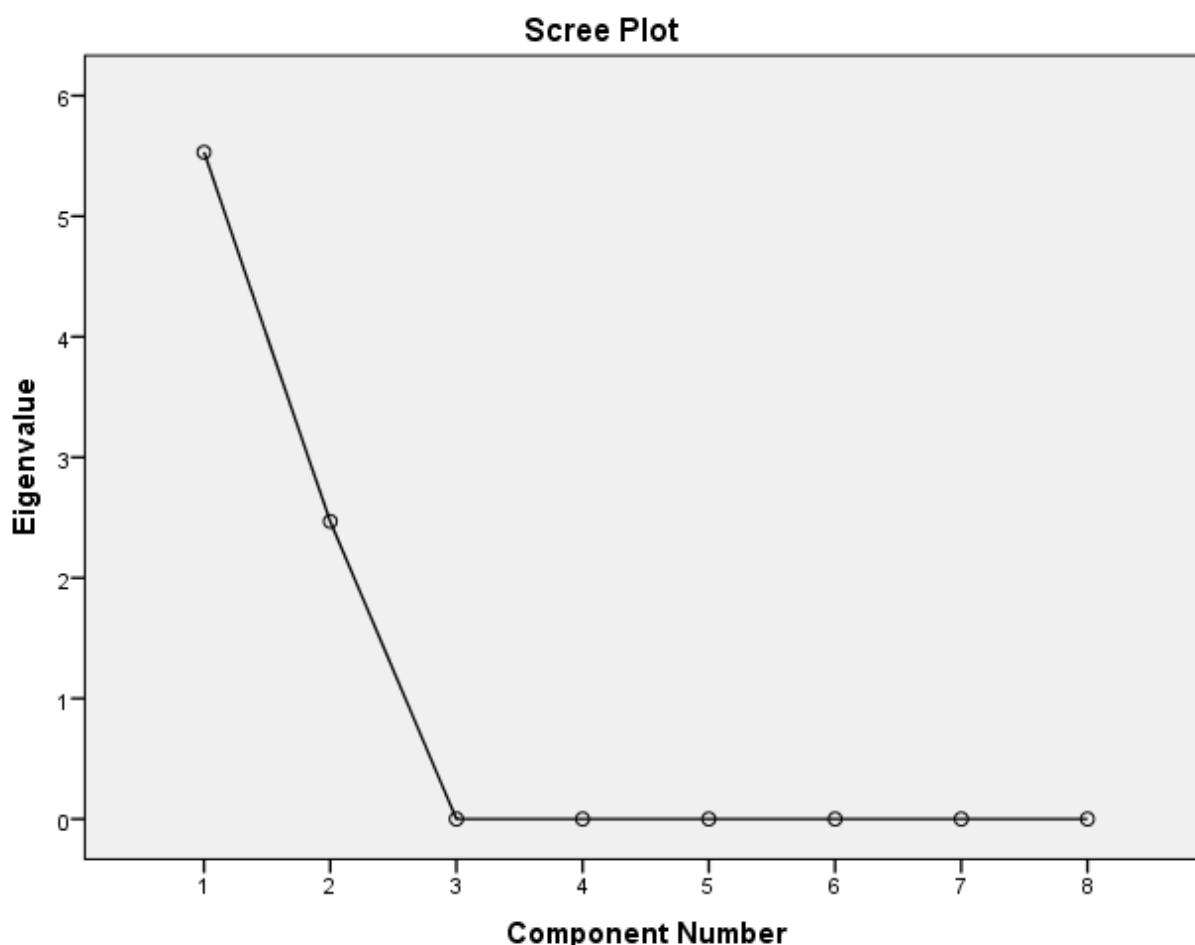


Figure 4 Scree plot for most valid components

3.4 Cluster analysis

A ward linkage dendrogram, based on correlation coefficient distance of the variables are given in Figure 5. Below, the cluster analysis confirms previous findings, showing great similarities between Zinc and lead supporting (Beckwith et al., 1985; Garty et al., 1996; Carreras and Pignata, 2002; Al-Khashman, 2004). Claim that both metals may have come from emissions due to plant activities and heavy traffic.

Copper and cadmium are also clustered together with CEC partially clustered with LOI. PH is weakly linked to all metals and soil properties.

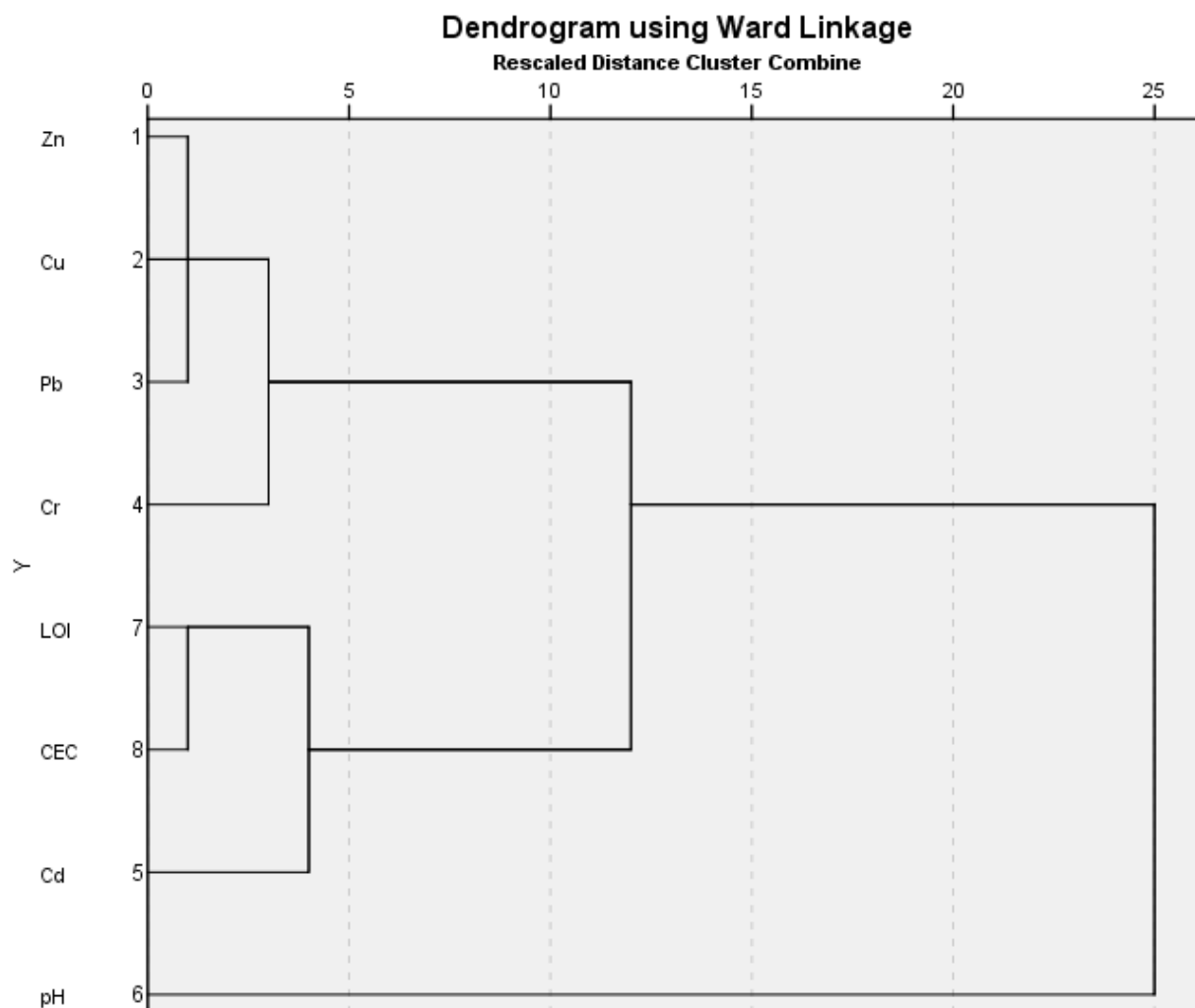


Figure 5: Dendrogram of the soil and sediment samples in Gboko based on the similarities of the heavy metals and some soil parameters.

4. CONCLUSION

The distribution of the metals in the soil of the study area indicated that this area has been affected by anthropogenic activities, in particular the cement industry, leading to a high accumulation of heavy metals compared with the natural background levels. The distribution of the metal concentration of the soil in study area indicated that the cement industry together with the agricultural activities and traffic emissions were mainly responsible for metal pollution,

as the highest metal concentrations were found close to the cement factory. No significant variations were found in pH values between the soil samples. This can be attributed to buffering effect of carbonate content in the cement industry in which carbonate materials are used as raw materials and form the major constituents of the emitted dust and aerosols released to environment. With regards to health risks, bioavailability and mobility of metals can be stated to be of minor significant in the soil. In future, further study is need not only to evaluate metal distribution but also to monitor

their variation across sites so as to detect pollution source and pre-empt a proper control measure.

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