

Multivariate Statistical Analysis and Enrichment of Heavy Metal Contamination of Soil Around Okaba Coal Mines

E.G. Ameh

Department of Earth Sciences Kogi State University, P.M.B 1008, Anyigba, Nigeria

Abstract: Eleven (11) soil samples were collected during the dry season from Okaba coal mine areas to establish the level of impact. Impact evaluation was carried out using regression analysis, factor and cluster analyses, determination of enrichment factor (EF), contamination factor (CF), pollution load index (PLI), anthropogenic factor (AF) and index of geo-accumulation (Igeo). The AF gave this order: Pb>Ni>Cu>Zn>Fe>Cd. Also, Igeo index, EF and CF reveals the same order as the AF. The pollution load index indicates that all sampled sites experienced deterioration with locations Ok06, Ok16, Ok17, Ok03, Ok10 and Ok08 as the most impacted. Strong relationships exist between the cations on one side, a few heavy metals and the cations on the other hand. The relationships between Cd and Pb; Cd and Ni were moderate. The R-mode factor suggests that factors one and three were both natural and anthropogenic while factor two was due to natural processes. The Q-mode factor indicates that factor two is anthropogenic while factors one, three, four and five maybe due to natural process. R-mode cluster analysis suggests that cluster one is anthropogenic and cluster two and three pseudo anthropogenic. Q-mode cluster indicates that cluster two may be anthropogenic ally influenced while one is not. This study brings to fore the impacts of coal mining on soil with Pb, Ni and Cu as the most impacted heavy metals. While detailed study is apt, the authors recommend immediate, total reclamation of the ponds and mines and treatment of the affected areas.

Key words: Contamination factor • Enrichment factor • Index of geo-accumulation • Okaba and Pollution load index

INTRODUCTION

Coal was discovered at Okaba in 1930 by the Geological Survey of Nigeria (GSN) along Otukpa stream near Okaba. Okaba is situated 16km NE of Ankpa at the base of Enugu escarpment. Exploratory boreholes sunk between 1954 and 1955 for depth and reservoir determination showed the presence of coal seams with an average thickness of 2.30m. The geological survey also carried out analysis on the Okaba coal and arrived at the following results: moisture content 6.9%, volatiles 41%, fixed carbon 42.6% and ash 7.0%. Okaba coal is sub bituminous and occurs in lower and upper coal measures. Total reserve of Okaba coal is put at 73million tones [1].

Presently at Okaba, there are two mine sites- one for Nigeria Coal Cooperation (NCC) and the other for Nordic. Both mines are closed and are hardly distinguished from

each other. On the entrant to the NCC mine is an abandoned mine and two other mines now ponds left by these companies. What quantity of coal has been mined by the various companies cannot be easily quantified but what is obvious is the stark reality of the various coal mining related activities and the attendant environmental impact. The mining method used is surface method.

Coal mining either by surface or underground methods has severe consequences on the environment. Surface and underground mining methods involve exploration for and removal of minerals from the earth. Associated with mining are physical, chemical and biological alterations of soil/sediment, alteration of drainage patterns, erosion and siltation of streams [2]. Also associated with coal mining is heavy metal pollution of soil/sediment and water bodies [3, 2].

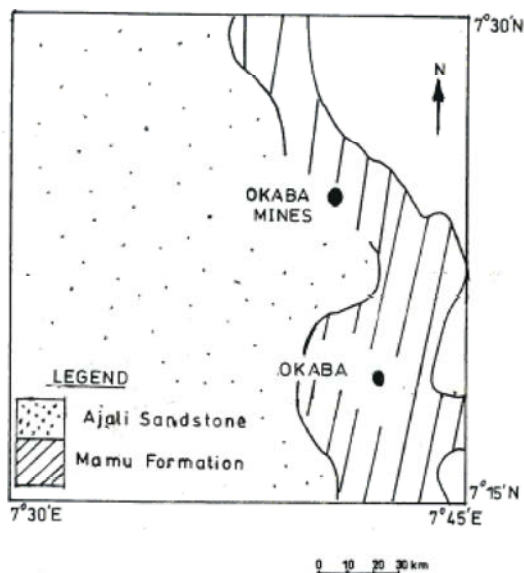


Fig 1: Geological map of the study area [4]

This study is imperative in order to determine the degree of contamination associated with coal mining on soils around Okaba.

Study Area: The coal measures found in Nigeria occur within the geological units represented by the Mamu Formation (Lower Maastrichtian) and Nsukka Formation (Upper Maastrichtian to Danian) [4]. Okaba coal mine is located in the Anambra Basin in eastern Nigeria. The area is underlain by two formations: the Mamu (Early to Late Maestrichtian) and Ajali (Middle to Late Maestrichtian) Formations [5, 4]. The coal bearing sequence is found in Mamu Formation (Lower Maestrichtian). This formation is underlain by Enugu shales (Campanian) and overlain by the false-bedded Ajali sandstones of Middle Maestrichtian age. Mamu Formation (Lower Coal Measures) consists of sandstone bands, mudstones, sandy shale/carbonaceous shale and coal measures at several horizons [6]. The shales and mudstones often alternate with thin bands and lenses of siltstones [1]. Ajali Formation (False bedded sandstones) is made up of friable coarse-grained, white sandstones and sometimes iron stained. The formation consists of gravelly and coarse sandstone within the upper horizons and grades into medium, fine-grained at greater depths. Clay and coal units occur towards the bottom indicating transition between Ajali and Mamu formations. Overlaying this Formation is red earthy sands due to weathering and ferruginisation [4].

MATERIALS AND METHODS

To evaluate the level of impact of coal mining in Okaba area, eleven (11) soil samples were collected in February during dry season.

Soil Sample Collection: Sample points were located and recorded using GPS (Figure 2). The samples were collected randomly but evenly distributed around the mines. The soil samples were sun-dried, disaggregated (not crushed) using a pestle and mortar and sieved to minus 80 meshes (0.177mm) with cellulose nitrate filter. 1.0g of each sample was digested with 3ml of 1:2 mixtures of perchloric acid and hydrofluoric acid. The concentrations of six heavy metals and four major cations were determined by AAS. Analytical procedures, operational parameters, calibration and standardization used in this study are according to [7]. All analysis was performed in Agriculture Faculty, Soil Science Dept. Kogi State University, Anyigba.

Analytical Methods: Insitu measurements of temperature, pH, Tds and EC were determined intrusively with appropriate probes. Spectrophotometer (Model Genesys 20) was used to determine the concentrations of K, Na and Ca. Atomic absorption spectrophotometer (Model 210 VGP) was used to determine the concentrations of Mg, Pb, Zn, Ni, Cu, Cd and Fe.

SPSS15.0 was used to perform all data analysis after auto-scaling for all parameters. Mathematically, PCA and PFA involve the following five major steps: i) code variables to have zero means and unit variance. ii) calculate covariance matrix iii) find eigenvalues and corresponding eigenvectors iv) discard any component that account for small proportion of variation in data set and v) develop the factor loading matrix and perform varimax rotation on the factor loading matrix to infer the principal parameters [8, 9]. In this study only components or factors exhibiting an eigenvalue greater than one were retained.

Hierarchical Cluster Analysis: Cluster analysis comprises of a series of multivariate methods used to find the true groups of data [10]. Objects are grouped such that similar objects fall into the same class. Hierarchical clustering which joins the most similar observations and successively the next most similar observations was employed. The levels of similarity at which observations

Table 1: Concentrations of cations and heavy metals in Okaba soils and their statistics summary.

Concentrations of cations and heavy metals mg/L										
Sample location	Na	K	Ca	Mg	Fe	Cu	Zn	Pb	Ni	Cd
OK11	94.7	26.7	21.3	0.0	97.8	0.3	0.2	0.4	5.8	0.5
OK12	126.4	29.1	36.0	0.2	195.3	0.3	1.7	0.5	3.7	0.5
OK03	211.6	44.8	28.2	5.7	220.3	1.0	0.9	0.5	3.8	0.6
OK06	106.2	33.4	42.7	4.1	507.5	0.7	2.4	0.4	5.8	0.8
OK08	189.6	45.7	33.3	3.2	279.3	0.2	1.7	0.5	5.6	0.5
OK10	196.8	37.9	32.8	4.2	203.8	0.4	1.1	0.9	3.4	0.8
OK16	172.2	31.2	34.7	1.3	100.1	1.3	1.7	0.7	5.5	0.7
OK17	181.3	27.1	25.6	0.8	150.2	0.6	1.9	0.5	5.1	0.6
OK18	100.1	25.6	19.3	1.0	89.5	0.2	0.7	0.5	3.8	0.5
OK19	80.6	26.0	35.4	0.3	210.3	0.6	1.8	0.3	1.5	0.4
OK20	99.6	20.7	30.4	0.4	95.1	0.5	1.8	0.4	1.3	0.1
Min	80.6	20.7	19.3	0.0	89.5	0.2	0.2	0.3	1.3	0.1
Max	211.6	45.7	42.7	5.7	507.5	1.3	2.4	0.9	5.8	0.8
Mean	141.7	31.7	30.9	1.9	195.4	0.5	1.5	0.5	4.3	0.6
Cp	36.7	15.3	30.4	4.1	86.5	0.2	0.5	0.1	0.9	0.4
Std. Dev.	48.7	8.08	6.87	2.0	121.4	0.3	0.6	0.2	1.7	0.2

Table 2: Correlation coefficients matrix of different cations and heavy metals in Okaba soils.

	Na	K	Ca	Mg	Fe	Cu	Zn	Pb	Ni	Cd
Na	1.000									
K	.765	1.000								
Ca	.034	.246	1.000							
Mg	.641	.844	.285	1.000						
Fe	.047	.459	.718	.587	1.000					
Cu	.347	.156	.306	.266	.032	1.000				
Zn	.017	-.011	.788	.046	.564	.267	1.000			
Pb	.654	.341	-.051	.316	-.218	.117	-.228	1.000		
Ni	.307	.375	-.019	.215	.294	.133	-.037	.140	1.000	
Cd	.536	.514	.211	.581	.406	.346	.009	.614	.644	1.000

Table 3: Anthropogenic factor of heavy metals in Okaba soils.

Heavy metals (mg/l)	Mean measured concentration	Control point concentration	Anthropogenic factor (AF) value	% AF	% Geogenic
Fe	195.36	86.52	2.26	69.31	30.69
Cu	0.535	0.18	2.97	74.81	25.19
Zn	1.447	0.54	2.68	72.83	27.17
Pb	0.517	0.05	10.35	91.19	8.81
Ni	4.098	0.86	4.77	82.65	17.35
Cd	0.554	0.35	1.58	61.27	38.73

AF = C_m/C_p , C_m = measured concentration; C_p = control point concentration

are merged are used to construct dendrogram. The squared Euclidean distance method is used to construct dendrogram. A low distance shows that the two objects are similar or close together whereas a large distance indicates dissimilarity [10, 11].

Factor analysis: The raw data were treated first to Z-scale transformation for standardization [12]. Multivariate data analysis was utilized to identify the correlations among the measured parameters. Principal component analysis was used to reduce the number of input variables. Spearman's correlation matrix was performed to illustrate the correlation coefficients among the variables.

Determination of Enrichment Factor: To evaluate the magnitude of contaminants in the soils, EF were computed for each location relative to the abundances of species in source materials to the control/background value and the following equation as proposed by [13,14 and 15] was employed to assess degree of contamination, understand the distribution of elements of anthropogenic origin. $EF = (C_m/C_{Fe})_{\text{sample}} / (C_m/C_{Fe})_{\text{control/background value}}$. Where $(C_m/C_{Fe})_{\text{sample}}$ is the ratio of concentration of heavy metal (C_m) to that of Fe (C_{Fe}) in the soil sample and $(C_m/C_{Fe})_{\text{control/background value}}$ is the reference ratio in the control/background value. Fe is selected as reference element because of its abundance and is one of the widely used reference elements [16, 15].

Table 4: Igeo index of Okaba soils and their classes according to [21].

	Sample location (OK)										
	3	6	8	10	11	12	16	17	18	19	20
Heavy metals	Igeo index										
Fe	0.76	1.97	1.11	0.65	-0.42	0.59	-0.38	0.21	-0.54	0.70	-0.45
Cu	1.82	1.29	-0.23	0.42	-0.11	0.10	2.28	1.10	-0.23	1.03	0.80
Zn	0.20	1.56	1.10	0.45	-0.88	1.09	1.05	1.25	-0.23	1.11	1.12
Pb	2.77	2.26	2.71	3.65	2.55	2.79	3.18	2.85	2.77	2.09	2.34
Ni	1.55	2.18	2.11	1.38	2.17	1.50	2.08	1.97	1.55	0.18	0.02
Cd	0.24	0.59	-0.04	0.68	-0.01	-0.22	0.5	0.26	-0.04	-0.54	-2.13

$I_{geo} = \log_2 [(C_m) / (1.5 * C_p)]$: Where; C_m = measured concentration; C_p = control point concentration; 1.5 = a factor for possible variations in reference concentration due to lithologic differences.

Table 5: R-mode varimax rotated factor analysis of Okaba soils.

Variable	R-mode varimax rotated factor			Communalities
	1	2	3	
Na	0.625	-6.497E-02	0.638	0.856
K	0.891	0.050	0.163	0.895
Ca	0.124	0.929	0.343	0.872
Mg	0.853	0.204	0.165	0.880
Fe	0.577	0.717	-0.335	0.971
Cu	0.280	0.377	0.674	0.743
Zn	-0.110	0.918	0.308	0.837
Pb	0.296	-0.275	0.748	0.714
Ni	0.744	0.021	0.181	0.924
Cd	0.693	9.482E-02	0.458	0.867
Eigenvalue	3.398	2.510	1.814	
% of variance	33.97	725.10	218.142	
Cumulative %	33.97	759.080	77.222	

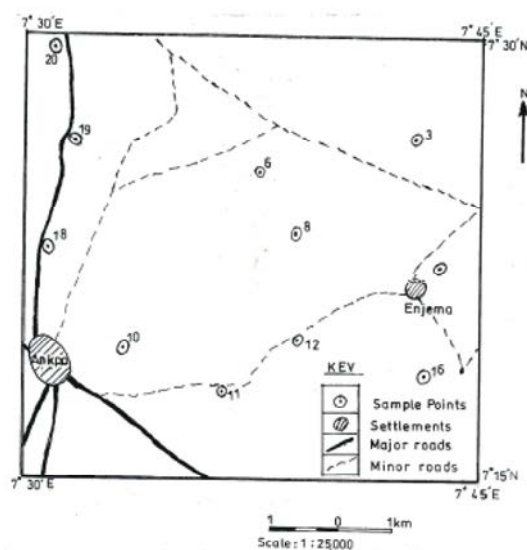


Fig. 2: Location map of Okaba soil samples.

Assessment of Pollution Load Index (PLI): The pollution load index (PLI) proposed by [17] was used in this study to measure PLI in soils of Okaba coal mine. The PLI for a single site is the nth root of n number multiplying the contamination factors (CF values) together. The CF is the quotient obtained as follows: $CF = C_{\text{metal concentration}} / C_{\text{control point concentration of same metal}}$ and $PLI \text{ for a site} = \sqrt[n]{CF_1 * CF_2 * \dots * CF_n}$. Where n is number of heavy metals study (six in this study) and CF= contamination factor. Other anthropogenic indices applied are geo-accumulation index [18, 19] and anthropogenic factor (AF) by [20].

Strong correlation ($r > 0.8$) exist between K and Mg. Moderate correlations ($r > 0.6$) were observed between Na-K, Na-Mg, Na-Pb, Ca-Fe, Ca-Zn, Pb-Cd and Ni-Cd. Weak correlations ($r > 0.4$) were recorded between Na-Cd, K -Fe, K-Cd, Mg-Fe, Mg-Cd, Fe-Zn, Fe-Cd, Pb-Cd and Ni-Cd.

Anthropogenic factor revealed AF of 91.19% for Pb, 82.65% for Ni, 74.81% for Cu, 72.83% for Zn, 69.31% for Fe and 61.27% for Cd (Table 3).

On the other hand, [21] calculate Igeo index according to the following equation; $I_{\text{geo}} = \log_2 [(C_m) / (1.5 * C_p)]$: Where; C_m = measured concentration; C_p = control point concentration; 1.5 = a factor for possible variations in reference concentration due to lithologic differences. He classified the pollution intensity in soils according to their heavy metals content as mentioned in the following table.

Igeo index	Pollution intensity
0	Background concentrations
0-1	Unpolluted
1-2	Moderately to unpolluted
2-3	Moderately polluted
3-4	Moderately to highly polluted
4-5	Highly polluted
>5	Very highly polluted

Also, the average Igeo index of accumulation reveals Pb to be moderately to highly polluted, Ni moderately polluted while Cu, Zn, Fe and Cd are unpolluted.

FA performed extracted three factors in all. Factor one consists of high factor loadings of K, Mg, Ni, Cd, Na and Fe with total variance of 33.98%. Factor two has variance of 25.10% and consists of high loadings of Ca, Zn and Fe. Factor three accounts for 18.14% of total variance and consists of Pb, Cu, Na and Cd. Given geochemistry of factor one, it maybe due to natural source while factor two and three are likely anthropogenic in nature. Fe, Cd and Na have dual sources, which imply natural or anthropogenic origins.

The Q-mode factor analysis extracted five factors (Table 6). Factor one consists of locations OK12, OK06, OK11, OK17 and OK19 with 27.83% variance. Factor two accounts for 23.82% of total variance and consists of OK03, OK16 and OK08. Factor three consists of OK18 and OK19 with total variance of 14.85%. Factor four accounted for 11.72% of total variance and consists of location OK10 and factor five is made up of OK20 and OK17 with total variance of 10.88%.

R-mode cluster analysis revealed two distinct clusters (Figure 3). Cluster one consists of K, Mg, Na, Ni, Cd, Pb and Cu. Cluster two consists of Ca, Zn and Fe. The highest similarity is exhibited in cluster one between K and Mg and in cluster two between Ca and Zn (Figure 3). This similarity was also exhibited given the high factor loadings in their respective factors one and two (Table 6). Except for Cu and Pb, cluster one is similar to factor one and cluster two is the same as factor two. Cluster two maybe anthropogenic – in this case mining related activities. Q-mode cluster analysis (Figure 4) also revealed two clusters. Cluster one consists of locations OK12, OK06, OK11, OK17, OK18, OK19 and OK10 while cluster two is made up of locations OK03, OK16, OK08 and OK20.

A closer look at the Q-mode cluster analysis (Figure 4) reveals that OK12 and OK06 bear first degree of similarity in that cluster, followed by OK12 and OK11. In cluster two (Figure 4), OK03 and OK16 have the maximum similarity, followed by OK03 and OK08. This similarity is also evident in the highest loadings displayed in their respective factors (Table 6). The same Q-mode factor analysis also revealed that factor four is made up of location OK10 only while factor five is made up of locations ITK17 and OK20.

[22] classes and the degree of soil enrichment from heavy metals content according to enrichment factor (EF) index as follows.

EF indices	Degree of enrichment
$EF \leq 1$	Background concentration
$EF \text{ 1-2}$	Depletion to minimal enrichment
$EF \text{ 2- 5}$	Moderate enrichment
$EF \text{ 5- 20}$	Significant enrichment
$EF \text{ 20- 40}$	Very high enrichment
$EF > 40$	Extremely high enrichment

Each EF location was calculated and result presented in Table (7). On the average, the order of enrichment factor is; $Pb (66.04) > Ni (29.64) > Cu (18.92) > Zn (15.35) > Fe (11.15)$ and $Cd (9.45)$. Except in locations OK12, OK08, OK06 and OK03, Pb has the highest value of EF in all remaining locations. This is followed by Ni, Zn, Cu, Fe and Cd is the least. In order of enrichment, location OK16

Table 6: Q-mode varimax rotated factor analysis of Okaba soils.

Q-mode varimax analysis					
Sample location	1	2	3	4	5
OK11	0.843	-8.972E-02	0.142	0.333	9.459E-02
OK12	0.892	0.177	0.204	-0.116	-0.106
OK03	0.137	0.919	0.354	0.158	0.183
OK06	0.867	0.266	0.123	0.309	-0.320
OK08	0.277	0.828	0.300	-0.292	-0.181
OK10	0.121	0.232	0.377	0.856	-0.235
OK16	-0.105	0.869	0.802	0.246	0.302
OK17	0.614	-0.356	0.174	0.372	0.410
OK18	0.119	0.282	0.949	0.370	0.350
OK19	0.525	0.020	0.720	0.274	0.102
Ok20	-0.122	0.193	-5.859E-02	-0.214	0.878
Eigenvalue	3.062	2.620	1.634	1.289	1.197
% of variance	27.834	23.821	14.85	11.720	10.883
Cumulative %	27.834	51.655	66.50	78.227	89.110

Table 7: Enrichment factor (EF) of heavy metals in Okaba soils and their classes according to [22].

Sample location											
Heavy metals (mg/l)	OK03	OK06	OK08	OK10	OK11	OK12	OK16	OK17	OK18	OK19	OK20
Fe	1.48	1.33	1.00	1.15	2.77	0.71	0.32	0.49	0.81	0.75	0.34
Cu	2.07	0.63	0.40	0.85	1.23	0.71	6.29	1.86	1.24	1.26	2.38
Zn	0.68	0.75	1.00	0.87	0.36	1.41	2.69	2.06	1.24	1.33	2.97
Pb	4.01	1.23	3.04	7.98	7.79	4.61	11.75	6.22	9.86	2.63	6.92
Ni	1.73	1.16	2.00	1.64	5.98	1.89	5.50	3.40	4.25	0.70	1.39
Cd	0.70	0.38	0.45	1.02	1.32	0.57	1.83	1.04	1.41	0.42	0.31

Table 8: Contamination factor (CF) and PLI of heavy metals in Okaba soils.

Sample location											
Heavy metals	OK03	OK06	OK08	OK10	OK11	OK12	OK16	OK17	OK18	OK19	OK20
	Contamination factor (CF)										
Fe	2.55	5.87	3.23	2.35	1.13	2.26	1.16	1.74	1.03	2.43	1.10
Cu	5.28	3.67	1.28	2.00	1.39	1.61	7.28	3.22	1.28	3.06	2.61
Zn	1.72	4.43	3.22	2.06	0.41	3.19	3.11	3.57	1.28	3.24	3.26
Pb	10.20	7.20	9.80	18.8	8.8	10.4	13.6	10.80	10.2	6.4	7.60
Ni	4.40	6.78	6.47	3.90	6.76	4.26	6.36	5.90	4.40	1.70	1.52
Cd	1.77	2.26	1.46	2.40	1.49	1.29	2.11	1.80	1.46	1.03	0.34
PLI											
	3.5	4.68	3.27	3.46	1.96	2.95	4.11	3.63	2.19	2.54	1.82

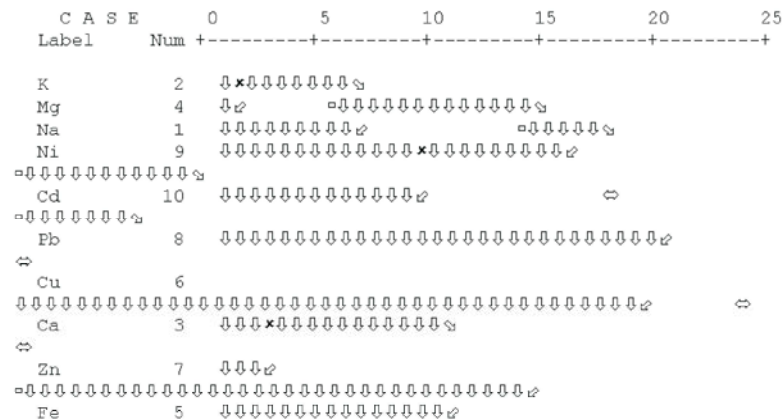


Fig. 3: R-mode cluster analysis of Okaba soils.

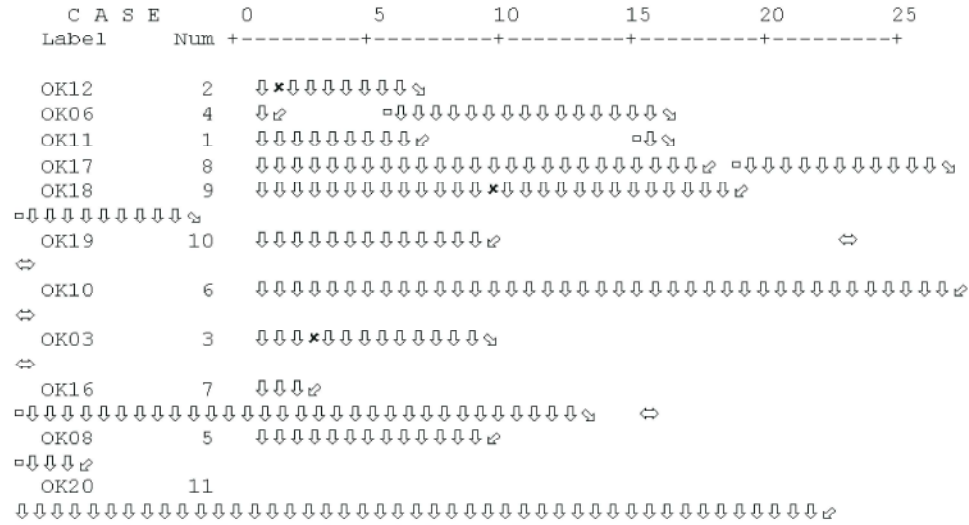


Fig 4: Q mode cluster analysis of Okaba soils.

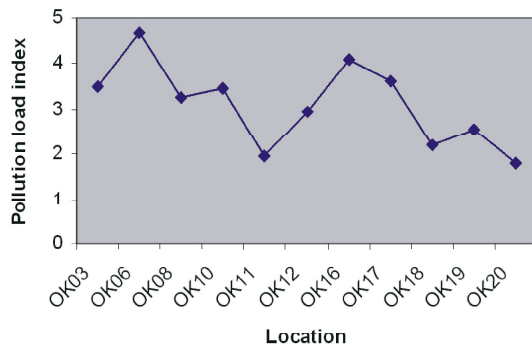


Fig. 5: Pollution load index (PLI) of heavy metals in different locations of Okaba soils.

is the most enriched followed by OK18, OK11 and OK17, while OK03, OK08, OK06 have least enrichment factors with respect to all the heavy metals considered (Table 7). In order of three heavy metals having highest impact, Pb have all six locations significantly polluted, four moderately polluted and OK06 is depleted to minimally enriched. Copper has one location OK16, significantly enriched and the rest moderately enriched. Nickel has two locations significantly enriched, six moderately enriched and two locations depleted to minimally enriched. The least of all EF is: $Cd < Fe < Zn$ with respect to all locations.

[17] classified the degree of soil contamination as indicated by contamination factor (CF) as follows;

Contamination factor (CF) indices	Degree of contamination
$CF < 1$	Low contamination
$1 \geq CF \geq 3$	Moderate contamination
$3 \geq CF \geq 6$	Considerable contamination
$CF > 6$	Very high contamination

Also, [17] classified the degree of soil contamination by heavy metals according to pollution load index (PLI) as follows;

PLI indices	Pollution level
0	Perfection
1	Only baseline levels of pollutants present

From the CF values illustrated in Table (8), Pb has the highest average CF values of (113.80) from all locations, followed by Ni (52.45), Cu (32.68), Zn (29.49), Fe (24.84) and Cd (17.41). Cadmium has the least CF value of 17.41. Iron has moderate contamination in nine locations and considerable contamination is the remaining two locations (OK08 and OK06). Copper has moderate contamination in six locations and considerable contaminations in locations OK03, OK06, OK17 and OK19. At location OK06, Cu has very high contamination with CF value of 7.28. Zink has low contamination at OK11, moderate contamination at locations OK03, OK10, OK18 and considerable contamination at locations OK06, OK08, OK12, OK16, OK17, OK19 and OK20. Lead has CF range of 6.4 to 18.8 and all eleven sample locations have very high contamination. Contamination factor values of Ni indicates that locations OK19 and OK20 are moderately contaminated, five other locations have considerable contaminations while OK06, OK08, OK11 and OK16 have very high contaminations. Cadmium has the least CF values and all eleven locations have CF values between 1 and 3, (moderate contamination) except location OK20 with low contamination. From Table (8), Pb has the highest CF value in all locations, followed by Ni in most locations, Cu and Zn while Fe and Cd are least. The most

contaminated locations are OK10, OK16, OK17, OK18, OK12, OK08, OK03 and OK20 in decreasing order. Thus, order of heavy metal CF is: $Pb > Ni > Cu > Fe > Zn > Cd$.

The pollution load index (PLI), Figure (5) shows that all the eleven locations have $PLI > 1$, indicating progressive deterioration of all the locations with OK06, OK16, OK17, OK03, OK08 as the most affected while locations OK11 and OK20 are the least affected by heavy metal contamination.

DISCUSSION

Coal and coal waste products contain toxic heavy metals including As, Pb, Hg, Ni, Cd, Cu, Zn, Fe etc which are dangerous if released to the environment [23, 18]. The potential environmental impacts of heavy metals in coal mining area is related not only to their total concentration and chemical forms, but also to the rate of weathering suffered by the samples. The pollution risk from heavy metals increases with time due to conversion from an inert state into an active state during weathering [24].

The major cations are present due to their abundance in rock forming minerals in the area. They show this trend: $Na (141.74) > K (31.65) > Ca (30.87) > Mg (1.92)$. Heavy metals such as Fe, Ni, Zn, Cd, Cu and Pb were also present in this order of decreasing concentration. Their presence is attributed to pyrite minerals and base metal deposits such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), covellite (CuS), galena (PbS), sphalerite (ZnS) [25].

Among the major cations, significant relationships were observed between Na-K and Mg-K while the rest relationships were not significant. Between heavy metals and major cations, few significant relationships were also observed. The relations between Ca-Fe, Ca-Zn were significant. The relationships among the heavy metals were generally less significant except that between Cd-Pb and Cd-Ni which were moderate. The absence of significant, statistical relationship could be attributed to the fact that these parameters do not share the same source [26, 27].

The R-mode factor analysis performed on the Okaba dry season soil samples suggest that factor one and three may be due to both natural and anthropogenic inputs while factor two could be due to natural processes based on their correlation regression analysis, EF and CF [28, 29]. Q-mode analysis extracted five factors. Factor two is directly linked to the mine areas while in factor one, only OK06 seems directly influenced by coal mining activities. Factors three, four and five on the other hand are not directly connected with mining activities. R-mode

cluster analysis generated three clusters. Cluster one is an association of K, Mg, Na, Ni, Cd and Pb. Nickel and Cd are connected to this cluster at a farther Euclidean while Pb is linked to this same cluster even at a farther distance (3rd order degree). Copper is the only element in cluster two. This solitary behavior was evident also in regression relationship where Cu did not significantly relate to any of the parameters analyzed for. The association in cluster three is made up of Ca, Zn and Fe. While cluster one is due to anthropogenic inputs related to coal mining, cluster two and three could both be due to natural processes [30].

Analysis of Q-mode cluster extracted two clusters. Cluster one consist of OK12, OK06, OK11, OK17, OK18, OK19 and OK10. Apart from OK06, this cluster consists of locations that may not have been influenced by coal mining. Cluster two on the other hand is made up of OK03, OK16, OK08 and OK20. This cluster is probably influenced by coal mining activities.

The AF, Igeo index, EF and CF indices all gave this order of enrichment/contamination of heavy metals present in Okaba coal mines and its surroundings: $Pb > Ni > Cu > Zn > Fe > Cd$. Cadmium and Fe are respectively the least contaminated. [31] investigated the distribution of heavy metals in coal and showed that As, Co, Cu, Ni, Cr, Pb, Zn, Cd etc were present. [18] also confirm the presence of heavy metals such as Pb, Cd and Ni in Enugu coal mining area. This study indicates that the dry season soil samples were contaminated/enriched with Pb, Ni, Cu and Zn. This observation is due to the presence of pyrite minerals in coal. Besides pyrites, base metal deposit contain other metal sulphide minerals such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), covellite (CuS), galena (PbS) and sphalerite (ZnS). In a strongly reducing environment and in the presence of sulphur, these elements form sulphides. This explains why coals which form in strongly reducing environment contain significant amounts of heavy metals [25]. Analysis of Nigerian coal shows the presence of heavy metals such as Cd, Cu, Cr, Hg, Ni, Zn, Pb, Ti, As, Ag, Al, Co, V and Si [32]. The acidic nature of the environment, leaching effects and the fact that these heavy metals are easily weathered on exposure contributed to the high concentration of these heavy metals [33].

While lower and generally no appreciable difference in PLI indicates less significant inputs from anthropogenic sources, $PLI > 1$ indicates progressive site deterioration. This means that all the dry season soil sample sites have experienced progressive deterioration. PLI of > 2.50 indicates appreciable enrichment/contamination and as

such locations OK06, OK16, OK17, OK03, OK10, OK12 and OK19 have experienced varying degrees of pollution arising from coal mining related activities [34].

CONCLUSION

Based on the indices used, Pb, Ni and Cu have significantly impacted on the soil. Factor and cluster analyses also complimented the indices for proper evaluation of the contaminated soils in the area. Efficient mining processes, improved maintenance and other practices are recommended for a sustainable environment.

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