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Evaluation of Heavy Metal Pollution and Metal Indices for Surface Water Around Okaba Coal Mines, Kogi State, Nigeria

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Abstract: This study became imperative given the importance of water to our lives and particularly those in the rural areas vis-à-vis the exploitation for coal. A total of ten (10) dry season surface water samples were analyzed for heavy metals and major ions. Regression analysis, factor and cluster analyses, anthropogenic factor (AF), heavy metal pollution (HPI) and metal indices (MI) were adopted to help in assessing the degree of pollution. trong relationship exists between the physiochemical and the anions especially with pH. Strong correlation also exists between Pb and EC, Tds; Cl and Ec but generally the relationships are weak. R-mode factor suggests that factor one and two are anthropogenic while factor three is natural. R-mode clusters reveal also that cluster two is anthropogenic in nature; one is a mixture of natural and anthropogenic sources. The Q-mode factor indicates that while some locations are directly influenced others are not. Q-mode cluster shows that cluster one is natural, clusters two and three are anthropogenic. The AF indicates this order of heavy metal impacts in the water samples: Cd>Zn>Ni>Fe>Pb> Cu. The HPI value of 56.21 obtained is below the critical pollution level of 100 at which the water is said to be contaminated. Metal indexing value of 460.46 obtained suggests "low water quality". This study has shown that heavy metal pollution of water resources around Okaba coal need to be evaluated in details. Control measures should be put in place to strike a balance while preventive measures and awareness are strongly recommended.

Key words: Anthropogenic factor (AF) · Heavy metal pollution indexing · Metal indexing · Multivariate analysis and Okaba

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, 2].

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 mining related activities and the attendant environmental impact. The mining method used at Okaba is surface method.

Coal mining either by surface or underground methods has 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, siltation of streams and heavy metal pollution of soil/sediment and water bodies [3, 4].

This study is necessary to evaluate the degree of contamination of surface, make data available to policy makers, companies and to create awareness on the dangers of these heavy metals on our health.

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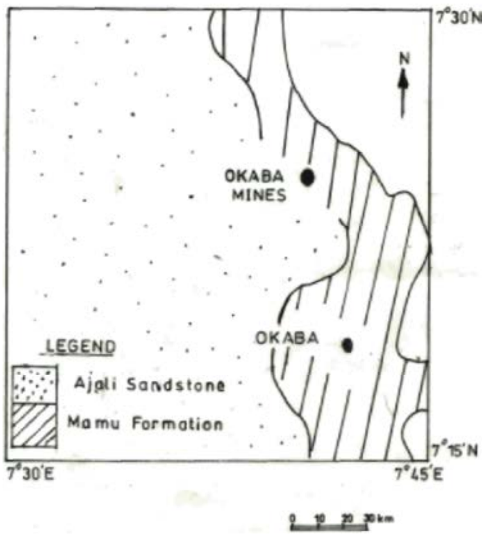

Fig. 1: Geological map of study area [2]

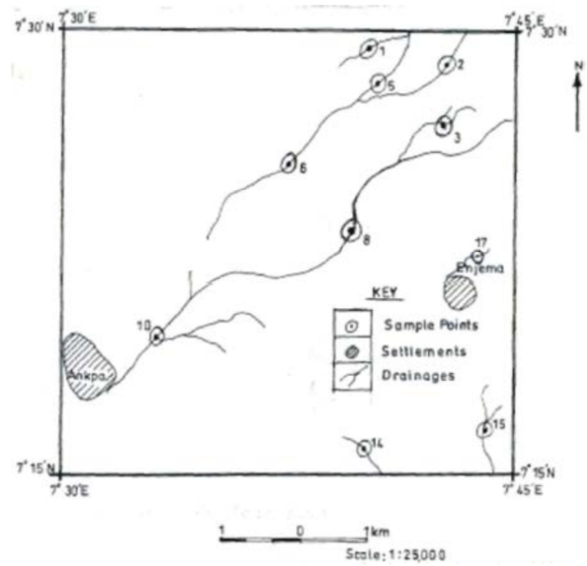

Fig. 2: Sample location map of Okaba water

Study Area: The coal measures found in Nigeria occur within the geological units represented by the Mamu Formation (Lower Maastrichtian) and Nsukka Formation (Upper Maastritchtian to Danian) [2]. Okaba coal mine is located in the Anambra Basin in eastern Nigeria. The area is underlain by two Formations: the Mamu (Early to Late Maestritchan) and Ajali (Middle to Late Maestritchtian) Formations [5, 2]. 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 [2]. The shales and mudstones often alternate with thin bands and lenses of siltstones [5]. 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 [2, 5].

MATERIALS AND METHODS

Sampling was carried out in the month of February (dry season). A total of ten (10) water samples were collected (Figure 2). Sampling was done randomly but evenly distributed. Samples were collected from mid-point and a foot below the surface water in duplicates-one for heavy metal and the other for anion analyses. Samples were filtered as soon as they were collected using cellulose nitrate filter with pores of 0.45 micron diameter. Polyethylene plastic bottles were used as sample containers. New bottles were cleaned with strong- metal free acid. The containers were rinsed with sample water prior to collection. Sufficient air space was allowed and sample stored upright. Teflon lined caps were screwed on tightly to prevent leakage. Water samples for cations and heavy metal analyses were acidified with metal free HNO_3 to a pH of 1- 2. The samples were stored between 1°C and 4°C on cool ice packs from the field to the laboratory for analyses [6].

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, Ca, NO_3 and SO4. AAS (Model 210 VGP) was used to determine the concentrations of Mg, Pb, Zn, Ni, Cu, Cd and Fe. Titration method was used for the determination of Cl and alkalinity concentrations. All analyses were performed according to [6] in the Dept. of Soil Science Laboratory, Faculty of Agriculture, Kogi State University, Anyigba.

Data Evaluations: Heavy metal pollution and metal indices approaches were used for this study. HPI is a method that rates the aggregate influence of individual heavy metal on the overall quality of water. It is defined as Wi, taken as inversely proportional to the recommended standard (Si) for each parameter. HPI model is given as HPI=Σ WiQi/ΣWi…….. (1). Where Qi = subindex of the ith parameter. Wi is the unit weightage of ith parameter and n is the number of parameters considered. The subindex (Qi) of the parameter is calculated by Qi =Σ (Mi (-) Ii)/ (Si-Ii)…….. (2). Where Mi is the monitored value of heavy metal of the ith parameter, Ii is the ideal/baseline value of ith parameter, Si is the standard value of ith parameter. The sign (-) indicates the numerical difference of the two values, ignoring the algebraic sign [7]. The critical pollution index value is 100 [8, 9, 10].

Another index used is the general metal index (MI) for drinking water [8] which takes into account possible additive effect of heavy metals on the human health that help to quickly evaluate the overall quality of drinking waters. MI = Σ [Ci/ (MAC)i] as proposed by [11, 8]. Where MAC is maximum allowable concentration and Ci is concentration of each metal. The higher the concentration of a metal compared to its respective MAC value, the worse the quality of water. MI value > 1 is a threshold of warning [8, 12].

Univariate and multivariate statistical methods of analysis were also used in the study. The software SPSS 11.0 was used for statistical analysis. The correlation matrix which is based on the Pearson's correlation coefficient was utilized for displaying relationships between variables {13]. Mathematically, PCA and PFA involve the following 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 [13]. In this study only components or factors exhibiting an eigenvalue greater than one were retained.

The obtained matrix was subjected to multivariate analytical technique. Factor analysis which aims to explain an observed relationship between numerous variables in terms of simple relations was applied. Cluster analysis was also used for investigating the similarities between variables found in the water samples. Evaluation of similarity was based on the average linkage between groups [14].

Table 1 is the summary statistics of all parameters measured in Okaba dry season water samples. Temperature ranges from 25.40 - 27.00°C with 26.15°C as mean. pH has a mean of 6.37 indicting slightly acidic water. Tds range from 1.80 - 1999.00 and has a mean of 886.38. EC has a mean of 1.70; alkalinity was 1.09, K 9.81mg/l, Na 4.38mg/l, Ca 6.42mg/l and Mg 0.13mg/l. Average concentrations order among major cations is: K>Ca>Na>Mg. Cl has a mean of 0.73mg/l, NO_3 8.27mg/l and SO_4 3.99mg/l. Average trend among major anions is: $NO_3 > SO_4 >$ Cl. Fe range from 0.35 - 20.17mg/l with a mean of 2.87mg/l, Cu has a mean of 0.11mg/l and range from 0.03 - 0.5mg/l. Zn range from 0.29 - 1.65mg/l with a mean of 0.85mg/l. Pb has a mean of 0.54mg/l and range between 0.21 - 0.92mg/l. Ni range from 2.55-7.81 mg/l but has a mean of 4.13 mg/l and finally Cd range from 0.40 - 0.87mg/l with mean value of 0.57mg/l. Ni > Fe > Zn > Cd > Pb > Cu was the average trend among the heavy metals.

Table 1: Descriptive statistics of Okaba dry season water

Variable	Min	Max	Mean	SD
Temp	25.40	27.00	26.15	.61
pH	3.50	7.70	6.37	1.35
Tds	1.80	1999.00	886.38	969.36
EC	.02	3.97	1.70	1.75
Alk	.01	6.15	1.09	1.86
K	3.00	18.90	9.81	5.57
Na	.44	6.58	4.38	2.05
Ca	.50	10.75	6.42	3.71
Mm	.02	.50	.13	.14
Cl	.03	1.77	.73	.84
NO_3	1.84	34.89	8.27	9.61
SO_4	.45	13.63	3.99	3.95
Fe	.35	20.17	2.87	6.11
Cu	.03	.50	.11	.14
Zn	.29	1.65	.85	.46
Pb	.21	.92	.54	.29
Ni	2.55	7.81	4.13	1.89
Cd	.40	.87	.57	.14

From the correlation coefficient (Table 2) above, strong correlation (r > 0.8 - 0.9) exists between Tds-Ec, Tds-Pb, Ec-Cl, Ec-Pb, NO_3-SO_4 and NO_3-Fe. These strong correlations suggests same environment. Moderate correlations (r > 0.6 - 0.7) were observed between these pairs of parameters, Tds-Cl, Ec-Ca, K-Cd, Na-Ca, Na-Cd, Cl-Pb and SO_4-Ni. Weak correlation (r = 0.4 - 0.5) were also observed as follows: temperature-Ni, pH-Cd, Tds-K, Tds-Ca, Tds-NO_3, Tds-Fe, Tds-Cu, Tds-Ni, Ec-K, Ec-Na, Ec-NO_3, Ec-Fe, Ec-Cu, K-Na, Ca-Cl, Ca-Ni, Ca-Cd, Cl-NO_3, Cl-SO_4, Cl-SO_4, Cl-Fe, Cl-Cu, Cl-Ni, NO_3-Pb, NO_3 -Ni, SO_4-Pb, Fe-Pb, Fe-Ni, Cu-Pb, Zn-Ni and Pb-Ni. Alkalinity, Mg shows only weak, negative correlations with few parameters analysed. Temperature and pH correlates weakly with Ni and Cd respectively.

Table 2: Okaba dry season water samples correlation coefficient

	Temp	pH	Tds	EC	Alk	K	Na	Ca	Mg	Cl	NO_3	SO_4	Fe	Cu	Zn	Pb	Ni	Cd
Temp	1.000																	
pH	-.199	1.000																
TDS	.310	-.376	1.000															
EC	.208	-.580	.903	1.000														
Alk	-.161	.380	-.329	-.493	1.000													
K	-.271	.183	.469	.514	-.418	1.000												
Na	.176	-.019	.262	.405	-.594	.498	1.000											
Ca	-.001	-.117	.576	.668	-.321	.705	.768	1.000										
Mg	-.152	.235	-.449	-.437	-.104	-.276	-.161	-.407	1.000									
Cl	.299	-.749	.665	.866	-.405	.305	.226	.488	-.324	1.000								
NO_3	.193	-.709	.432	.490	-.258	-.250	.291	.257	-.129	.410	1.000							
SO_4	.226	-.708	.370	.387	-.222	-.180	.221	.255	-.149	.416	.885	1.000						
Fe	.265	-.766	.407	.494	-.237	-.331	.250	.238	-.102	.474	.978	.849	1.000					
Cu	.169	-.308	.438	.440	-.283	.208	-.286	-.007	-.178	.469	-.227	-.253	-.127	1.000				
Zn	-.429	.271	.096	.160	.281	.206	.113	.187	-.079	-.050	.062	-.242	-.002	-.340	1.000			
Pb	.292	-.515	.934	.807	-.205	.297	-.008	.366	-.508	.652	.454	.478	.430	.495	-.071	1.000		
Ni	.547	-.402	.420	.397	-.053	.034	.381	.456	-.361	.484	.547	.753	.526	-.287	-.212	.445	1.000	
Cd	-.245	.492	.074	.079	-.159	.635	.649	.532	-.398	-.249	-.195	-.276	-.310	-.319	.431	-.140	-.053	1.000

Table 3: R-mode varimax rotated factor analysis of heavy metals

	Factor			
Variable	1	2	3	Communalities
Fe	.839	-.104	.088	.723
Cu	-.313	-.335	.867	.962
Zn	-.027	.857	-.062	.739
Pb	.527	.041	.819	.950
Ni	.883	-.080	-.062	.790
Cd	-.144	.810	-.142	.696

Eigenvalue 1.881 1.521 1.458

% total variance 31.351 25.345 24.304

Cumulative % 31.351 56.696 81.000

Table 4: Q-mode varimax rotated factor analysis.

	Factor				
Variable	1	2	3	4	Communalities
Ok01	-.269	.873	-.105	.070	.850
Ok02	-.265	-.326	-.352	.823	.977
Ok03	.076	-.034	.884	-.016	.789
Ok05	.038	.480	.016	.844	.944
Ok06	.272	.858	-.065	.015	.815
Ok08	-.221	-.127	.778	-.185	.705
Ok10	.991	.035	.012	-.027	.984
Ok15	.991	.035	.012	-.027	.984
Ok14	.871	-.049	-.214	-.143	.828
Ok17	.991	.035	.012	-.027	.984

Eigenvalue 3.977 1.858 1.573 1.451

% total variance 39.768 18.581 15.730 14.507

Cumulative % 39.768 58.349 74.079 88.586

R-mode varimax rotated factor analysis performed for Okaba dry season water samples extracted three factors. Factor one has eigenvalue of 1.881 and total variance of 31.351%. Factor one is characterized by high factor loadings of Ni, Fe and weak loading of Pb. Factor two consists of Zn and Cd with eigenvalue of 1.521 and total variance of 25.345%. High, positive loadings of Cu and Pb were recorded in factor three. This factor has eigenvalue of 1.458 and 24.304% total variance (Table 3).

The R-mode cluster analysis of the heavy metals extracted two clusters. Cluster one consists of Fe, Ni, Cu and Pb with Fe and Ni showing highest similarities. Cluster two is an association between Zn and Cd (Figure 3).

Q-mode factor analysis of the heavy metals yielded four factors. Factor one consist of high, positive loadings of OK10, OK15, OK14 and OK17. This factor has significant eigenvalues and total variance of 3.977 and 39.768% respectively. Factor two has high loadings of OK01, OK06 and weak loading of OK05. This factor has eigenvalue of 1.858 and total variance of 18.581%. Both factors three and four have high, positive loadings of OK03, OK08 and OK02, OK05 respectively (Table 4). Factor three has eigenvalue of 1.573 and total variance of 15.730% while factor four has total variance of 14.507% and eigenvalue of 1.451.

The Q-mode cluster analysis performed extracted three distinctive clusters. Cluster one consist of OK15, OK17, OK10 and OK14. OK14 is linked at Euclidean distance of 5 to the rest cluster. Cluster two is an association between locations OK01, OK06, OK02 and OK05. The last cluster consists of only OK03 and OK08 (Figure 4).

Table 5: Anthropogenic factor (AF) of heavy metals in Okaba water

Heavy metals (mg/l)	Mean value	Cp value	AF value	AF %	Geogenic %
Fe	2.872	1.02	2.84	73.79	26.21
Cu	0.109	0.06	1.82	64.50	35.50
Zn	0.849	0.02	42.45	97.70	2.30
Pb	0.54	0.22	2.45	71.05	28.95
Ni	4.134	1.42	2.91	74.43	25.57
Cd	0.565	0.01	56.5	98.26	1.74

AF $=C_m/C_p$; C_m = measured concentration; C_p = control point concentration.

Table 6: Heavy metal pollution indexing (HPI) and metal indexing (MI) of Okaba water

Heavy metals (mg/l)	Mean value (m/l) (Mi)	Standard value (Si) FEPA	Baseline Value (Ii)	Unit weightage (Wi)	Subindex (Qi)	Wi *Qi
Okaba dry season water HPI = 56.21						
Fe	2.87	0.3	1.02	3.333	2.57	8.57
Cu	0.11	1	0.06	1	0.05	0.05
Zn	0.85	3	0.02	0.333	0.28	0.09
Pb	0.54	0.01	0.22	100	1.52	152
Ni	4.13	0.02	1.42	50	1.94	97
Cd	0.57	0.003	0.01	333.333	80	26666.64
				ΣWi = 487.999		ΣWi *Qi = 26924.35

Okaba dry season water MI = 460.46

Heavy metals (mg/l)	Ci	MAC	MI
	Metal Indexing (MI) table of Okaba dry season water		
Fe	2.87	0.3	9.57
Cu	0.11	1	0.11
Zn	0.85	3	0.28
Pb	0.54	0.01	54
Ni	4.13	0.02	206.5
Cd	0.57	0.003	190

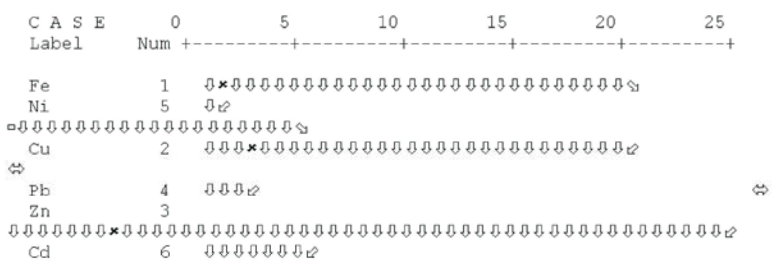

Fig. 3: R-mode cluster analysis of heavy metals

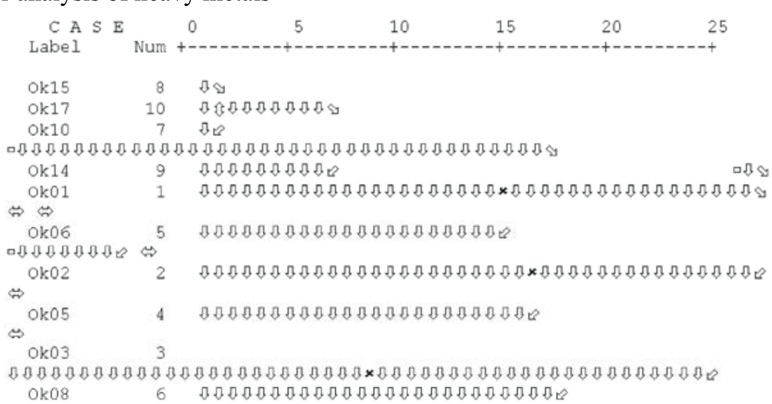

Fig. 4: Q-mode cluster analysis

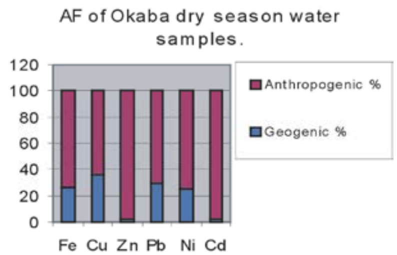

Fig. 5: AF of Okaba dry season water samples

The anthropogenic factor (Table 5), using average heavy metal concentrations reveals the following percentages: Cd 98.26%, Zn 97.70%, Ni 74.43%, Fe 73.79%, Pb 71.05% and Cu has the lowest AF of 64.50%. AF trend of Okaba dry season water samples is: Cd > Zn > Ni > Fe > Pb > Cu (Figure 5).

The HPI of Okaba dry season water samples is 56.21 (Table 6). This is below the critical pollution index value of 100. Metal indexing (MI) also is 460.46. This MI value (Table 6) indicates low water quality because MI>1 is a threshold of warning [7, 9, 10].

DISCUSSION

The major cations and heavy metal trends in Okaba dry season water are: K (9.81) > Ca (6.42) > Na (4.38) > Mg (0.13) and Ni (4.13) > Fe (2.87) > Zn (0.85) > Cd (0.57) > Pb (0.54) > Cu (0.11). The average pH of the dry season water is 6.37. This is attributable to the presence of pyrite, sulphide minerals which are reactive to atmospheric oxygen and water under humid conditions. The initial products of oxidation are ferrous and ferric sulphates, suphuric acid and hydrated ferric oxide [15, 16]. Apart from the association of the major cations, anions and heavy metals to pyrite and sulphide minerals, their generally higher concentration at dry season can be related to the fact that they are susceptible to leaching out by surface and infiltrating waters [17]. Low water pH also favours the residence of heavy metals in solution leading to an amplification of water contamination [17, 11].

The relationship between heavy metals and physiochemical, major ions and among the heavy metals are relatively weak except between Fe – pH, Pb – Tds, Fe – NO_3, Fe – SO_4 and Ni – SO_4 (r = > 0.70). These pairs with relatively strong correlation are significantly related. Weak relationships were also experienced between major ions and physiochemical and among themselves, the exception being the significant relation between Cl, NO_3, SO_4 and pH; Cl – Ec, Ca – K, Ca – Na and SO_4 – NO_3. Where significant regression occurs may suggest same anthropogenic source [18, 19].

R-mode factor analysis yielded three factors. Factors one and two which consists of Ni, Fe, Pb and Zn, Cd suggests anthropogenic source as the dominant source while factor three may be related to natural processes. The R-mode cluster extracted two clusters. Cluster one suggests a mixture of natural and anthropogenic sources while cluster two implies anthropogenic input [20, 21, 13].

Both Q-mode factor and cluster analyses were performed. Four factors and three clusters were extracted in the Q-mode analyses. In factor one, only OK17 was directly affected while in factor two, the locations may have been influenced by mining activities. In factor three, (OK08) and in factor four, (OK02) are also not directly influenced by coal mining. This cluster indicates that all locations in cluster one are not directly linked, while in cluster two, OK01, OK06 and OK05 may have been influenced to various degrees. In cluster three, OK08 is not influenced while OK03 may have been influenced.

The anthropogenic factor (AF) used for heavy metal evaluation of Okaba dry season water samples revealed this trend: Cd > Zn > Ni > Fe > Pb > Cu. Dissolved Fe was lower than expected since Fe may have been oxidized, hydrolyzed and precipitated rapidly, which explains the yellow-red ferric precipitates observed in the channels. The relatively lower concentrations of Pb may be attributable to the sulphides in the study area, their immobile nature and strong affinity for sediments and suspended particles [22]. While lower acidities of water allows heavy metals such as Cd, Zn, Ni, Fe, Pb and Cu to enter into solution phase and be transported from the water, the total heavy metal content was very high in the case of Cd, Zn and Ni, high for Fe and lower for Cu and Pb as these metals appear associated to sulphides in this type of mine [22]. Heavy metals are highly mobilized under moderate acid/acidic conditions. The potential for acid mine drainage and the release of toxic heavy metals from mine wastes exists throughout Okaba area. This poses major environmental hazard to fresh water resources and has enhanced the levels of heavy metals. The implication of this is increasing bioavailability, bioaccumulation and toxicity which may result to serious health and environmental consequences [18, 23].

The HPI for Okaba dry season water samples is 56.21, below the critical pollution level of 100 [9, 10]. Metal indexing on the other hand is 460.46 which implies low water quality [7, 8].

CONCLUSION

Heavy metal pollution (HPI) and metal indices (MI) were used to aggregate the quality of water. HPI indicates no contamination and MI shows that the water quality is low. This study also reveals the effect of coal mining on water with Cd, Zn and Ni as the most impacted heavy metals.

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