

## Research Article

### Cluster Analysis of Metal Concentrations in River Kubanni Zaria, Nigeria

A.W. Butu and E.O. Iguisi

Department of Geography, Ahmadu Bello University, Zaria, Nigeria

**Abstract:** The cluster analysis was used to assess the degree of association of the metal concentrations in river Kubanni Zaria, Nigeria. The main sources of data for the analysis were the sediment from four distinct locations along the long profile Kubanni River which were analyzed using Instrumental Nitrogen Activities Analysis (INAA) techniques. The Nigerian Research Reactor-1(NIRR-1) which is Miniature Nitrogen Source Reactor (MNSR) was used to analyze the data. The result of the laboratory analysis was subjected to cluster analysis. The analysis shows a stable clustering system where the metal concentrations in the four different locations were grouped into two main groups with one outlier. The level of concentration of elements that were sampled in the dry months were cluster in group I and those collected in the raining months were in group II. This strongly support that there is temporal variation in the levels of concentration of metal contaminants between wet and dry seasons in river Kubanni and also confirms the fact that the elements that were collected in the wet season are from the same source and those in the dry season are also from common source.

**Keywords:** Catchment area, cluster analysis, group levels of concentration, metal contaminants

## INTRODUCTION

Cluster analysis is the assignment or grouping of a set of observations into subsets called clusters so that observations in the same cluster are similar in some sense (Wikipedia, 2010). The term cluster analysis encompasses a number of Algorithms and method of grouping of objects of similar kind into respective categories and it was first used in 1939 by Tyron (Satsoft Inc., 2012). The cluster programme produce a pattern that allows for a more resolved visualization of the similarities existing between objects as related to some determined variables (i.e., elemental concentration) especially when the variable are very large (Ewa, 2004).

This method (cluster analysis) is most useful where most statistical methods cannot satisfactorily interpret existing trend in spatially multi-elemental concentrations associated with sedimentary environment of the earth's as is usually the case with geochemical data (Ewa *et al.*, 1992). There are different types of clustering, viz; joining (Hierarchical or tree cluster), two-way joining clustering, k-means clustering and Expectation Maximization (EM) clustering. The hierarchical clustering allows a cluster to be within another cluster but overlapping with another cluster. Cluster method based on hierarchal procedures begins by taking each observation as a cluster itself followed by merging of the two clusters to form a new cluster thereby replacing the two old clusters. Merging of two closer clusters is then repeated until only one cluster is left at the final stage. Tree

hierarchical clustering therefore emanates (n-1). Fusion steps starts from n-cluster with each step being assigned a similarity coefficient.

The cluster analysis is aimed at investigating existing similarities for different zones of the study area based on the concentration of the metallic elements in the zones in river Kubanni Zaria, Nigeria. The method also helps to identify the most dominant element in the study area. The results obtained could be used as a quick-guide in the knowledge of metal concentration in Kubanni River with regard to the contributing factor from the four distinct zones of the study area. Cluster analysis is a Multivariate technique that is useful in statistical analysis of data when the sample size is very large. The aim of this study is therefore to use this efficient statistical method (cluster analysis) to correlate the environmental variables with the levels of concentration of metals in river Kubanni Zaria, Nigeria.

## MATERIALS AND METHODS

The main sources of data for this study are sediments from four different sampling points along the long profile of river Kubanni Zaria, Nigeria. The Kubanni River spans to about 21 km. The sampling points were code named KP1- KP4. The sample period spanned for eleven months starting from December 2007 to October 2008. The sediments collected were prepared in the laboratory and finally analysis. The Certificate reference materials IAEA-SL-3 (sediment) was used to determine the calibration factors for all the elements. The Instrumental Nitrogen Activation

Analysis (INAA) technique was adopted in the analysis of the data using Nigeria Research Reactor-(NIRR-I) which is a Miniature Neutron Source Reactor (MNSR). To analyze the data, two irradiation schemes were adopted based on the half life of the product radionuclide.

For elements leading to short-lived activation products, the samples were irradiated in the outer irradiation channel B4 where the neutron spectrum is soft. Following the short-lived irradiation regime the first round of counting was done for 10 min (i.e., S1) after a waiting time of 2-5 min, the second round of

Table 1: The level of concentration of metals in the sediment in Kp1 (at the Kampagi Hills)

Element/Metals (ppm)		KP1 19/1	KP1 16/2	KP1 4/4	KP1 10/5	KP1 5/7	KP1 2/8	KP1 4/10	KP1 8/12
Magnesium	Mg	BDL	BDL	BDL	4200	BDL	BDL	4500	2600
Aluminium	Al	35000	30000	32000	53000	84000	27000	4500	31000
Calcium	Ca	1600	BDL	BDL	2000	2000	BDL	BDL	BDL
Titanium	Ti	1600	1400	2000	BDL	4500	1300	2600	1500
Vanadium	V	25	33	34	30	53	23	46	25
Manganese	Mn	589	290	304	313	152	179	308	211
Dysprosium	Dy	6.4	3.8	7.1	6.5	8	4.3	8.7	4
Sodium	Na	4000	1300	2000	3600	2000	1500	2000	2000
Potassium	K	20000	18000	28000	24000	17000	15000	20600	18000
Arsenic	As	1	2	2.8	2.6	0.63	2	2.5	1.07
Bromine	Br	BDL	0.3	BDL	BDL	BDL	1.53	BDL	0.51
Lanthanum	La	36	18	27.5	31	20	44	46	45
Samarium	Sm	7.2	4.4	6.3	7.1	5.4	7.1	8.6	7.8
Ytterbium	Yb	9.8	1.6	8.6	9.1	7.7	7.1	4.2	5.5
Uranium	U	5	4.2	5.4	6.4	4.1	5.7	5.2	6.8
Scandium	Sc	3.4	2.5	3.4	4.5	1.7	4.9	4.6	5.2
Chromium	Cr	10	14	18	12	13	28	20	32
Iron	Fe	13000	13000	20000	20000	8000	22000	18000	16000
Cobalt	Co	4.5	4	5.8	5.1	2.6	5	7.4	4
Zinc	Zn	28	40	BDL	BDL	23	226	40	BDL
Rubidium	Rb	155	106	173	238	99	131	156	123
Caesium	Cs	4.7	6	6.1	11	3.2	3	11.6	3.5
Barium	Ba	464	521	715	549	357	374	518	419
Europium	Eu	0.8	BDL	1	1	0.6	0.8	1.4	1.1
Lutetium	Lu	1	0.25	1	1	1.3	0.8	0.6	0.63
Hafnium	Hf	16	6.5	13	12	8	15.3	16.6	38
Tantalum	Ta	1.8	1.7	2	2	1	1.5	1.8	2.4
Antimony	Sb	BDL	0.22	BDL	BDL	BDL	6.2	BDL	0.6
Thorium	Th	20	6.5	15	15	14	18	18.3	32

BDL = Below detectable limit; Field studies 2007/2008

Table 2: The level of concentration of metal in sediment at Kp2 (ABU Dam)

Element/Metals (ppm)		KP2 19/1	KP2 16/2	KP2 4/4	KP2 10/5	KP2 5/7	KP2 2/8	KP2 4/10	KP2 8/12
Magnesium	Mg	BDL	BDL	BDL	2600	BDL	1800	BDL	BDL
Aluminium	Al	30000	2600	30000	32000	37000	35000	46600	43000
Calcium	Ca	1200	1300	BDL	2000	1200	BDL	BDL	BDL
Titanium	Ti	1100	4500	3000	4000	2500	2200	2600	2000
Vanadium	V	24	31	32	35	25	40	36	106
Manganese	Mn	308	336	400	346	224	218	287	181
Dysprosium	Dy	6	6.2	3.1	4.4	4.7	4	6	3.2
Sodium	Na	2000	1800	2000	2400	1500	1500	600	2000
Potassium	K	21000	20000	21000	34000	14000	20000	13800	21000
Arsenic	As	0.52	0.7	2	1.9	0.62	1.3	1.38	1.1
Bromine	Br	BDL	0.6	BDL	0.3	BDL	BDL	0.73	0.34
Lanthanum	La	27	30	34.7	17	57	16.2	29	17
Samarium	Sm	4.8	5.1	6	3	15.5	3.1	322	3.1
Ytterbium	Yb	3	2.8	2.5	1.23	14.5	2	8	1.6
Uranium	U	4.4	4.6	5	4	BDL	3.5	13	3.3
Scandium	Sc	1.8	3.5	2.2	1.8	2.1	2.2	4.4	2
Chromium	Cr	14	22	21	23	28	22	25	15.4
Iron	Fe	10200	14000	23000	16300	16000	15000	16000	14000
Cobalt	Co	1.7	4.2	2.8	4.1	2.5	2.7	6.3	2.6
Zinc	Zn	BDL	49	13.4	24	67	32	BDL	27
Rubidium	Rb	99	107	110	144	80	94	64	107
Caesium	Cs	1.3	2.7	2	2.1	1.5	2	3	1.6
Barium	Ba	428	476	344	496	319	436	139	347
Europium	Eu	0.43	0.54	0.6	0.6	0.5	1	1	0.7
Lutetium	Lu	0.43	0.4	0.32	0.2	2.1	0.3	0.4	0.2
Hafnium	Hf	19	19	20	10	23	15.2	10	10
Tantalum	Ta	2.15	2	2.4	1.2	5.2	1.1	2	2.5
Antimony	Sb	0.4	0.2	0.22	BDL	BDL	BDL	BDL	0.2
Thorium	Th	18	15	25	10	42	10	11	11

BDL: Below detectable limit; Field work 2007/2008

Table 3: The level of concentration of metals in sediment at kp 3

Element/Metals (ppm)		KP3 19/1	KP3 16/2	KP3 4/4	KP3 10/5	KP3 5/7	KP3 2/8	KP3 4/10	KP3 8/12
Magnesium	Mg	2100	BDL	BDL	2400	4000	4000	BDL	2400
Aluminium	Al	34000	34000	BDL	23000	75000	69000	27000	55000
Calcium	Ca	BDL	BDL	8000	3000	4500	17000	BDL	4000
Titanium	Ti	3000	4000	BDL	2500	4100	3500	3600	4100
Vanadium	V	25	24	BDL	25	61	57	19	42
Manganese	Mn	151	154	145	244	340	289	263	220
Dysprosium	Dy	6	8.1	4	5.1	11.1	7.3	9	7.7
Sodium	Na	2100	2700	4300	2600	2000	1400	1600	1500
Potassium	K	23000	27000	26000	13000	17000	13000	20000	1700
Arsenic	As	1.7	1.1	15.7	1.7	1.7	2.4	BDL	1.5
Bromine	Br	BDL	0.7	7	BDL	BDL	2	0.42	1
Lanthanium	La	21	54	30.2	26	19	59	41	44
Samarium	Sm	6.4	10.1	5	4.3	5.1	10	375	8.1
Ytterbium	Yb	5.9	3.9	2	2	8.5	9.5	12	4
Uranium	U	4.2	6.2	2	2.7	4.3	6.7	11.6	5.8
Scandium	Sc	4.3	3.2	7.2	2	2.3	7	2.3	5.3
Chromium	Cr	26	12	45	46	18	42	15	30
Iron	Fe	15400	13000	22000	25400	13000	30000	10000	22000
Cobalt	Co	3.4	3.2	7.1	2.5	3	7.3	3	6.4
Zinc	Zn	83	97	103	133	BDL	495	BDL	349
Rubidium	Rb	147	132	42	67	145	152	60	121
Caesium	Cs	3.3	2.5	5.1	BDL	4.1	4	2	3
Barium	Ba	419	392	113	199	561	508	176	370
Europium	Eu	1.1	0.8	1	0.45	0.7	1	0.6	1
Lutetium	Lu	0.76	0.4	0.3	0.24	1	1.1	0.5	0.6
Hafnium	Hf	32	27	5.1	9	12	20	24	23
Tantalum	Ta	2.14	2.4	1	3.5	1.4	2.2	3	2
Antimony	Sb	0.44	0.47	2.1	1	1	8.5	BDL	1
Thorium	Th	31	30	7	19	10	30	22.2	22

BDL: Below detectable limit; Field work 2007/2008

Table 4: The level of concentration of metals in the sediment in kp4 (near the confluence with river Galma Gyelesu area)

Element/Metals (ppm)		KP4 19/1	KP4 16/2	KP4 4/4	KP4 10/5	KP4 5/7	KP4 2/8	KP4 4/10	KP4 8/12
Magnesium	Mg	BDL	1300	2700	BDL	BDL	BDL	BDL	2400
Aluminium	Al	35000	34000	41000	29000	65000	20000	43000	35000
Calcium	Ca	1600	BDL	BDL	1000	BDL	BDL	2000	2000
Titanium	Ti	3600	2300	5000	2000	4000	1400	BDL	4000
Vanadium	V	26	22	41	38	41	15	39	22
Manganese	Mn	148	122	227	225	162	279	105	208
Dysprosium	Dy	7	5.3	7.1	10.3	8	4.4	4.1	12
Sodium	Na	2100	2000	1400	1400	2000	2300	2000.00	2000.00
Potassium	K	23000	25000	16000	16000	21000	24000	23000	22000
Arsenic	As	1.7	1	2	2	0.47	1.5	1.1	BDL
Bromine	Br	BDL	0.5	0.54	0.44	BDL	0.3	BDL	0.45
Lanthanium	La	21	32	35	52	83	50.7	49	88
Samarium	Sm	6.4	5.4	5.8	8.9	12.2	8.4	49	12
Ytterbium	Yb	2.64	0.3	3.8	4.4	4.8	4.6	12.2	17.6
Uranium	U	4.2	3.7	5.7	5.8	5.7	6.2	8	7
Scandium	Sc	2.7	3	4.3	6.3	3.7	5.8	3.7	3.2
Chromium	Cr	13	16	37	34	30	44	26	26
Iron	Fe	14200	10000	18000	23000	15000	20000	13000	10000
Cobalt	Co	4.9	3.1	3.7	4.7	4	5.1	3.7	3
Zinc	Zn	BDL	68	77	237	39	57	109	BDL
Rubidium	Rb	148	85	97	123	154	145	139	152
Caesium	Cs	7	2.4	2.5	3.7	3.3	4.2	1.5	1.4
Barium	Ba	366	189	307	412	340	583	757	272
Europium	Eu	0.76	0.6	0.7	1.1	1	1.2	0.6	1
Lutetium	Lu	0.36	0.1	0.6	0.63	0.5	0.7	1.3	1.7
Hafnium	Hf	7	14	27	28	21	23	29.3	51
Tantalum	Ta	1.17	1.4	2	2.5	1.6	2.3	1.8	2.6
Antimony	Sb	0.5	0.0	0.7	BDL	BDL	0.3	2	1.2
Thorium	Th	13	13	19	28	44	27	43	47

BDL = Below Detectable Limit; Field Work 2007/2008

counting was carried out for another 10 min (S2) after a waiting Period of 3-4 h. For elements leading to long lived activation products, samples were irradiated for 6 h in the inner irradiation channel and the first round of counting was carried out for 30 min after a waiting time of 4-5 h then the second round of counting was performed for 60 min. Finally the identification of

gamma-ray of product radionuclide through their energies and quantitative analysis of their concentrations were obtained by using the gamma-ray spectrum analysis software WINSPAN 2003.

The metal concentrations from the four different sampling points (Table 1 to 4) were subjected to cluster analysis. Each sample could be regarded as a point in

an *n*-dimensional space. Cluster analysis begins with the calculation of the separation of the points (concentration of elements for each sample) in the *n*-dimensional space.

The mathematical calculations are translated into scoring levels of the computer with resulting dendrogram illustrating the way the samples are clustered.

## RESULTS AND DISCUSSION

Figure 1 shows the cluster out-put in the form of a dendrogram or tree diagram (top down). From the cluster routines of the data sets from all the zones (Kps). It is clear from the dendrogram that there are two clearly defined cluster groupings (Group I and II).

**Group I:** All the sediments in the group were collected within the months of October (Kp3, Kp1, Kp4, Kp2) December (Kp4, Kp2, Kp1) January (Kp1, Kp2, Kp3, Kp4, Kp2), February (Kp3, Kp4, Kp2) April (Kp1, Kp2, Kp4, Kp4) May (Kp2, Kp4, Kp1) July (Kp2) and August (Kp2, Kp4). Group I has three main branches or subgroups namely group IA, IB and group IC and an outlier.

**Group II:** It is clear from the grouping that all the samples in these four distinct locations were collected during the dry season (October-May) and in the August. The elements groupings in subgroup IC were collected in the peak of the dry season, in the months of October-December and January. The ones in group IB were collected in the months of April, May and August, while those in group IC were also collected in the dry months of April, May, October and July.

The result of cluster analysis (Fig. 1) shows how the elements clustered in group I. It is convincing evidence that there is a temporal variation in the levels

of concentration of metals in river Kubanni, because all the metals collected in four different zones in the dry season are clustered in one group. This therefore suggests abundantly that these metals have similar characteristics or sources. It is a possible evidence that the metals in these group must have been eroded into the river from the surrounding catchment area which is dominated by human activities such as agricultural, research activities, mechanical works, quarrying and other artisan works during runoff and must have been in a cemented or consolidated form in the sediment in the dry period. Another possible reason for this grouping could be that the elements are in high levels of concentration in the surrounding soil or they are from the same geologic formations.

The elements in Kp3 (Jim Harrison/Green-area) in the month of April remained as an outlier from other groups, standing out alone. This is a convincing proof of the success of the cluster analysis (Fig. 1). It therefore reveals the probability of different type or levels of concentration of elements which must have been eroded into this zone of the river from either the vast farmlands that are heavily cultivated annually and are been treated with large quantity of chemical fertilizer and herbicides or from CERT, Nigeria College of Aviation Training Centre or the densely populated area of Kwangila, Zango and Palladan which are all located up stream of KP3. The input data also revealed that the concentration of the elements determined in Kp3 in April is grossly different from the rest.

The clustering of elements in group II, shows that all the samples in the four different locations were generally collected in the months of raining season. Group II has two major branches or sub groups, namely group IIA and group IIB. The elements in group IIA were all collected in the months of July in three different locations (Kp1, Kp3 and Kp4). This strongly

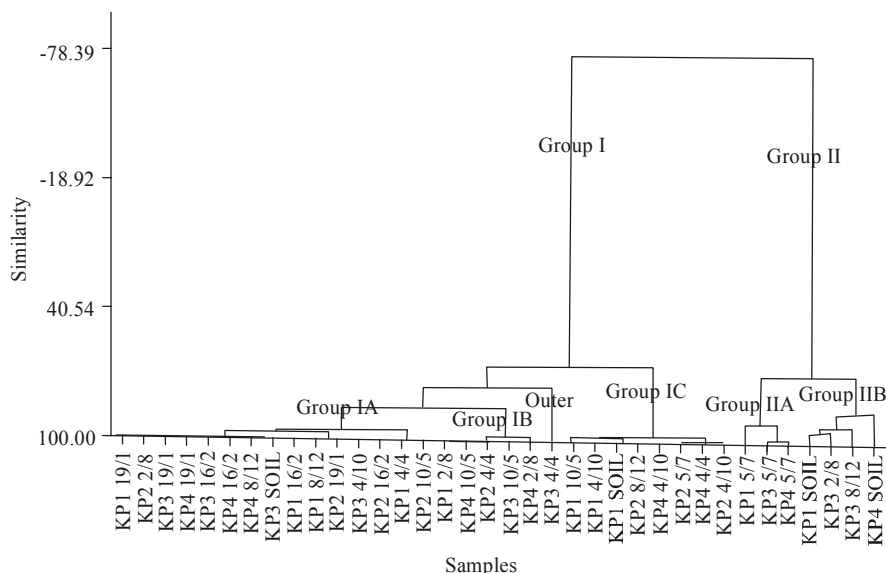


Fig. 1: Dendrogram showing the cluster analysis of all the metal contaminants in river Kubanni

proved that the elements in group IIA have similar characteristics in terms of sources and levels of concentration. The grouping of elements in group IIA which were all collected in the peak of the raining season further suggests strongly that these metal contaminants have a common source or origin. Kp1 (Kampangi Hill), Kp3 and Kp4 (Gyelesu area) are all known to have similar characteristics. These areas are known to be intensively cultivated areas where application of chemical fertilizers is high and the areas are also highly populated with different types of human activities. It is therefore obvious that most of the fertilizers from the vast farm lands and other effluents as well as synthetic products from household and waste from mechanical workshop and electronic waste such as used Tv, used batteries, used bulbs, etc from the numerous heaps of refuse dumps that dot the entire catchment area must have drained into these zone of river Kubanni during storm or these elements are released and gradually drained from the refuse dumps into the river by surface or subsurface flow during the raining season in July, consequently resulting into the clustering of these elements in one group because of their similarity in nature and source. Clustering has been confirmed by two groupings and by exclusion of outlier which proved the effectiveness of the technique. Finally clustering of elemental concentration from river Kubanni shows that elements that were collected in the dry season have similar sources as well as those in the wet season.

## CONCLUSION

Metal concentrations from four different sections of river Kubanni were subjected to Cluster analysis. From the cluster routines of the data sets from all the Zones, the dendrogram shows two clearly defined cluster groupings (group I and II).

The analysis shows a stable clustering system where the elements that were collected in the wet season in group II with one outliers. This clearly indicates that there is temporal variation in the level of concentration of metals in river Kubanni. The grouping of the metal concentration also indicates that the metals in group I are from a common source and also the ones in group II are from other sources too.

## REFERENCES

- Ewa, I.O., 2004. Data evaluation of trace elements determined in Nigerian coal using cluster procedures. *Appl. Radiat. Isot.*, 60(5): 751-758.
- Ewa, I.O.B, M.O.A Oladipo and L. Dim, 1992. Cluster analysis of elemental concentration of cored Nigeria sediment. *J. Environ. Sci. Heal. A.*, 29(1): 1-11.
- Satsoft Inc., 2012. Electronic Statistical Textbook. Reactors of Statistical Data Analysis Software and Services. Retrieved from: [http://www.statsoft.com/textbook/cluster analysis](http://www.statsoft.com/textbook/cluster%20analysis).
- Wikipedia, 2010. The Free Encyclopaedia. Retrieved from: <http://www.wikipedia.com>.