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Using Factor-Cluster analysis and Enrichment methods to evaluate impact of cement production on stream sediments around Obajana cement factory in kogi state, North Central Nigeria

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ABSTRACT
The objective of the study is to evaluate the degree of stream sediments pollution around the cement factory. The heavy metals were assessed by factor and cluster analyses. Factor results revealed four sources of pollutants as explained by the four factors (84.83%) to include vehicular, effluents from factory, natural processes of dissolution/ co precipitation and ionic exchange. The R and Q- mode clusters yielded three clusters each. Also used for heavy metal assessment are, enrichment factor, contamination factor and pollution load index. EF indicates that Fe, Zn, Ni and Cd in the sediment range from depletion to minimal enrichment while in few locations Fe are moderately enriched. CF also show that the sediments have moderate contamination with respect to Fe, Zn, Ni and Cd. PLI revealed progressive deterioration of locations Obj01, Obj07 and Obj21.

Key words: Factor analysis; Cluster analysis; Anthropogenic; Pollution load index.

INTRODUCTION

The main raw materials needed to manufacture cement are limestone/marble, clay, laterite and gypsum. Cement production involves the grinding of the limestone/marble, sandstone and clay to the required size and consistency. The mixture is then fired in the kiln calciner where the limestone, clay and sandstone form a clinker (fig.1). The clinker is ground and gypsum is added to control the hardening period of the cement.

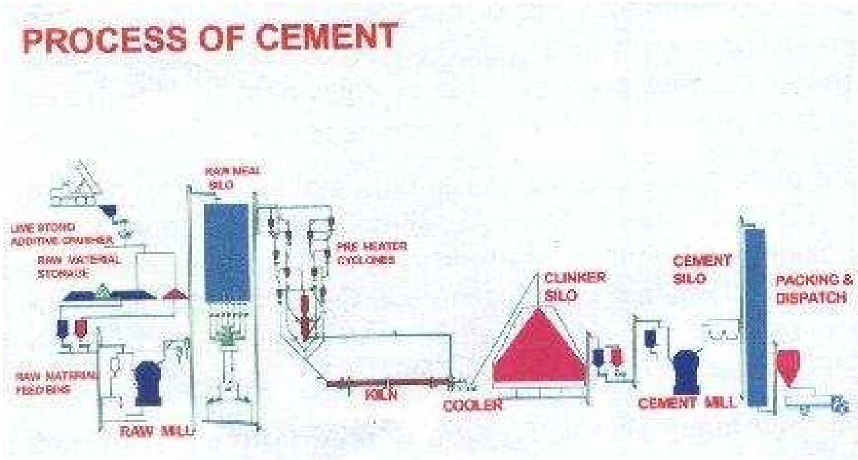

Fig 1: Cement production stages.

The ground clinker and gypsum mixture is now ready for marketing as cement. The potential impacts of production could result from construction and operation of the ropeway; on-site storage of the crushed limestone, clay, laterite, sandstone and gypsum; dust from grinding and mixing of raw material; dust and combustion by products from the calciner; dust from clinker grinding and bagging; wastewater used for bearing cooling, and sewage discharge from staff housing and offices and disposal of solid wastes.

The major constituents in dust from cement manufacturing plants are alumina, silica, metallic oxides and clay, trace amounts of organic chemicals (dioxins and furans), heavy metals (cadmium, lead and selenium) and radio nuclides (Nitish, 2008). Typical gaseous emissions to air from cement manufacturing plants include nitrogen oxides (NOx), sulphur dioxide (SO_x), carbon oxides (CO and CO_x) and dust.

During cement manufacturing operations, effluent discharge is generated from cooling process equipment, wet scrubbing kiln stack emission for recovering cement kiln dust and runoff water from the outdoor areas. Effluents contain mainly dissolved solids (potassium and sodium hydroxides, chlorides and sulphates), suspended solids (calcium carbonate) and waste heat. Other issues to consider around production area are the existing condition of any water body or groundwater that may be changed as a result of waste disposal during construction and operation, run-off from wash-down areas, fuel storage facilities, roads and parking areas, waste disposal (litter or solid waste), toxic and hazardous waste (Nitish, 2008).

Geology of study area:

These study areas lies within the Benin-Nigeria shield, situated in the Pan-African mobile zone extending between the ancient Basements of West African and Congo Cratons in the region of Late Precambrian to Early Palaeozoic orogenies (Rahaman, 1976; Odigi, 2002 Ekwueme , 2003). The Basement Complex rocks of Nigeria are composed predominantly of migmatite gneiss complex; slightly migmatised to unmigmatised paraschists and metaigneous rocks; charnockitic, older granite suites and unmetamorphosed dolerite dykes. (Rahaman, 1976).

The Precambrian Basement rocks of Obajana area, Southwestern Nigeria comprise of schists and gneisses which have been subjected to major supracrustal tectonic events such as the Dahomeyan (3000± 200Ma), Eburnean (1850 ± 250Ma), Kibaran (1000± 100Ma), and Pan-African (550± 100Ma). (Ezepue and Odigi, 1993).

The Obajana gneisses (fig.2) comprise of three types of rocks designated as quartz-biotite gneiss; quartz-biotite-hornblende-pyroxene gneiss and quartz-biotite-garnet gneiss (Odigi and Ezepue, 1993; Ezepue and Odigi, 1994; Odigi, 2002). According to these authors above, igneous rocks of this area occur as small, circular to oval outcrops and include members of the older granite suite mainly granites, granodiorites and syenites while associated schists in the area are: quartz-biotite schist, amphibolite schist, muscovite schist and quartzitic schist.

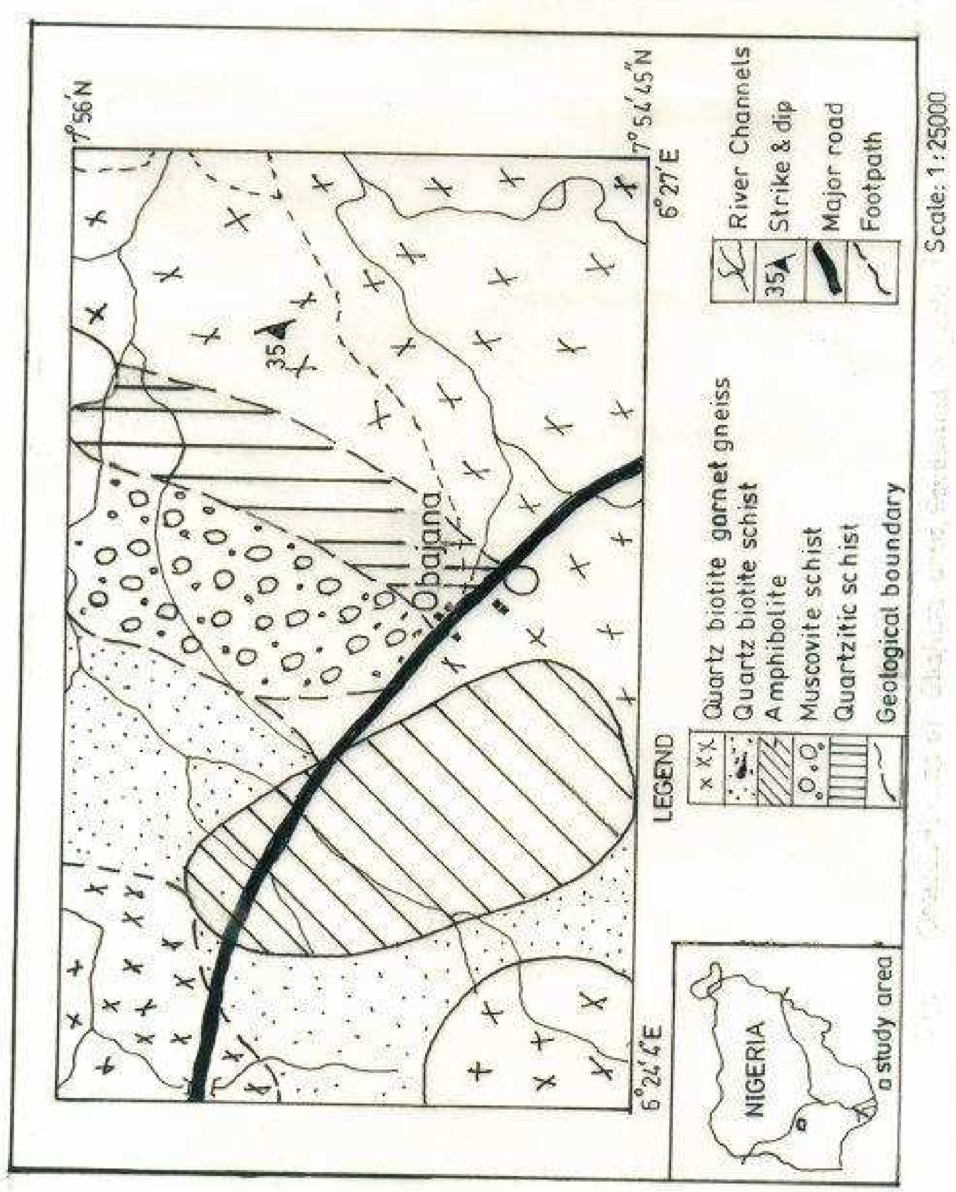

Fig.2: Geological map of study area (after Odigi, 2002)

MATERIALS AND METHODS

A total of nine ((9) stream sediments were collected from tributaries around the cement production area (fig.3). Sample points were located and recorded using GPS. The samples were collected randomly but evenly distributed along the stream channels. The sediments were sun-dried, disaggregated (not crushed) using a pestle and mortar and sieved to minus 80 meshes

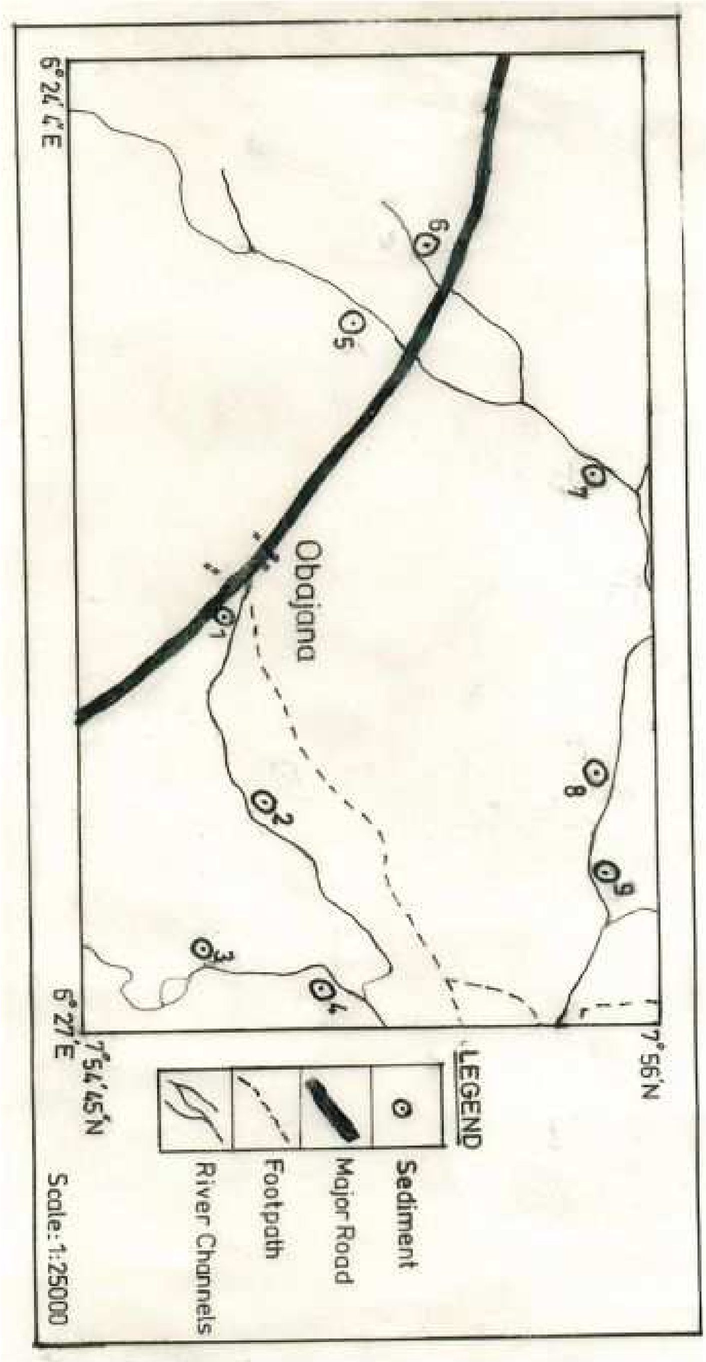

Fig 3: Sample location map of study area.

(0.177mm) with cellulose nitrate filter. 0.1g of each sample was digested with 3ml of 1:2 mixtures of perchloric acid and hydrofluoric acid. The concentrations of six trace metals and four major cations were determined by AAS. Analytical procedures, operational parameters, calibration and standardization use in this study is according to APHA, 2002. All analysis was performed in Agriculture Faculty, Soil Science Dept., Kogi State University, Anyigba.

Data Analysis: Analytical results expressed in parts per million (ppm) were log-transformed and statistically treated using SPSS version 11.0 software. Factor and cluster analyses were computed for the ten variables in the stream sediments using the SPSS version 11.0 software. The total variance in each factor is re-expressed by the eigenvalue provided by the principal component solution as an initial set of uncorrelated linear transformations of original variables. The factor loadings, which can be regarded as combination between the elements, were then computed after rotating the original principal component solution according to Kaiser's varimax criterion (Praveena, et al., 2007). In this study factors with eigenvalues greater than 1 were retained and only variables with loadings greater than 0.40 were considered significant groups of a particular factor. Cluster analysis was also used for investigating the similarities between major variables and heavy metals from the sediment samples. Evaluations of similarity were based on the average linkage between groups (Praveena, et al., 2007).

Determination of enrichment factor: To evaluate the magnitude of contaminants in the sediments, 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 Simex and Helz (1981); Atgrin etal., 2000 was employ to assess degree of contamination, understand the distribution of elements of anthropogenic origin from sites by individual elements in sediments.

EF= (C_m/C_{Fe}) sample/ (C_m/C_{Fe}) control/background value. Where (C_m/C_{Fe}) sample is the ratio of concentration of trace metal (C_m) to that of Fe (C_{Fe}) in the sediment sample and (C_m/C_{Fe}) control/background value is the reference ratio in the control/background value. Fe is selected as reference element because in wet lands, it is mainly supplied from sediments and is one of the widely used reference elements (Sekabira et al., 2010).

Assessment of pollution load index (PLI): the pollution load index (PLI) proposed by Tomlinson et al. 1980 has been used in this study to measure PLI in sediments of Obajana cement production area. 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 for a site = nth√ CF1*CF2….*CFn. Where n number of metals study (six in this study) and CF= contamination factor.

RESULTS AND DISCUSSION

Univariate and multivariate statistical analyses:

The sediment sample results statistics are shown in table 1 below. The multivariate statistics shows the correlation coefficients between measured parameters in sediment samples.

Table 1: Descriptive statistics of major cations and heavy metals in stream sediments from Obajana cement production area

Na	K	Ca	Mg	Zn	Cu	Cd	Pb	Fe	Ni
1.44	19.05	16.08	4.63	1.37	.45	.52	.68	1647.002.50	
1.27	15.51	6.19	8.40	1.07	.37	.62	.48	1498.50.89	
1.83	18.03	17.38	4.41	1.25	.35	.47	.30	1533.001.75	
10.42	10.01	16.04	10.41	2.39	1.20	1.21	.42	1686.00	1.20
2.80	17.30	16.80	5.36	1.50	.54	.45	.41	1395.00.81	
1.59	10.42	18.84	3.81	2.00	.49	.38	.44	1851.00	1.00
2.30	9.65	21.75	5.30	1.66	1.01	.57	.40	1365.00.68	
2.04	22.80	19.70	9.42	2.38	.76	.69	.50	1971.001.01	
1.62	8.90	43.21	4.32	1.43	.16	.89	.33	1339.501.15	
Min	1.27	8.90	6.19	3.81	1.07	.16	.38	.30	1339.00.68
Max	10.42	22.80	43.21	10.41	2.39	1.20	1.21	.68	1971.001.75
Mean	2.81	14.63	19.55	6.23	1.67	.59	.64	.44	1587.331.22
Cp	1.93	13.70	20.42	6.32	1.84	.87	.60	.50	1547.001.03
SD	2.89	5.03	9.88	2.48	.48	.34	.26	.11	220.43 .57

Table 2: Correlation coefficients matrix of elements from Obajana dry season sediment samples.

	NA	K	CA	MG	ZN	CU	CD	PB	FE	NI
NA	1.000									
K	-.324	1.000								
CA	-.122	-.422	1.000							
MG	**.621**	.188	-.391	1.000						
ZN	**.591**	-.063	.055	**.528**	1.000					
CU	**.734**	-.178	-.272	**.599**	**.706**	1.000				
CD	**.784**	-.367	.269	**.654**	**.452**	**.453**	1.000			
PB	-.118	**.440**	-.412	.155	.054	.072	-.144	1.000		
FE	.128	**.404**	-.299	.378	**.689**	.247	.002	**.418**	1.000	
NI	-.085	.370	-.060	-.262	-.253	-.286	-.088	**.497**	.152	1.000

Table 3: Varimax rotated R mode factor matrix for Obajana stream sediment samples.

	Factor				
Variable	1	2	3	4	Communalities
NA	**.943**	7.244E-02	-3.870E-02	-4.780E-02	.899
K	-.311	.299	**.580**	**.407**	.688
CA	-.105	-3.965E-03	-.945	-5.199E-02	.907
MG	**.745**	.272	**.420**	-8.507E-02	.812
ZN	**.523**	**.816**	-.116	-.170	.981
CU	**.742**	.311	.218	-.254	.759
CD	**.887**	-5.414E-03	-.330	4.769E-02	.899
PB	-1.284E-02	.260	**.436**	**.668**	.704
FE	6.483E-02	**.904**	.224	.217	.920
NI	-9.890E-02	-7.050E-02	-3.369E-02	**.948**	.915
Eigenvalue	3.177	1.822	1.819	1.666	
% of Variance	31.770	18.219	18.186	16.657	
% Cumulative	31.770	49.988	68.174	84.831	

Factor analysis: R mode factor analysis of all chemical constituents from Obajana sediments were carried out. The analysis generated four factors which together account for 84.8% of the total variance. The rotated loadings, eigenvalues, percentage of variance and cumulative percentage of all four factors are given in table 3. The first eigenvalue is 3.18, it account for 31.77% of the total variance. This constitutes the first and main factor. The second and third factors eigenvalues are 1.82 and 1.81 respectively and these accounts for 18.22% and 18.20% respectively of the total variance. The fourth factor has eigenvalue of 1.67 and account for 16.66% of variance. Factor one which account for 31.77% of total variance is characterized by high loadings of Na, Cd, Mg, Cu and Zn. The Cd, Cu and Zn may be associated with Na and Mg rich rocks found in the area. Factor two accounts for 18.22% of total variance and consists of high loadings of Fe and Zn. These two heavy metal associations could be due to natural/anthropogenic mixture because both Fe and Zn have high EF and CF values. Factor three accounts for 18.19% of total variance with high loadings of K, Mg, and Pb. The high loading for Pb could also be associated with K and Mg rich rocks release due to natural processes. Factor four accounts for 16.66% of total variance. This factor consists of Ni, Pb and K. The association of Ni and Pb with K is likely due to anthropogenic factors. Pb and Zn has been distributed between 3^{rd} and 4^{th} factors and 1^{st} and 2^{nd} factors respectively indicating that dual sources may have contributed to their concentrations (Sekabira et al., 2010).

Cluster Analysis: Is a series of multivariate methods which is used to find true groups of data or stations. In clustering the objects are grouped such that similar objects fall into the same class (Reghunath et al, 2002). The hierarchical method of cluster analysis, which is used in this study, has the advantage of not demanding for prior knowledge of the number of clusters which the non- hierarchical method does. As a distance measure, the squared euclidean distance was used, which is one of the most commonly adopted measures (Reghunath et al, 2001). The output of cluster analysis is given as a dendrogram (fig. 4). There are two major clusters: cluster one consists of Na, Cd, Mg, Zn and Cu which corresponds to factor one. Cluster two consists of Pb, Ni and k linked weakly to Fe. This cluster also corresponds to factor four except the weak bond with Fe. As evident from the cluster diagram, cluster two could be attributed to anthropogenic source (Harikumar and Jisha 2010). Ca is distinctive from these factors and have high but negative loading in R-mode factor analysis suggesting distinct process from the rest clusters.

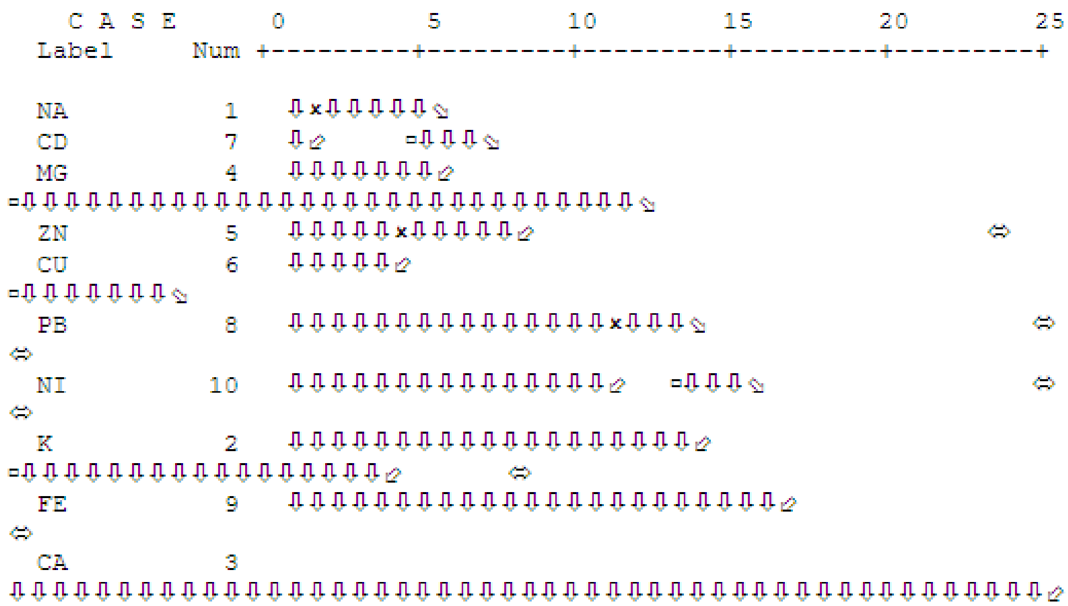

Fig 4: R mode cluster analysis of Obajana stream sediment samples.

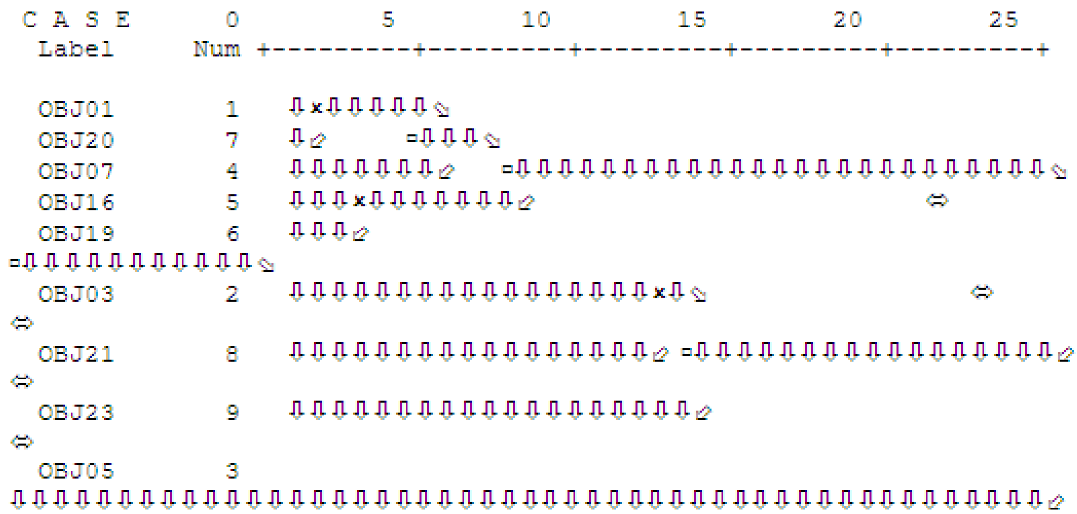

Fig 5: Q mode cluster analysis of Obajana stream sediment samples.

The Q-mode cluster analysis of the same stream sediment shows three clusters (fig.5). Cluster one consists of locations Obj01, Obj20, Obj07, Obj16 and Obj19. Cluster two is made up of locations Obj03, Obj21 and Obj 23. The third cluster is distinctively made up of Obj05. In the R-mode dendrogram, the highest similarity is observed between Na and Cd; Zn and Cu; Na and Mg; Cd and Zn and Pb and Ni in that order while the Q-mode cluster shows maximum similarity between locations Obj01, Obj20, Obj16, Obj19, followed by locations Obj03 and Obj21 and Obj05 distinct.

Tables 5a&b: Enrichment factor (EF) of heavy metals with respect to each location and class classification (after Sutherland, 2000)

Heavy metals	Sample locations								
	Obj01	Obj03	Obj05	Obj07	Obj16	Obj19	Obj20	Obj21	Obj23
Fe	14.18	1.67	1.46	0.84	1.11	1.1	0.98	0.99	1.11
Cu	0.49	0.04	0.41	1.27	0.69	0.47	1.32	0.69	0.21
Zn	0.7	0.6	0.69	1.19	0.9	0.91	1.02	1.02	0.9
Pb	1.28	0.99	0.61	0.77	0.91	0.74	0.91	0.78	0.76
Ni	2.28	0.89	1.71	1.1	0.87	0.81	0.75	0.77	1.29
Cd	0.08	0.11	0.79	1.85	0.83	0.53	1.1	0.9	1.71

EF Indices	Degree of Enrichment	Heavy Metals
EF ≤ 1	background concentration	
EF 1-2	depletion to minimal enrichment	Fe, Zn, Cd and Ni
EF 2- 5	moderate enrichment	Fe
EF 5- 20	significant enrichment	
EF 20- 40	very high enrichment	
EF > 40	extremely high enrichment	

EF is a convenient measure of geochemical trends and it is used for making comparisons between areas. Except Fe at Obj01 and Ni at Obj01 that are significantly enriched and minimally enriched respectively, every other location has EF values below one.

From the EF values in table 5a, EF values of Fe in Obj01 (14.18) is significantly enriched while Obj03 (1.67), Obj05 (1.46), Obj16 (1.11), Obj19 (1.10) and Obj23 (1.11) tends towards depletion to minimal enrichment. Cu at Ob07 (1.27) and Obj 20 (1.32) are also minimally enriched with respect to Cu. Zn is only minimally enriched at Obj 07 (1.17), Obj20 & 21 (1.02) each. Pb is minimally enriched Obj01 (1.28). Ni on the other hand is moderately enriched at Obj01 (2.28) and minimally enriched at Obj05 (1.71), Ob07 (1.10) and Obj 23 (1.29). Cd is minimally enriched in locations Obj07 (1.85), Obj20 (1.10) and Obj23 (1.71). On the basis of EF values, Obj01, Obj05, Obj07, Obj20 and Obj23 have been minimally to moderately contaminated.

Elements which are naturally derived have an EF value of nearly unity while elements of anthropogenic origin have EF values of several orders of magnitude (Sekabira etal. 2010). According to Harikumar and Jisha 2010, EF values greater than 1.5 have such heavy metals derived from other sources suggesting environmental contamination by those particular heavy metals. It is presumed that high EF values indicates an anthropogenic source of trace metals mainly from activities such as industrialization, deposition of industrial wastes etc (Harikumar and Jisha, 2010). Since the bioavailability and toxicity of any heavy metal in sediment depend on chemical form and concentration of the metal (Kwon, et al. 2001), it can be inferred that trace metals in sediments samples with high EF values, along with higher labile fractions in sediments are potential sources for mobility and bioavailability in the aquatic ecosystems.

EF values indicate that Fe, Zn, Cd and Ni concentrations need to be monitored to avoid potential pollution risk in the future.

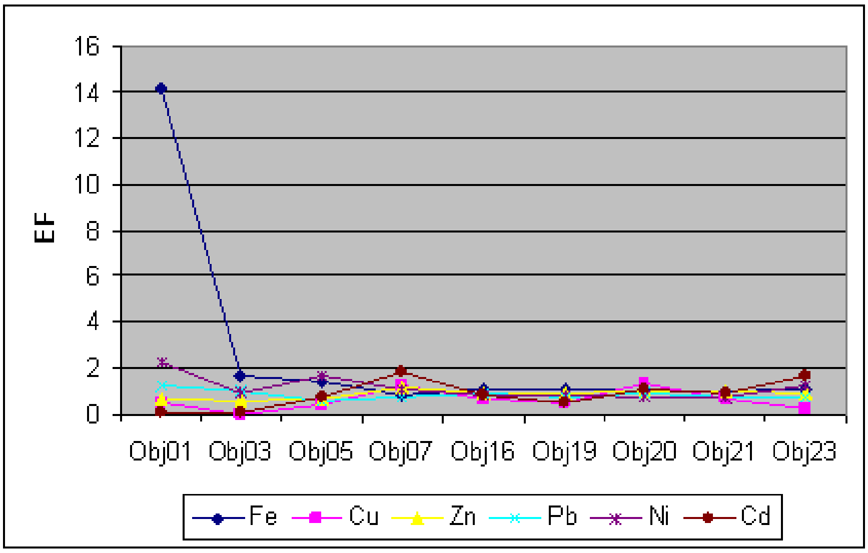

Fig 6: EF against sample locations of Obajana sediments.

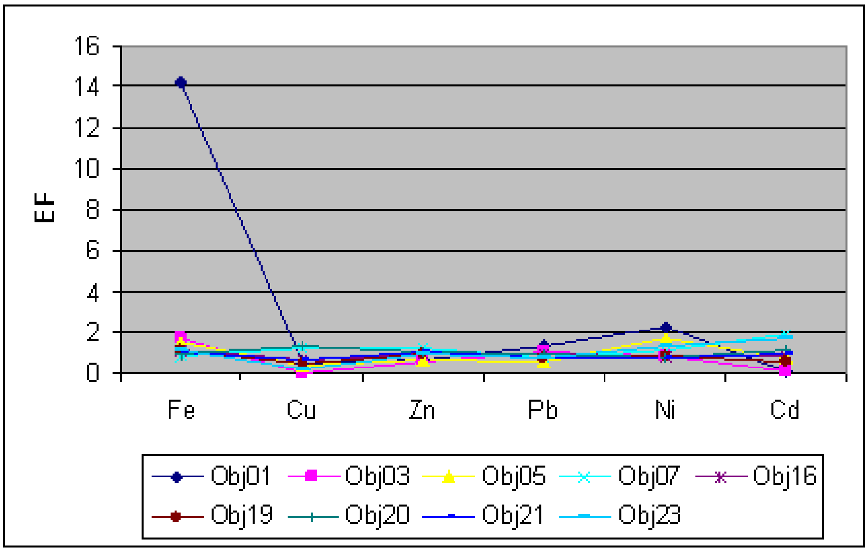

Fig 7: Plot of EF against heavy metals from Obajana sediment samples.

EF versus locations and EF versus trace metals distributions and pattern are shown in figs 6 and 7. From fig. 6 values of EF with respect to the metals are seen and fig. 7 shows each trace metal at various locations.

Tables 7a&b: Contamination factor (CF), Pollution Load Index (PLI) of heavy metals in sediments and classes (after Hakanson, 1980).

Heavy metals	Sample locations								
	Obj01	Obj03	Obj05	Obj07	Obj16	Obj19	Obj20	Obj21	Obj23
Fe	1.06	0.97	0.99	1.09	0.9	1.2	0.88	1.27	0.87
Cu	0.52	0.43	0.4	1.38	0.62	0.56	1.16	0.87	0.18
Zn	0.74	0.58	0.68	1.3	0.82	1.1	0.9	1.29	0.78
Pb	1.36	0.96	0.6	0.84	0.82	0.88	0.8	1	0.66
Ni	2.43	0.86	1.7	1.17	0.79	0.97	0.66	0.98	1.12
Cd	0.87	1.03	0.78	2.02	0.75	0.63	0.95	1.15	1.48
PLI	**1.03**	**0.77**	**0.77**	**1.25**	**0.78**	**0.86**	**0.88**	**1.08**	**0.72**

Contamination Factor (CF) Indices	Degree of Contamination	Heavy Metals
CF < 1	Low contamination	
1 ≥ CF ≥ 3	Moderate contamination	Fe, Zn, Ni and Cd
3 ≥ CF ≥ 6	Considerable contamination	
CF > 6	Very high contamination	

Contamination factor (CF): With respect to heavy metal contamination, CF values (table 7a) indicates that Fe is moderately contaminated in locations Obj01 (1.06), Obj07 (1.09), Obj19 (1.2) and Obj21 (1.27) while Cu is moderately contaminated in locations Obj07 (1.38) and Obj20 (1.16).Zn is moderately contaminated at locations Obj07 (1.3), Obj19 (1.10) and Obj21 (1.29). Pb also is moderately contaminated at locations Obj01 (1.36), and Obj21 (1.0). Ni at locations Obj01 (2.43), Obj05 (1.70), Obj07 (1.17) and Obj23 (1.12). Cd at locations Obj03 (1.03), Obj07 (2.02), Obj21 (1.15) and Obj23 (1.48) are moderately contaminated. As observed with EF values, locations Obj01, Obj07, Obj19, Obj21 and Obj23 are most contaminated when viewed generally (tables 5a and 7a). Also fewer locations are moderately. From these values of CF, monitoring of concentrations of Fe, Zn, Ni and Cd are desirable.

Table 9: Pollution load Index of heavy metals concentration (After Tomilson et al., 1980)

PLI Indices	Pollution Level	Locations
0	Perfection	
1	Only baseline levels of pollutants present	
> 1	Progressive deterioration of the site	Obj 01, 07 & 21

Fig.8 shows the CF values of each element along sample points and fig.9 shows the CF values of each element in all sampled locations and how these elements varies from one location to another.

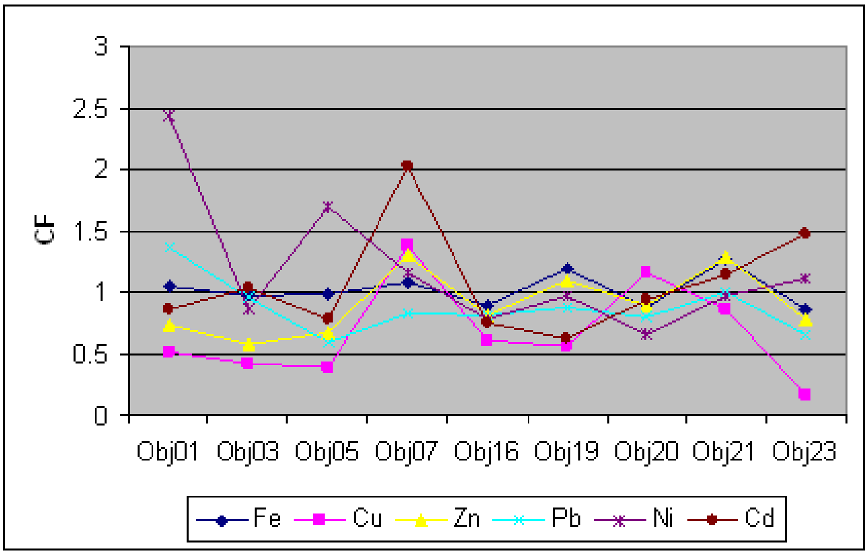

Fig 8: CF against sample locations of Obajana sediment samples.

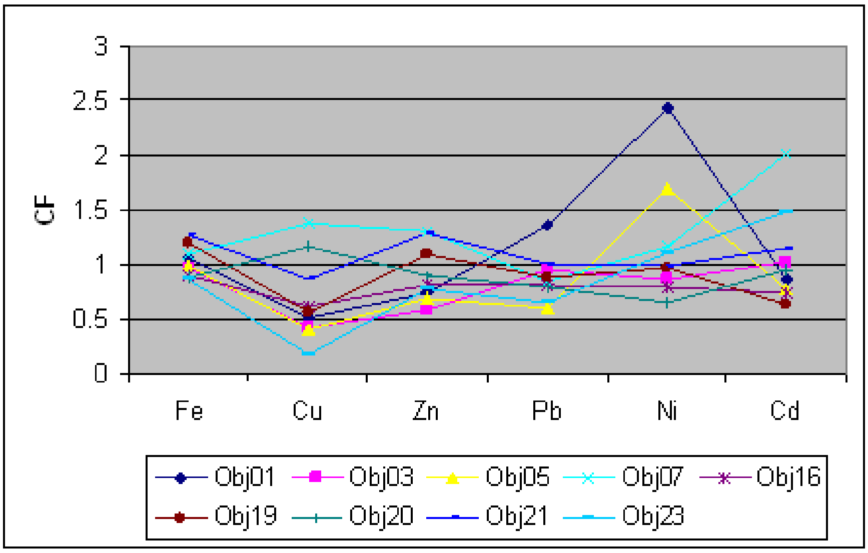

Fig 9: CF plot against heavy metals from Obajana sediment samples.

According to Tomilson et al., 1980, PLI greater than one is said to be a progressive deterioration of that very site. From fig. 10, locations Obj01, Obj07 and Ojb21 are experiencing progressive deteriorations and need to be monitored.

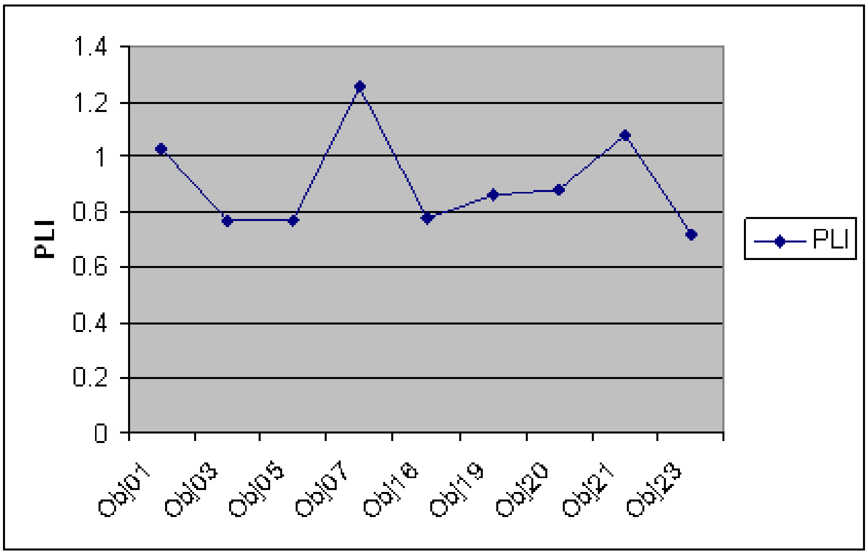

Fig 10: PLI against sample locations of Obajana sediments.

CONCLUSION

This study revealed that the enriched concentration and contamination factor values of sediments around Obajana cement production are due to strong anthropogenic influences. The distribution pattern of the heavy metals according to EF and CF in the stream suggest that sediments are polluted with respect to Fe, Zn, Cd and Ni and locations Obj01, Obj07, Obj20 and Obj23 and Obj01, Obj07 and Obj21 respectively. PLI also shows that locations Obj01, Obj07 and Obj21 confirmed that sediment quality is deteriorated with same heavy metals and these may have severe impact on the ecosystem. To prevent heavy toxic metal pollution at and within the vicinity of communities exposed to anthropogenic-derived metal inputs, it is imperative to implement timely monitoring and remediation strategies to alleviate the loadings and cumulative concentrations of these heavy metals found in the study area.

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