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Research Article

Integrated Environmental Quality Assessments of Surface Water around Obajana Cement Production Area

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Abstract: Due to industrialization, there is enormous amount of heavy metals been released from anthropogenic sources into the environment. Heavy metals are considered as one of the main sources of environmental pollution since they have significant effect on the ecological quality and water in particular. These pollutants are hazardous to consumers of water that have significant quantity of these heavy metals. The population most exposed to cement polluted water includes workers in cement factories, families of workers living in Staff houses of factories like in Obajana and other neighborhood habitations. The Obajana cement factory consists of cement kilns/coolers with clinkers. The kilns are equipped with pre-heaters and Electro-Static Precipitators (ESP). The facility has raw mills, crushing operations, cement mills that are potential source of pollutants into the water bodies. Storage silos, conveyors, vehicular travel, and other unquantified fugitive source of water contamination exist in the factory. Monitoring the contamination of water with respect to heavy metals is of interest due to their influence on humans, animals and to some extent plants. A good approach to estimate how much of the water is impacted is by using the heavy metal pollution index and metal index for metal concentrations above the control points in water bodies around Obajana cement.

Keywords: Heavy metal pollution indexing, metal indexing, multivariate analysis, obajana

INTRODUCTION

Obajana plant has two production lines with a combined capacity of 15,000 metric tons of cement per day. All the raw materials-marble, schist, clay and laterite are available within the mines. The raw materials are spread over 900 ha with an average depth of 130 m. Transport of the raw materials from the quarry to the plant site is through a conveyor belt line of 8.0 km long. The raw materials are crushed at the mines into smaller pebbles and transported by the conveyor belt to the raw material storage shed at the factory. The raw meal is passed through a pre-heater where it is heated up to 900°C before it is fed into kilns where the raw meal is heated up to a temperature of 1400°C. The resulting product-clinker-is cooled in coolers and stored in clinker silos. The clinker is mixed with gypsum and ground in the cement mills to produce cement. The cement is stored in cement silos. From the cement silos, the cement is distributed through automatic truck loaders.

The potential impacts of production could result from construction and operation of the ropeway; on-site storage of the crushed limestone, clay, laterites 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 (Ziadat *et al.*, 2006; 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. 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), waste heat and heavy metals (Legator *et al.*, 1998).

The objective of the study is to analyzed the water samples, use heavy metal pollution and metal indexing in conjunction with factor and cluster analysis to evaluate cement impacts on surface water.

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Geology of study area: The study area 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±200 Ma), Eburnean (1850±250 Ma), Kibaran (1000±100 Ma) and Pan-African (550±100 Ma) (Ezepue and Odigi, 1993). The Obajana gneisses (Fig. 1 and 2) comprise of three

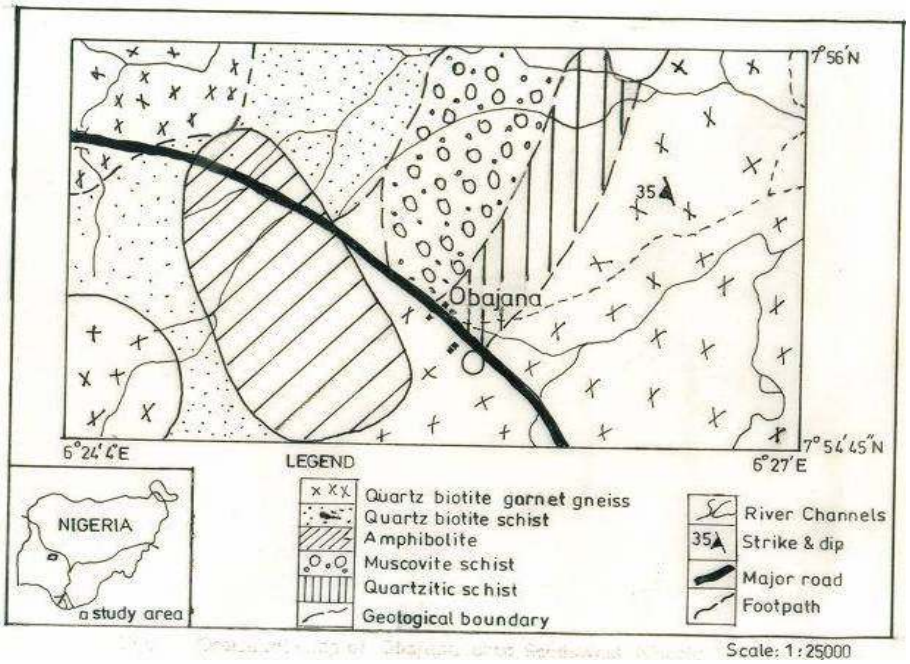

Fig. 1: Geological map of study area (Odigi, 2002)

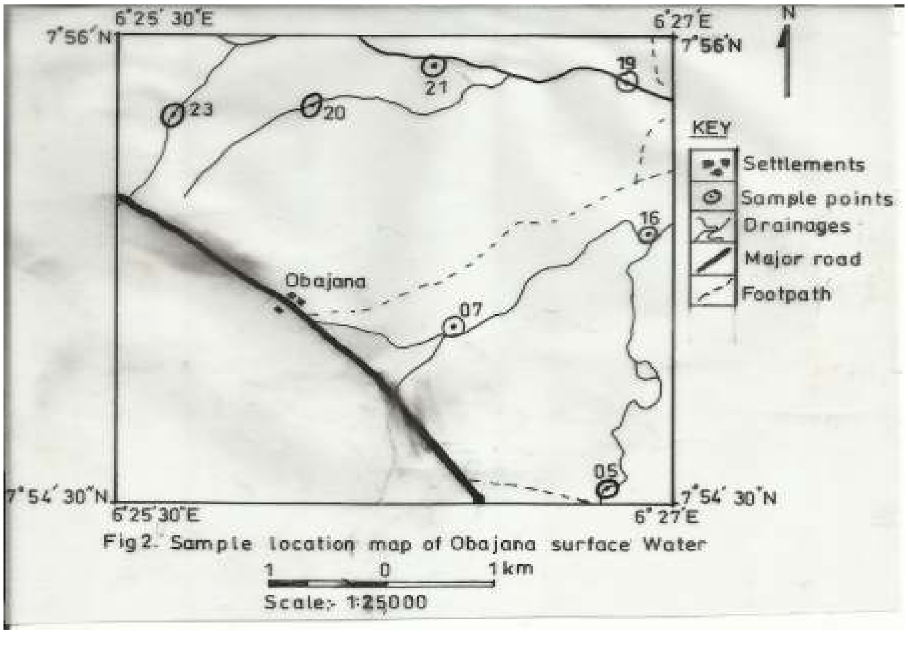

Fig. 2: Sample location map of obajana

types of rocks designated as quartz-biotite gneiss; quartz-biotite-hornblende-pyroxene gneiss and quartz-biotite-garnet gneiss (Ezepue and Odigi, 1993, 1994; Odigi, 2002). According to these authors above, igneous rocks of this area include members of the older granite suite mainly granites, granodiorites and syenites. The associated schists in the area are: quartz-biotite schist, amphibole schist, muscovite schist and quartzitic schist.

MATERIALS AND METHODS

Sampling was carried out in February (dry season). A total of (8) water samples were collected (Fig. 2). Sampling was random but evenly distributed. Samples were collected from mid-point and a foot below 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 and 4°C on cool ice packs from the field to the Lab. for analyses.

Analytical methods: Insitu measurements of temperature, pH, Tds and EC were carried out intrusively with appropriate probes. Spectrophotometer (Model Genesys 20) was used to determine the concentrations of K, Na, Ca, NO_3 and SO_4 while 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 the concentrations of Cl and alkalinity. All analyses were performed according to APHA (2000) in the Dept. of Soil Science Lab, Faculty of Agriculture, Kogi State University, Anyigba.

Data evaluations: Heavy metal pollution index and metal index 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:

$$HPI = \sum WiQi / \sum Wi \qquad (1)$$

where,

Qi = Subindex of the i^{th} parameter

Wi = The unit weightage of i^{th} parameter

n = The number of parameters considered

The subindex (Qi) of the parameter is calculated by:

$$Qi = \sum (Mi\ (-)\ Ii) / (Si-Ii) \qquad (2)$$

where,

Mi = The monitored value of heavy metal of the i^{th} parameter

Ii = The ideal/baseline value of i^{th} parameter

Si = The standard value of i^{th} parameter

The sign (-) indicates the numerical difference of the two values, ignoring the algebraic sign (Prasad and Bose, 2001). The critical pollution index value is 100 (Reza and Singh, 2010; Bakan *et al*., 2010).

Another index used is the general Metal Index (MI) for drinking water (Caeiro *et al*., 2005) 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 = ∑ [Ci/ (MAC) i] proposed by Caeiro *et al*. (2005). 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 (Caeiro *et al*., 2005).

Univariate and multivariate statistical methods of analysis were also used in the study. The software SPSS 15.0 was used for statistical analysis. The correlation matrix which is based on the Pearson's correlation coefficient was utilized for displaying relationships between variables. 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 River Mimi and its tributaries. Evaluations of similarity were based on the average linkage between groups (Praveena *et al*., 2007; Harikumar and Jisha, 2010).

RESULT ANALYSIS

Analytical results expressed in milligram per liter (mg/L) were log-transformed and statistically treated using SPSS version 15.0 software. Factor and cluster analyses were computed for the variables using the SPSS version 15.0 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

Table 1: Descriptive statistics of obajana dry season water

Variable	Min.	Max.	Mean	S.D.	CP
Temp	26.00	27.00	26.43	0.45	26
pH	7.20	9.50	8.01	0.78	7.900
Alk	18.00	86.00	41.00	25.36	22
Tds	74.00	317.00	225.00	81.90	85
EC	0.15	0.43	0.32	0.10	0.110
Na	1.38	5.34	3.80	1.68	1.360
K	2.82	8.18	4.82	1.71	3.580
Ca	0.84	5.02	2.16	1.35	0.500
Mg	0.19	9.23	5.63	3.35	7.510
Zn	0.01	0.02	0.02	0.01	0.020
Cu	0.03	0.08	0.05	0.02	0.060
Cd	0.01	0.04	0.02	0.01	0.020
Pb	0.23	0.63	0.40	0.14	0.180
Fe	0.19	7.12	1.85	2.71	6.850
Ni	0.72	1.90	1.24	0.48	0.510
Cl	0.04	0.05	0.04	0.00	0.044
SO_4	0.06	0.09	0.07	0.01	0.062
NO_3	0.71	10.95	5.19	3.84	2.200
CO_3	4.23	21.72	14.53	6.00	7.110

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 in the samples. Evaluations of similarity were based on the average linkage between groups (Praveena *et al*., 2007; Aprile and Bouvy, 2008).

Table 1 shows the summary of parameters measured in Obajana dry season water samples. The order of mean concentration among the physiochemical is Tds>alkalinity>temperature>pH>Ec. pH of the area is generally alkaline because of the presence of Carbonates (CO_3). The major cations have this order of concentration: Mg>K>Na>Ca. Because of cement production and the geology of the area, this order among the major cations is expected. The order observed also among the anions is: CO_3>NO_3>SO_4>Cl. CO_3 is expected to dominate the anions because of its presence in marble while NO_3 maybe from fertilizer application to improve yields. The heavy metals show this concentration trend: Fe>Ni>Pb>Cu>Cd/Zn. Fe is generally high in Nigeria because of our tropical climatic conditions (Fagbote and Olanipekun, 2010) but the relatively higher concentrations of Ni and Pb is worthy of note.

Temperature shows (Table 2) negative, weak correlations with K, Ni; moderate correlation with Ca and strong correlation with Mg. Moderate correlations were recorded with pH-alkalinity and pH-K while strong correlations exists between pH-Zn, pH-NO_3. Alkalinity shows negative and weak correlations with Tds, weak correlations with Zn and Cl while the correlation between Fe and NO_3 is moderate. The same alkalinity correlates moderately with Ni but negative. Tds recorded very strong correlations with Ec and Na, moderate relationship with K and Pb, negative and moderate relation with Fe. Tds exhibits negative and weak relationships with Cd and Cl and weak correlation with Cu. Ec-Na shows very strong correlation. Moderate correlation exists between Ec-Pb and negative, moderate relations exist between Ec-Fe. The correlations between Ec-K, Cu-Cd are weak. Between Ec-Cd is negative. Na shows very strong correlation with Pb ($r>0.8$), strong but negative correlation with Cd and a moderate correlation with Cu. Weak, negative correlation also exist between Na-Fe. The relationship between Na-Pb is very strong, with Cd it is negative but strong, moderate correlation exists with Cu. Weak and negative correlation was evident between Na-Fe. Weak correlations were observed with K-NO_3, K-CO_3 while same weak but negative correlations exists with K-Fe and K-Cl. K-Mg shows strong but negative correlation. The correlation between Ca-Mg, Ca-NO_3 is weak while that between Ca-Zn is moderate. Mg shows negative, weak correlations with Cd and Ni, weak correlation with SO_4. Zn shows weak correlation with Cl, weak and negative correlation with SO_4 and moderate correlation with NO_3. Interestingly, Zn shows no correlation with any of the heavy metals. Cu correlates negatively but weakly with Cd, SO_4 and CO_3 and a positive, weak correlation with Cl. The correlation between Cu-Pb is moderate. Cd correlates negatively but moderate with only Pb among the heavy metals. Lead on the other hand has weak, negative correlations with only Fe. Fe shows negative and weak correlations with Ni, SO_4 and a weak correlation with Cl. Ni correlates negatively and weakly with NO_3 and CO_3.

Table 2: Correlation matrix of obajana dry season water samples

	Temp	pH	Alk	Tds	EC	Na	K	Ca	Mg	Zn	Cu	Cd	Pb	Fe	Ni	Cl	SO_4	NO_3	CO_3
Temp	1.000																		
pH	-0.259	1.000																	
Alk	-0.007	0.624	1.000																
Tds	0.020	0.108	-0.406	1.000															
EC	0.076	0.130	-0.338	0.978	1.000														
Na	0.139	-0.128	-0.232	0.844	0.887	1.000													
K	-0.427	0.620	-0.111	0.627	0.527	0.199	1.000												
Ca	0.670	0.131	-0.137	0.243	0.277	0.012	0.056	1.000											
Mg	0.746	-0.624	-0.135	-0.136	-0.086	0.098	-0.719	0.487	1.000										
Zn	0.198	0.701	0.406	0.080	0.206	-0.058	0.179	0.611	-0.077	1.000									
Cu	-0.029	0.278	0.190	0.431	0.575	0.655	0.091	-0.162	-0.267	0.371	1.000								
Cd	-0.371	0.184	-0.141	-0.421	-0.535	-0.772	0.308	-0.148	-0.522	-0.125	-0.545	1.000							
Pb	0.325	-0.223	-0.099	0.623	0.655	0.887	0.015	-0.131	0.145	-0.241	0.609	-0.690	1.000						
Fe	-0.153	0.046	0.624	-0.670	-0.615	-0.434	-0.537	-0.170	0.278	0.091	-0.244	-0.147	-0.449	1.000					
Ni	-0.485	-0.117	-0.555	0.089	0.107	-0.021	0.186	-0.310	-0.508	-0.067	0.280	0.397	-0.136	-0.447	1.000				
Cl	0.108	0.164	0.471	-0.471	-0.281	-0.180	-0.554	-0.009	0.103	0.548	0.488	-0.228	-0.156	0.461	0.137	1.000			
SO_4	0.397	-0.747	-0.840	0.219	0.129	0.099	-0.133	0.355	0.532	-0.471	-0.502	0.059	0.093	-0.432	0.071	-0.559	1.000		
NO_3	0.302	0.797	0.593	0.228	0.244	0.043	0.440	0.523	-0.118	0.682	0.134	-0.113	0.027	-0.008	-0.573	0.002	-0.421	1.000	
CO_3	-0.270	0.064	-0.018	0.380	0.230	0.214	0.473	-0.083	-0.061	-0.381	-0.400	-0.068	0.103	0.048	-0.474	-0.798	0.154	0.195	1.000

Table 3: R-mode varimax factor analysis

Variable	Factor 1	2	3	Communalities
Zn	-0.014	-0.077	0.945	0.899
Cu	0.718	0.354	0.518	0.908
Cd	-0.867	0.367	-0.147	0.908
Pb	0.947	0.163	-0.249	0.986
Fe	-0.253	-0.812	0.191	0.759
Ni	-0.215	0.871	0.124	0.820
Eigenvalue	2.275	1.710	1.296	
% total variance	37.914	28.497	21.599	
Cumulative %	37.914	66.411	88.010	

Table 4: Q-mode rotated factor analysis of obajana heavy metals

Variable	Factor 1	2	3	Communalities
Obj05	0.188	-0.080	0.629	0.438
Obj07	0.833	0.352	0.397	0.976
Obj16	-0.828	0.432	-0.117	0.886
Obj19	0.888	0.015	-0.386	0.938
Obj20	-0.320	-0.630	0.594	0.852
Obj21	-0.096	0.949	0.126	0.925
Obj23	0.222	-0.433	-0.751	0.801
Eigen value	2.363	1.802	1.650	
% of variance	33.762	25.738	23.566	
Cumulative %	33.762	59.500	83.066	

From the correlation (Table 2), the heavy metals shows no correlations among themselves, where it exist, they are weak and negative. This suggests anthropogenic source for the heavy metals. The correlation between Cl-CO_3 is strong ($r>-0.7$) but negative. Between Cl and SO_4 is weak and also negative. SO_4 correlates negatively and weakly with NO_3. As observed with the heavy metals, the anions show no relations among themselves. Where relationship exists, they are negative and weak. This is also an indication of anthropogenic inputs for these anions. Overall, strong and positive correlations exist among the physiochemical and major cations while this is not true for the heavy metals and anions.

R-mode varimax factor analysis revealed three factors. Factor one consist of high factor loadings of Cu, Cd and Pb with eigenvalue of 2.275 and total varimax of 37.914%. Factor two also consists of high loadings of Fe and Ni with eigenvalue of 1.710 and total variance of 28.497%. The association in factor three is between Zn and Cu with Zn having high, positive loading and weak factor loading for Cu. Factor three has eigenvalue of 1.296 and total variance of 21.599% (Table 3).

R-mode cluster extracted two clusters. Cluster one consist of Cu, Pb, Zn and Fe while cluster two is an association between Cd and Ni (Fig. 3).

Q-mode varimax rotated factor analysis of heavy metals yield three factors. Factor one consists of high factor loadings of locations Obj07, Obj16 and Obj19 with total variance of 33.762% and eigenvalue of 2.363. Factor two has eigenvalue of 1.802 and total variance of 25.738%. Factor two is an association of locations Obj16, Obj20, Obj21 and Obj23. Obj21 has high factor loading and the rest showed weak factor loading. Factor three consists of locations Obj05, Obj19 and high loading for Obj23. Factor three has eigenvalue of 1.650 and total variance of 23.566 (Table 4).

Q-mode cluster extracted two clusters Figure 4. Cluster one consists of locations Obj07, Obj19, Obj23, Obj05 and Obj20. Cluster two on the other hand consists of locations Obj16 and Obj21.

The HPI of Obajana samples calculated is 0.43. This is well below the critical pollution index value of 100. Metal Indexing (MI) also calculated is 114.90.

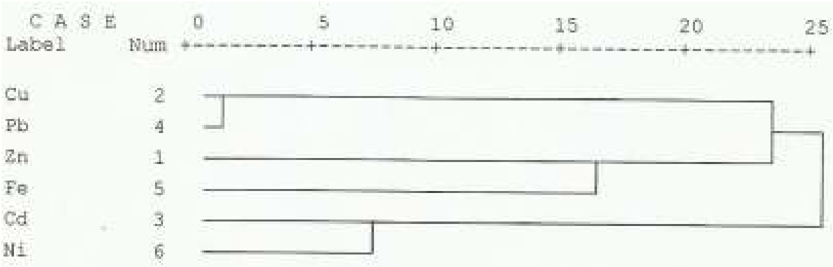

Fig. 3: R-mode cluster analysis of heavy metals

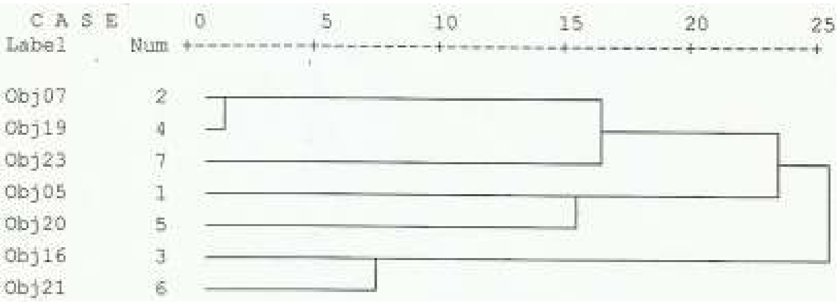

Fig. 4: Q-mode cluster analysis of obajana heavy metals

Table 5: HPI and MI indices of obajana dry season water samples

Heavy metals (mg/L)	Mean value (mg/L) (Mi)	Standard value (Si) NSDWQ, 2007	Baseline value (Ii)	Unit weightage (Wi)	Sub-index Qi	Wi*Qi
Zn	0.02	3	0.02	0.333	0	0
Cu	0.05	1	0.06	1	0.01	0.01
Cd	0.02	0.003	0.02	333.333	0	0
Pb	0.40	0.010	0.18	100	1.29	129
Fe	1.85	0.300	6.85	3.333	0.76	2.53
Ni	1.24	0.020	0.51	50	1.49	74.50
				∑Wi = 478.999		∑Wi *Qi = 206.04

Heavy metals (mg/L)	Ci	MAC	MI
Zn	0.02	0.02	0.01
Cu	0.05	0.05	0.05
Cd	0.02	0.02	6.67
Pb	0.40	0.40	40
Fe	1.85	1.85	6.17
Ni	1.24	1.24	62

Obajana dry season water HPI = 0.43; Obajana dry season water MI = 114.90

MI>1 is a threshold of warning This MI value indicates low water quality (Prasad and Bose, 2001; Reza and Singh, 2010; Bakan *et al*., 2010) (Table 5).

DISCUSSION

Moderate to strong correlation exist (in few cases) between the cations and the physiochemical, a clear indication of the contribution of these ionic components to the overall Tds and Ec (Abimbola *et al*., 2005). Among the major cations, strong correlation also exist between Mg-K while the rest variables show weak to no correlation-suggesting diverse origin for the major cations (Abimbola *et al*., 2005; Olayinka and Olayiwola, 2001). The heavy metals exhibit weak to moderate correlations and in most cases negative with one another as well as with Ec and Tds. This may be attributed to the fact that dissolution of metals in the aqueous phase is controlled by the chemical character and solubility (mobility) of the respective metals (Tijani *et al*., 2004). Correlation between heavy metals and major cations were also very weak, moderate and negative in most cases except that between Na-Cd; Na-Pb which is strong and is a reflection of a source area deposited together under similar conditions (Tijani *et al*., 2004). The relationship between cations and physiochemical were weak except between pH-SO_4; pH-NO_3; alkalinity-SO_4 which were strong, an indication of same source and affinity of the physiochemical for NO_3 and SO_4. Between major cations and anions, it is generally weak, same for between anions and heavy metals. Among the anions, strong but negative relationship was observed between CO_3 and Cl, an indication also of same source/origin of deposition (Olayinka and Olayiwola, 2001; Tijani *et al*., 2004).

The R-mode factor analysis of heavy metals extracted three factors. Factor one which consists of high loadings of Cu, Cd and Pb and showed fairly significant correlation is an indication of similar source related to anthropogenic inputs considering the presence of Cd and dual sources for Cu (Shakeri *et al*., 2009). Ni and Fe in factor two shows high factor loadings, weak and negative relationship (r = -0.447) indicating that the dynamics of the two heavy metals though linked are not closely related (Idowu *et al*., 2007). Zn and Cu in factor three shows high and moderate factor loadings. It is a normal association but the weak relationship that exists (r = 0.371) may implies psudo anthropogenic factor (Alkarkhi *et al*., 2008). The R-mode cluster (Fig. 3) is characterized by Cu, Pb, Zn and Fe in the first cluster. In this cluster, Cu and Pb shows first degree of similarity reflecting their strong common sources. Zn and Fe are not related to Cu and Pb but bounded loosely to them at a farther Euclidean distance. Cluster two also show similar pattern. Though Cd and Ni are in a cluster, there seems to be little relationship which could imply diverse origin (Pathak *et al*., 2008).

Q-mode rotated varimax analysis extracted three factors (Table 4). High factor loadings of locations Obj07, Obj10 were recorded. Obj07 in this factor is close and under the influence of Obajana cement production activities while Obj16 and 19 are far from the factory's direct influence. Factor two has high, positive loadings of Obj21 while the rest factor loadings are low and negative for Obj23 and Obj20. All the locations in this factor are far from the influence of the factory suggesting similar concentrations (Tauhid-Ur-Rahman *et al*., 2008). High but negative factor loadings was recorded for location Obj23 while weak to moderate factor loadings were observed for Obj20 and Obj25 respectively. These locations also are far from the factory and hence little influence from it (Tauhid-Ur-Rahman *et al*., 2008).

Q-mode cluster analysis revealed two clusters. Cluster one include locations Obj07, 19, 23, 05 and 20. The closest association is between location Obj07 and Obj19 while the rest locations may not have been influenced by same process as in Obj07 and Obj19. These two locations are directly under the influence of the factory while the rest are not. Cluster two though consist of locations 16 and 21 are not strongly linked indicating a mixture of factors/influences (Ziadat *et al*., 2006).

The HPI value for dry season water samples is 0.43 while the MI = 114.90. This HPI imply that the water is not contaminated with respect to heavy metals. The MI value of 114.90 suggests that the water is contaminated because MI value>1 is a threshold of warning (Caeiro *et al*., 2005; Reza and Singh, 2010; Bakan *et al*., 2010).

CONCLUSION

Mean concentration of Fe, Ni and Pb were relatively higher compared to other heavy metals. Factor and cluster analysis showed various degree of anthropogenic influence on the water. Heavy metal pollution index reveals that pollution has not reached the critical level while metal index suggests low water quality. Pollution prevention at source through substitution of less hazardous materials, improved maintenance and effective production processes is recommended for a sustainable environment and healthy living.

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