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A PRELIMINARY ASSESSMENT OF GROUNDWATER SAMPLES AROUND A FILLING STATION IN DIOBU, PORT HARCOURT, RIVERS STATE, NIGERIA.

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ABSTRACT

This paper is a preliminary assessment of groundwater samples around a filling station in Diobu area of Port Harcourt for four years at intervals of two years with a view to determine the level of groundwater pollution. It examines the physiochemical, major ions and heavy metal aspect of groundwater quality around the study area.

Both factor and cluster analysis for the period under investigation shows that variables such as OG, NO_3, PO_4 that recorded high factor loadings and closer clusters may have been introduced from anthropogenic sources while Ec, TDS, Cl, Fe, TSS, salinity, hardness may be due to saltwater intrusion from the sea. The anthropogenic factor (AF) value also indicates significant influences from natural processes.

Significant influences may have been from natural process but were enhanced by over pumping/nearness to the sea and oil/agricultural activities.

KEY WORDS: Multivariate Analysis; Anthropogenic Factor; Physico-Chemical**;** Diobu; Nigeria

INTRODUCTION

South-south Nigeria and Port-Harcourt in particular is generally underlain by sedimentary formation and so groundwater is usually present in abundance. This partly is as a result of the climate that foster heavy rainfall and hence adequate aquifer recharge together with suitable aquifers and impervious sediments that favour the storage of the recharging water (Ofoma, *et al*., 2005). In spite of these, ground water is still unwholesome because its quality is considerably degraded by physical, chemical and bacterial contamination that results from the activities of man. A closer assessment therefore of the physical, chemical and bacterial constituents of groundwater is often necessary for effective monitoring of its quality status.

In Diobu area of Port-Harcourt, groundwater constitutes the predominant source of water for domestic use. This is due to pollution of available surface water as a result of indiscriminate disposal of solid and liquid wastes and activities of the oil companies. This paper examines the heavy metal and physiochemical aspect of ground water quality around a filling station in Diobu area. It is a preliminary assessment of the area surrounding the filling station for four years at intervals of two years with a view to determine level of ground water pollution.

Previous work: Previous works in the area include aspects of hydrogeochemistry. Etu-Efeotor, 1981 observed the presence of two hydrogeochemical regimes in the area, one inland and the other towards coastal area. He also confirmed that iron content is higher than acceptable values for drinking water. Etu-Efeotor and Odigi (1983) observed some water supply problems in the area to include: salinity, bacterial contamination and presence of undesirable ions. They also concluded that variation in water chemistry exists from one aquifer to the other. Amadi and Amadi (1990) observed that the chemistry of natural waters in Port Harcourt area changes with season as a result of dissolution, dilution and dispersion. Ngah (2002) in his study of pattern of groundwater chemistry observed that rainwater showed more enrichment of NO_3^-, SO_4^{2-} and relatively lower pH than the groundwater. Other authors who have carried out similar researches in the same geological environment include Amojor (1986) and Egboka (1986). Both observed relative enrichment of major ions and some heavy metals.

Location of the study Area and Geology

Diobu is a district in Port Harcourt, Southern Nigeria and located within the Niger Delta Basin, delimited by Latitude 4^0 40'N and 5^0 00'N and Longitude 6^0 45'E and 7^0 10'E (Fig 1). The area lies within the subequatorial wetland climate that spreads across a number of ecological zones.

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Niger Delta consists of three dichronous units, namely from bottom, the Akata, Agbada and Benin Formations (Olobaniyi, *et al.*, 2007). The study area is underlain by the Miocene-Recent Benin Formation. The formation is aquiferous and is probably the most prolific groundwater producer in Southern Nigeria (Oteze 1981; Ofodili, 1992; Ofoma, *et al.*, 2005). The formation which is about 2100m thick at the basin centre generally consists of unconsolidated and friable sandy beds with intercalation of gravely units and clay lenses (Olobaniyi *et al.*, 2007). The upper section of the formation is the quaternary deposits which is about 40-150m thick and comprises rapidly alternating sequences of sand and silt/clay with the later becoming increasingly more prominent seawards (Etu-Efeotor and Akpkoje, 1990; Ofoma *et al.,* 2005).

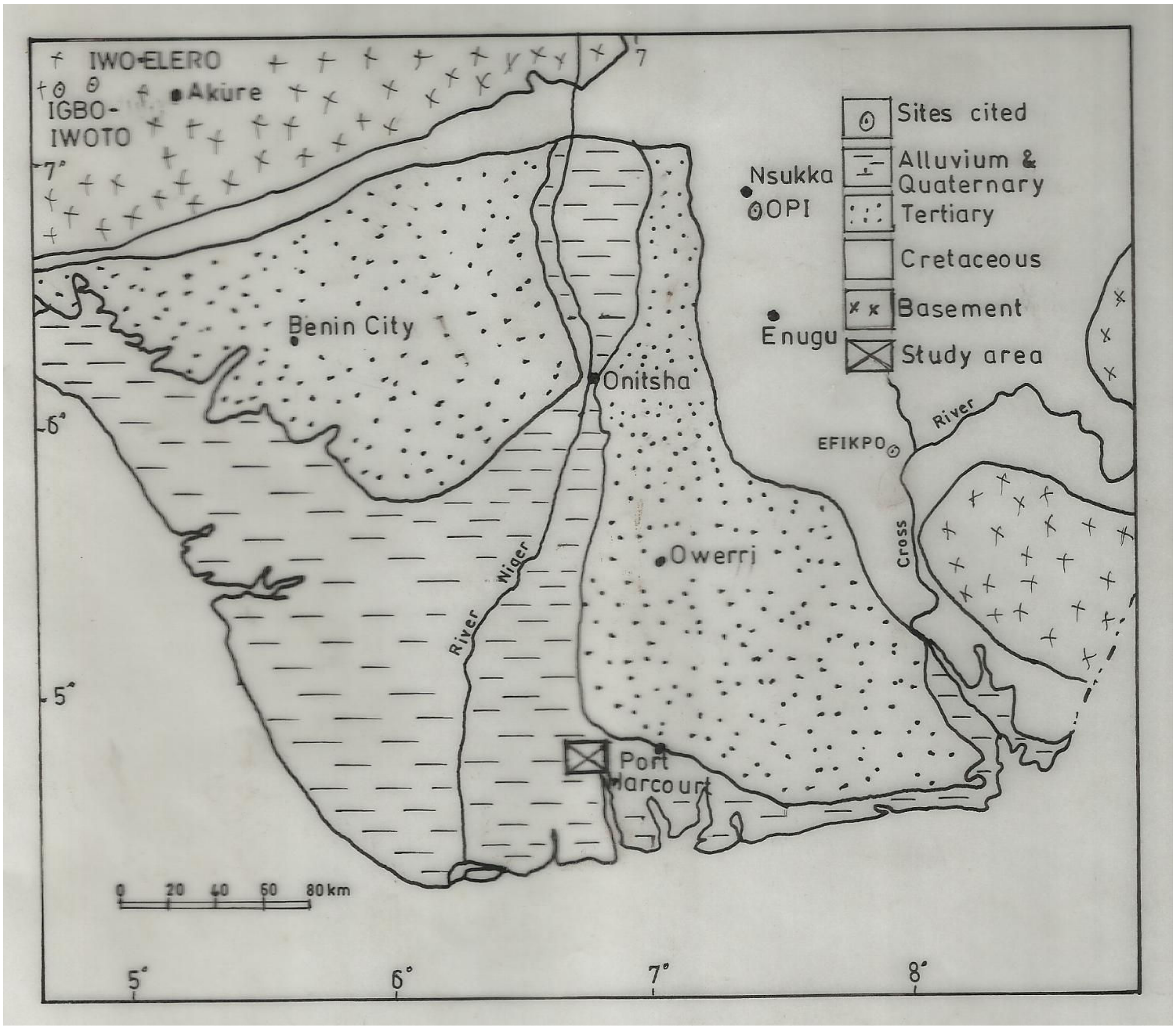

Fig.1: Geological map of study Area (after Etu-Efeotor and Akpoje, 1990)

MATERIALS AND METHODS

Sample and Analysis: Ground water samples were collected from three boreholes within and around the filling station between 2000 and 2004 in the month of April and a total of 15 parameters were determined. At each borehole site, the well was pumped for 5 minutes to remove stagnant water and fresh water was allowed to run before samples were collected. Duplicate samples were collected- one for heavy metals and cations and the other for anions and the unstable parameters. Samples were collected in clean 1 liter plastic bottle from each borehole. The plastic bottle for heavy metal and cations were stabilized with acid while the other bottles were kept on ice pack and the unstable parameters such as pH, EC, TDS were measured in situ with appropriate probes. Borehole sections were obtained to determine the lithological profiles, characteristics and sequence correlations within the study area (Fig 2). Water depths were taken to determine flow line direction of boreholes.

Analytical method: The water samples were analyzed for heavy metals using AAS. Anions were analyzed by titration method according to APHA, 2002. All analyses were carried out at Fugro Nig. Ltd, Laboratory, Port Harcourt.

Data evaluation

SPSS v 11.0 was used to perform all data analysis after performing 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 the covariance matrix iii) find eigenvalues and corresponding eigenvectors iv) discard any component that only 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 (Pathak et al., 2008; Yang et al., 2009). In this study, only components or factors exhibiting an eigenvalues greater than one were retained. Component loadings were used to determine the relative importance of variables as compared to other variables in a PC and do not reflect the importance of the components (Lokhande et al., 2008).

Factor analysis: The raw data were treated first with Z-scale transformation to make the data standardized.
Multivariate data analysis was utilized to identify the correlations among the measured parameters. Principal component analysis was done to reduce the number of input variables. Spearman's correlation matrix was performed to illustrate the correlation coefficients among the variables (Reghunath et al., 2002; Pathak et al., 2008).

Hierarchical cluster analysis: Cluster analysis was used to find the true groups of data. In clustering, objects are grouped such that similar objects fall into the same class. Hierarchical clustering joins the most similar observations and successively the next most similar observations. The levels of similarity at which observations are merged are used to construct dendrogram. In this study, squared Euclidean distance method was used to construct dendrogram. A low distance shows the two objects are similar or close together whereas a large distance indicates dissimilarity (Reghunath et al., 2002).

Anthropogenic Factor (AF): Is a quantification method use for degree of contamination relative to either average crustal composition of the respective metal or to measured background values from geologically similar and uncontaminated area was used. It is expressed as: $AF=C_m/B_m$ where C_m is the measured concentration in soil, B_m is the background concentration (value) of metal, either taken from the literature (average shale/average crustal abundance) or directly determined from a geologically similar area (Tijani *et al*., 2004). Correlation coefficient matrix was also calculated for ease of data evaluation.

Table 1: Borehole water parameters

Parameter Sampled mg/g	2000 and 2004 Borehole 1 2004		2000 and 2004 Borehole 2 2004 Borehole 3		2000 and 2004 Borehole 3 2004		Mean 2000	Std D 2000	Mean 2004	Std D.2004
Turbidity	0.2	0.8	ND	0.2	ND	0.3	.2	0.07	0.2	0.04
pH	5.2	7.8	6.5	7.9	4.4	6.9	5.6	0.91	7.2	1.02
Temp (oC)	27	27	27	27	27	27	27.6	0.30	26.8	0.22
Salinity	12.5	ND	ND	ND	ND	ND	28.5	7.01	20.3	2.33
TDS	20.4	130	22.2	100	31.2	15	75.0	94.7	1.89	1.67
Cond.uS/cm	139	250	42.2	190	60.6	29	17377	1708	216	77.54
Hardness	ND	7.5	2	60	5	10	4.8	1.63	0.33	0.1
Alkalinity	ND	45	10	39	8.5	52	9.1	3.1	0.14	0.1
NO_3^-	2.9	1	ND	ND	1	1	1.0	0.8	30.3	3.01
PO_4^{3-}	0.5	0.9	ND	ND	0.8	0.8	0.1	0.02	106	40.39
SO_4^{2-}	ND	ND	ND	ND	1	ND	1.2	0.15	0.1	0.03
Cl^-	ND	31	ND	ND	9.5	34	81.9	54.38	48.2	19.0
Mn	ND	0.4	0.1	0.2	0.3	0.5	.03	0.01	42.85	37.7
Zn	0.3	0.5	0.5	0.4	0.4	0.6	0.23	0.12	0.10.03	0.02
Fe	0.5	0.6	0.4	0.4	0.4	0.8	0.09	0.2	0.03	0.01

Table 1 revealed significant changes in boreholes 1 to 3 within the period 2000 to 2004 with respect to turbidity, pH, TDS, conductivity, hardness and alkalinity. The observed increase could be due to over pumping thereby shifting the equilibrium/interface between fresh and salt waters and its consequent ionic increases. Among the cations, no significant changes were observed while the heavy metals show relative enrichment. This enrichment may have arisen from human inputs and salt water intrusions (Ofoma et al., 2005)

Table 2: Shows correlation matrix for the 2000 borehole waters

Variables	Turbidity	pH	Temp	Salinity	TDS	Ec	NO_3	PO_4	SO_4	Cl	Mn	Zn	Fe	Hardness	Alkanity	TSS	OG
Turbidity	1.00																
pH	-.093	1.000															
Temp	.431	-.543	1.000														
Salinity	.358	-.007	.242	1.000													
TDS	.256	-.162	-.046	.299	1.000												
Ec	.406	-.288	-.098	.232	.897	1.000											
NO_3	-.102	-.181	.014	-.909	-.159	-.039	1.000										
PO_4	-.557	-.500	.072	.127	-.282	-.337	-.257	1.000									
SO_4	-.369	-.390	.587	-.119	-.146	-.400	.066	.484	1.000								
Cl	.608	.074	-.038	-.212	.414	.600	.349	-.836	-.439	1.000							
Mn	.484	-.389	.251	.376	.171	.496	-.150	-.172	-.328	.436	1.000						
Zn	.033	-.700	.147	-.034	.029	.110	-.033	.615	.277	-.169	.023	1.000					
Fe	.036	-.186	-.038	-.833	-.223	-.089	.868	-.110	-.003	.242	-.270	.272	1.000				
Hardness	.741	.056	.126	.266	.425	.419	-.239	-.480	-.230	.605	.121	.230	-.065	1.000			
Alkalinity	-.597	-.204	-.071	.085	-.096	-.233	-.338	.745	.581	-.577	-.196	.478	-.214	-.308	1.000		
TSS	.574	.529	-.066	.332	.037	-.031	-.431	-.416	-.290	.269	-.144	-.025	-.133	.758	-.162	1.000	
OG	.204	.191	-.342	.572	.450	.478	-.503	-.192	-.646	.112	.249	-.245	-.572	.261	-.401	.131	1.000

OG= oil and grease

Apart from the strong correlation recorded for a handful of the variables in 2000 boreholes, most relationships were moderate to weak. This seemingly lack of sympathy among parameters indicate different sources (Table 2).

Table 3: Shows factor analysis of 2000 borehole sample

	Factors					
	1	2	3	4	5	6
Turbidity	.044	.756	-.141	.144	.586	.118
pH	.153	.231	-.662	-.243	-.484	-.412
Temp	.074	.131	.049	-.085	.386	.889
Salinity	.933	.187	.057	.088	.234	.055
TDS	.184	.112	-.020	.960	-.011	-.013
EC	.046	.116	.048	.901	.338	-.193
NO_3	-.956	-.197	-.159	.032	.083	.087
PO_4	.230	-.464	.776	-.285	-.154	.106
SO_4	-.024	-.233	.274	-.089	-.374	.840
Cl	-.384	.473	-.367	.504	.345	-.102
Mn	.204	-.018	.016	.209	.849	.001
Zn	-.145	.181	.963	.066	.049	.078
Fe	-.950	.096	.142	-.103	.004	-.028
Hardness	.084	.900	.035	.350	.073	.001
Alkanity	.247	-.288	.623	-.062	-.504	.194
TSS	.241	.916	-.122	-.126	-.206	-.136
OG	.564	.031	-.194	.333	.255	-.561

Eigenvalue:	3.463	3.009	2.694	2.483	2.275	2.126
% of variance:	20.369	17.702	15.845	14.603	13.381	12.507
Cumulative %:	20.369	38.071	53.916	68.519	81.900	94.407

Factor analysis extracted six factors. Factor 1 has highest variance of 20.37% and eigenvalue of 3.46. Factor 1 consists of high factor loadings on NO_3, Fe, salinity and OG. Factor 2 was an association of TSS, hardness, turbidity, Cl and PO_4 with variance of 17.70% and eigenvalue of 3.00. Factor 3 has eigenvalue of 2.694 and variance of 15.845%. Factor 3 consists of high factor loadings on Zn, PO_4, pH and alkalinity. Factor 4 consists of TDS, EC and Cl with eigenvalue of 2.483 and variance of 14.603%. Factor 5 has eigenvalue of 2.275 and variance of 13.381%. It consists of Mn, turbidity, alkalinity and pH. Factor 6 has eigenvalue of 2.126 and variance of 12.507%. It was an association of temperature, SO_4, OG and pH (Table 3).

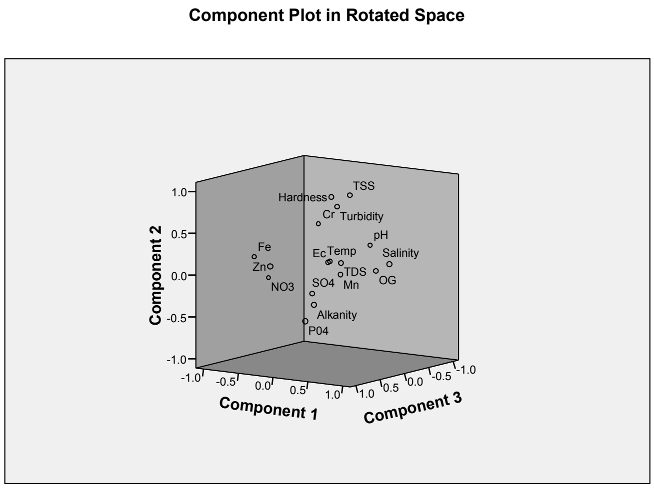

Fig 2: Factor plot in rotated space for the 2000 borehole samples

From the rotated factor plot (Fig. 2), factors 3 and 2 were the dominant.

```
  C A S E     0        5       10       15       20       25
 Label     Num +---------+---------+---------+---------+---------+

 TDS         5
 Ec          6
 Cl         10
 Mn         11
 Hardness   14
 TSS        16
 Turbidit    1
 Salinity    4
 OG         17
 pH          2
 NO3         7
 Fe         13
 Temp        3
 SO4         9
 P04         8
 Alkanity   15
 Zn         12
```

Fig. 3: 2000 borehole water dendrogram.

From the cluster analysis (Fig. 3), cluster 1 consists of TDS, EC, Cl, Mn, hardness, TSS, turbidity, salinity, OG and pH. Among these, the highest similarity exists between TDS-EC; hardness-TSS and alkalinity. This association suggests seawater/freshwater (Nganje et al., 2010) interaction. Cluster 2 consists of NO_3, Fe, temperature, SO_4, PO_4, alkalinity and Zn. Maximum similarities where however, observed between NO_3-Fe; PO_4- alkalinity. This cluster could suggest anthropogenic inputs from agriculture/domestic activities.

Table 4: Correlation matrix of 2004 borehole samples

Parameters	Turbidity	pH	Temp	Salinity	NO_3	Ec	Cl	TDS	PO_4	Alkalinity	Hardness	Fe	Mn	Zn	OG
Turbidity	1.000														
pH	-.737	1.000													
Temp	.340	-.389	1.000												
Salinity	.127	.421	-.013	1.000											
NO_3	-.275	.464	.530	.569	1.000										
Ec	.064	.597	-.239	.897	.415	1.000									
Cl	.706	-.135	.199	.663	.248	.671	1.000								
TDS	.156	.510	-.082	.919	.428	.954	.646	1.000							
PO_4	.050	-.422	-.460	-.232	-.641	-.402	-.353	-.381	1.000						
Alkanity	-.210	.724	.141	.793	.819	.831	.468	.806	-.716	1.000					
Hardness	-.520	.516	.412	.442	.878	.217	-.150	.299	-.354	.638	1.000				
Fe	.211	.457	-.314	.513	.002	.809	.565	.782	-.464	.554	-.203	1.000			
Mn	.400	.302	-.099	.659	.204	.866	.841	.810	-.543	.650	-.145	.908	1.000		
Zn	-.396	.756	-.826	.410	-.059	.683	.102	.521	-.050	.428	-.082	.662	.507	1.000	
OG	-.433	.862	-.339	.323	.230	.625	.012	.592	-.565	.647	.217	.761	.533	.721	1.000

Greater proportions of correlations from 2004 boreholes were significant and this suggests sympathetic relationships among variables. It could imply same source for most variables (Table 4).

Table 5: Rotated Component Matrix for 2004 borehole Samples

	Factor			
	1	2	3	4
Turbidity	.524	-.695	-.478	-.016
pH	.136	.827	.474	.269
Temp	-.060	-.817	.429	.356
Salinity	.853	.146	.475	-.148
NO_3	.230	-.094	.916	.268
Ec	.876	.402	.233	.128
Cl	.908	-.324	-.069	.133
TDS	.875	.278	.286	.119
PO_4	-.244	.027	-.352	-.894
Alkalinity	.590	.279	.650	.381
Hardness	-.043	.057	.988	.040
Fe	.729	.427	-.239	.450
Mn	.889	.152	-.120	.403
Zn	.388	.902	-.096	-.008
OG	.259	.746	.137	.560

Eigenvalue:	5.385	3.866	3.464	1.967
% of Variance:	35.898	25.773	23.095	13.112
Cumulative %:	35.898	61.672	84.767	97.879

Borehole data from 2004 yielded four factors. Factor 1 has eigenvalue of 5.385 and 35.898%. This factor consists of high factor loadings on Cl, Mn, Ec, Tds, salinity, Fe, alkalinity and turbidity. Factor 2 was made up of Zn, pH, temperature, OG, turbidity and Fe. It has eigenvalue of 3.866 and 25.77% variance. Factor 3 has high factor loadings on hardness, NO_3; moderate loading of alkalinity and weak factor loadings on turbidity, pH, temperature and salinity. It has eigenvalue of 3.464 and variance of 23.095%. Factor 4 has eigenvalue of 1.967 and variance of 13.112%. Factor 4 consists of PO_4, OG, Fe and Mn (Table 5).

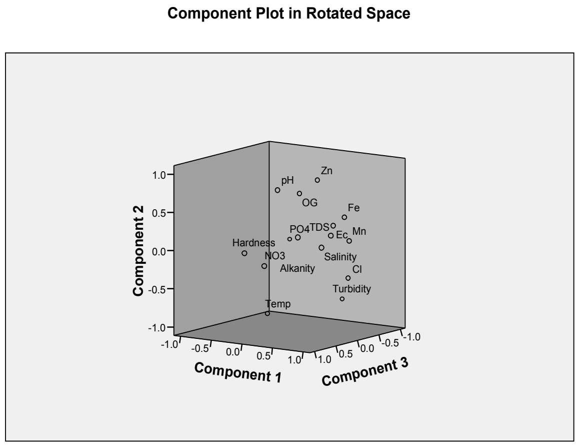

Fig. 4: Component plot in rotated space for 2004 borehole samples.
Borehole 2004 component (factor) rotated plot also indicates that factors 3 and 2 were most dominant (Fig. 4).

```
2000 C A S E      0        5        10        15        20        25
  Label      Num +---------+---------+---------+---------+---------+

  Ec          6   □□
  TDS         8   □□□□□□□
  Salinity    4   □□  □□□□□□
  Alkanity   10   □□□□□□□  □□□□□□□□
  Fe         12   □□□□□□□□□□□□   □
  Mn         13   □□        □□□□□□□□□□□□□□□□□□
  pH          2   □□□□□□□□□    □       □
  OG         15   □□□□□  □□□□□□□□□□□      □□□□□□
  Zn         14   □□□□□□□□□□         □  □
  Turbidit    1   □□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□  □□□□□□□□□□□□□□□□□□□□□
  Cl          7   □□□□□□□□□□□□         □       □
  NO3         5   □□□□□□□□□□□□□□□□□□□□□□      □       □
  Hardness   11   □□□□□      □□□□□□□□□□□□□□□□□□□□□      □
  Temp        3   □□□□□□□□□□□□□□□□□□□□□□            □
  PO4         9   □□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□
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Fig. 5: Dendrogram for 2004 borehole samples.

Cluster analysis of borehole 2004 extracted two clusters. Cluster 1 consists of Ec, TDS, salinity, alkalinity, Fe, Mn, pH, OG, Zn, turbidity and Cl. Maximum similarities were however, observed between Ec, TDS and salinity; Fe-Mn; pH-OG. Cluster 2 on the other hand consists of NO_3, hardness and temperature while cluster 3 was made up of only PO_4 (Fig. 5).

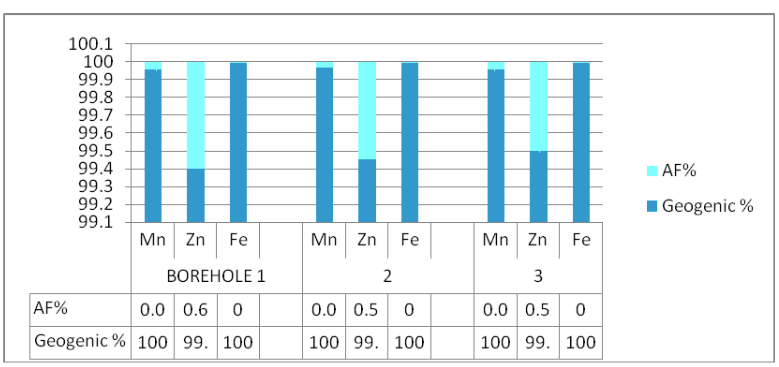

Fig. 6. Anthropogenic and geogenic factor plots for boreholes in the study area.
From the borehole AFs, significant contributions were as a result of natural proceses rather than anthropogenic inputs (Fig.6).

Fig.

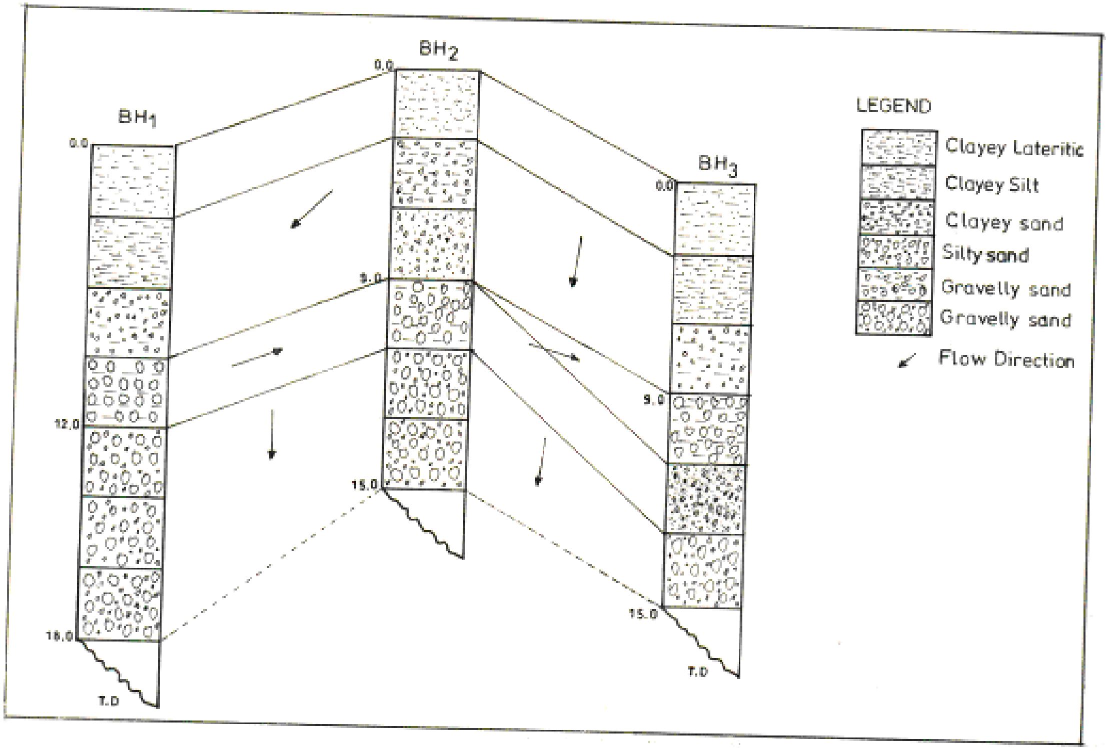

Fig. 7: The correlation panel of the three boreholes and directions.
Correlation panel of borehole flow direction shows that borehole 2 was at higher water level and so, the flow directions were towards borehole 1 and 3.

DISCUSSION

In 2000, the correlation (Table 2) relationships were generally weak. This observation could suggests diverse origin for the variables measured (Tijani et al., 2004; Abimbola et al., 2005). Factor 1 (Table 3) maybe due to natural processes such as saltwater intrusion; the generally high Fe content could be due to tropical climatic conditions (Nganje et al., 2010). The NO_3 and OG could also be due to anthropogenic inputs from agriculture and oil/gas related activities. The high factor loadings of TSS, hardness, turbidity and Cl suggest natural processes; PO_4 implies also agricultural/denitrification inputs (Lokhande et al., 2008). Factor 3 suggests wholly natural processes except the presence of PO_4. Factors 4 and 5 suggest natural processes of saltwater intrusion (Reghunath et al., 2002). In factor 6, the presence of SO_4 and OG implies human related inputs. The OG in particular means oil related sources (Table 3). Cluster 1 in the cluster analysis (Fig. 3) shows more of natural influences while cluster 2 suggests anthropogenic influences (Chakravarty et al., 2009).

In 2004, correlation (Table 4) coefficient shows that the variables were mostly sympathetic to each other. Apart from an indication of increase in human influence, it also suggests an overall water deterioration (Praveena et al., 2007). Factors 1, 2 and 3 (Table 5) were due to pseudo anthropogenic influences (Abbas et al., 2006), while in factor 4, the dominant influence was from human activities. In the cluster analysis (Fig. 5), cluster 1 was related to both natural and human inputs while in cluster 2, it maybe anthropogenic in puts from domestic/manure applications (Pathak et al., 2008).
The AFs for all the boreholes within the period of study revealed significant influence from natural processes (Fig. 6).

CONCLUSION

This study has revealed traces of OG from the filling station. Other human inputs from domestic/agriculture were also observed. Slow but steady deterioration of the borehole waters were also evident over the period under study. Based on these observations, proper monitoring and control measure are recommended.

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