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Research Article

A Preliminary Assessment of Soil Samples Around a Filling Station in Diobu, Port Harcourt, Rivers State, Nigeria

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Abstract: This research study is carried out to evaluate the effects of fuel station on surrounding soil. Twelve (12) soil samples were collected at intervals of four years (2000 and 2004) and were analyses. Generally, in both years, strong correlation coefficients suggest anthropogenic inputs while weak to moderate correlations implies natural sources. The 2000 and 2004 data also revealed higher concentrations at 2000 than 2004. This observation could be due to dilution, diffusion and dispersion over the period. The data acquired were subjected to multivariate statistical analysis and Contamination Factor (CF) index calculation. Both factor and cluster analyses show that natural and anthropogenic influences contributed to the variable sources. Directly linked to the fuel station were TOC, N, OG, Pb, Ni and Mn while PO_4 and NO_3 were related to chemical fertilizer application on farmlands. Other variables such as Cu, Ca, Mg, Zn and Fe may be due to natural processes. Contamination Factor (CF) for Zn, Fe and Cu in both years suggests some degree of enrichment. While the rest heavy metals recorded low contamination, Fe revealed moderate contamination.

Keywords: Anthropogenic factor, cluster analysis, contamination factor, diobu, factor analysis

INTRODUCTION

Soils constitute part of the vital environmental, ecological and agricultural resource that has/must be protected for sustainable development and for generations yet unborn. The determination of elemental and organic status of cultivated lands is necessary to identify yielding limiting deficiencies/enrichment of essential micronutrients, polluted soils and groundwater resources. This is important in Diobu because the inhabitants are mostly farmers and fishermen.

This study focuses on the organic constituents of oil and gas related activities and the heavy metals associated with it. The potential for these to constitute pollution nuisance in the area is high. The availability of these heavy metals and the presence of factors capable of mobilizing, distributing and storing them in pedologic system are critical. The heavy metals and other organic constituents of oil and gas have been implicated in various disease conditions in many other areas (Adaikpoh *et al*., 2005). There are concerns about the potential harmful effects of these heavy metals in soils in the area (Adaikpoh *et al*., 2005). So far, studies on heavy metals and organic constituents of oil and gas has been scanty, local and therefore, there is the need for regional update and integration to determine the geological and geochemical affinities of these oil and gas constituents and their consequences on soil at higher/ critical concentrations.

The objective of study is to determine the various constituents of oil and gas due to the fuel station, distribution and concentrations by comparing acquired values with standards.

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° 40'N and 5° 00'N and Longitude 6° 45'E and 7° 10'E (Fig. 1). The area lies within the subequatorial wetland climate that spreads across a number of ecological zones.

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; Ofodile, 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 40-150 m thick and comprises rapidly alternating sequences of sand and silt/clay with the later becoming increasingly more prominent seawards (Etu-Efeotor and Akpokodje, 1990; Ofoma *et al*., 2005).

MATERIALS AND METHODS

To evaluate the level of effects of the filling station on soils, a total of 12 soil samples were collected

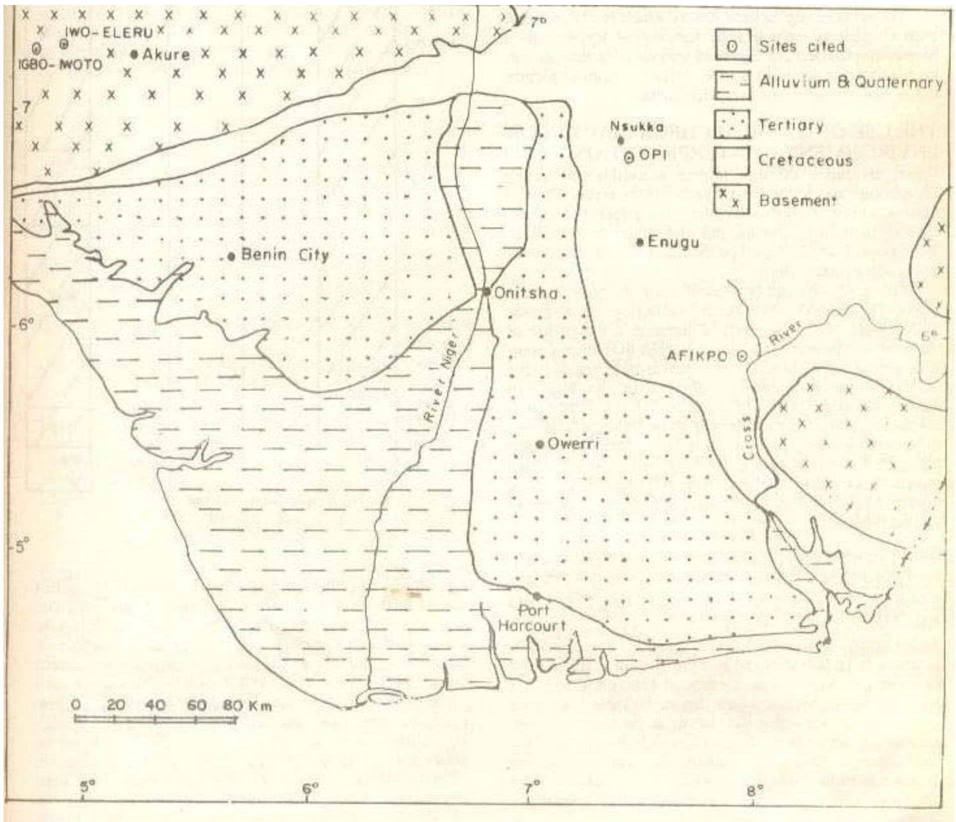

Fig. 1: Geological map of study Area (Etu-Efeotor and Akpokodje, 1990)

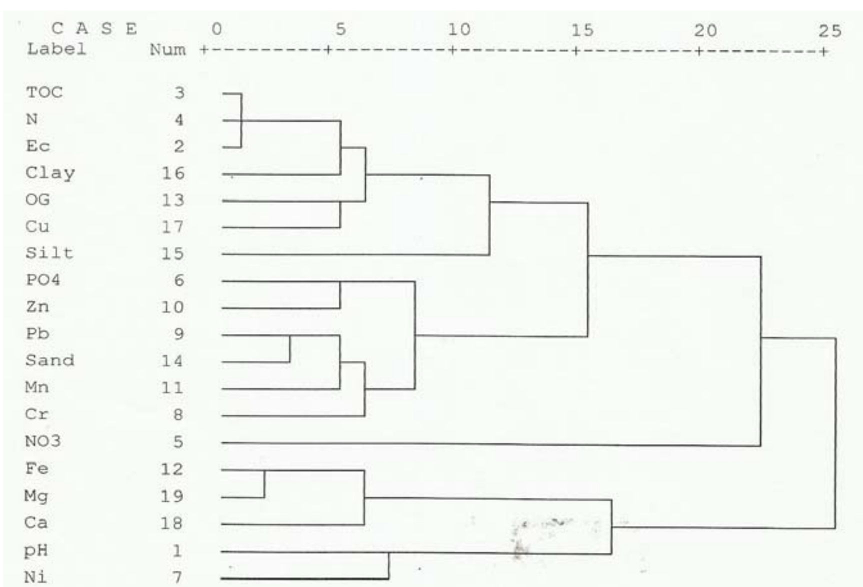

Fig. 2: R-mode cluster result of 2000 soil

radially over intervals of few meters from the filling station between the period of 2000 and 2004.

Soil sample collection: Sample points were located and recorded using GPS (Fig. 2). The samples were collected radially from the filling station and evenly distributed around the filling station. The soil samples were sun-dried, disaggregated (not crushed) using a pestle and mortar and sieved to min 80 meshes (0.177 mm) with cellulose nitrate filter. 1.0 g of each sample was digested with 3 mL of 1: 2 mixtures of perchloric acid and hydrofluoric acid. The concentrations of seven heavy metals were determined by AAS. Analytical procedures, operational parameters, calibration and standardization used in this study are according to APHA (2002). All analyses were performed in Fugro Nig. Ltd. Laboratory, Port Harcourt, Nigeria.

Analytical methods: Insitu measurements of pH and Ec were determined intrusively with appropriate probes. Spectrophotometer (Model Genesys 20) was used to determine the concentrations of Ca. Atomic absorption spectrophotometer (Model 210 VGP) was used to determine the concentrations of Ni, Cr, Pb, Zn, Mg, Mn and Fe. PO_4^{2-} and NO_3^- were determined by titration while TOC and N were analysed using CHN/S analyzer and OG was determined using standard methods (APHA, 2002).

SPSS 15.0 was used to perform all data analysis after auto-scaling for all parameters. Mathematically, PCA and PFA involve the following five major steps:

- Code variables to have zero means and unit variance.
- Calculate covariance matrix
- find eigenvalues and corresponding eigenvectors
- Discard any component that account for small proportion of variation in data set
- Develop the factor loading matrix and perform varimax rotation on the factor loading matrix to infer the principal parameters (Afshin and Moore, 2007; Ata *et al*., 2009).

In this study, only components or factors exhibiting an eigenvalue greater than one were retained.

Hierarchical cluster analysis: Cluster analysis comprises of a series of multivariate methods used to find the true groups of data (Praveena *et al*., 2007). Objects are grouped such that similar objects fall into the same class. Hierarchical clustering which joins the most similar observations and successively the next most similar observations was employed. The levels of similarity at which observations are merged were used to construct dendrogram. The squared Euclidean distance method is used to construct dendrogram. A low distance shows that the two objects are similar or close together whereas a large distance indicates dissimilarity (Praveena *et al*., 2007; Reghunath *et al*., 2002).

Factor analysis: The raw data were treated first to Z-scale transformation for standardization. Multivariate data analysis was utilized to identify the correlations among the measured parameters. Principal component analysis was used to reduce the number of input variables. Spearman's correlation matrix was performed to illustrate the correlation coefficients among the variables (Aprile and Bouvy, 2008).

Determination of contamination factor: To evaluate the degree of contaminants in the soils, CF 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 Hakanson (1980) and used by Mohiuddin *et al*. (2010) and Sekabira *et al*. (2010) was employ to assess degree of contamination, understand the distribution of elements of anthropogenic origin. The CF = $C_{metal\ concentration}/C_{background\ value}$.

RESULTS

The heavy metal mean concentrations (Table 1) in 2000 revealed this trend: Fe (847.82 mg/L) >Zn (39.58 mg/L) >Cu (37.86 mg/L) >Mn (17.39 mg/L) >Ni (0.05 mg/:) >Cr/Pb (0.03 mg/L). The cations and anions show these trends: Ca (485.0 mg/L) >Mg (77.0 mg/L) and NO_3 (52.49 mg/L) >PO_4 (0.54 mg/L), respectively. The organic constituents varied thus: OG (35.30) >TOC (1.80) >N (0.09). The percentage of soil components varies thus: sand> silt> clay for the same year. pH mean was 6.09 and Ec was 196 NTU.

In 2004, mean concentration trend of the heavy metals were Fe (816.33 mg/L) >Zn (32.70 mg/L) >Cu (29.55 mg/L) >Mn (13.95 mg/L) >Ni (0.04 mg/L) > Cr/Pb (0.02 mg/L). The cations and anions varied thus: Ca (492.0 mg/L) >Mg (73.0 mg/L) and anions NO_3 (40.98 mg/L) >PO_4 (0.38 mg/L). The organic components recorded thus: OG (33.08) >TOC (0.86) >N (0.04). The soil percentages recorded this order:

Table 1: Results of 2000 soil samples

Location	pH	Ec	TOC	N	NO3	PO4	Ni	Cr	Pb	Zn	Mn	Fe	OG	Sand %	Silt %	Clay%	Cu	Ca	Mg
CSA	6.2	92.58	1.25	0.06	56.12	0.36	0.07	0.00	0.00	30.82	13.1	1795.7	30.1	32.1	4.5	3.4	26.06	484	75
NBH	6.3	76.12	0.76	0.04	48.33	0.59	0.05	0.03	0.02	36.4	19.86	893.6	15.5	93.3	4.2	2.5	19.66	526	84
OUF	5.9	186.1	1.53	0.08	54.68	0.63	0.05	0.04	0.03	43.16	17.11	931.4	42.63	89.5	6.8	3.9	36.52	493	81
200M	5.75	219.5	2.06	0.11	53.06	0.69	0.04	0.02	0.04	45.8	19.93	716.3	45.8	90.2	5.1	4.7	29.14	475	70
800M	6.1	322.6	2.56	0.13	52.1	0.43	0.05	0.03	0.04	37.1	18.76	936.8	39.66	91.4	4.8	3.8	37.86	490	80
1KM	6.3	284.5	2.63	0.13	50.64	0.52	0.06	0.02	0.03	44.22	15.55	813.1	38.1	89.2	5.5	5.3	35.32	485	77
Mean	6.09	196	1.80	0.09	52.49	0.54	0.05	0.03	0.03	39.58	17.39	847.82	35.30						

* CSA: Cylinder Storage Area; NBH: Near Borehole; OUF: Outside the Fence; OG = Oil and Grease

Table 2: Results of 2004 soil samples

Location	pH	Ec	TOC	N	NO_3	PO_4	Ni	Cr	Pb	Zn	Mn	Fe	OG	Sand %	Silt %	Clay%	Cu	Ca	Mg
CSA	6.43	35.4	0.73	0.04	42.1	0.29	0.06	0.00	0.00	25.93	11.75	720	22.7	86.5	6.8	6.7	22.14	396	63
NBH	7.75	45	0.57	0.03	36.1	0.36	0.04	0.02	0.01	32.51	16.22	812	12.4	87.9	6.2	5.9	16.35	492	73
OUF	7.7	58.1	1.03	0.05	40.62	0.47	0.03	0.03	0.02	35.52	14.1	897	71.3	86.8	5.5	7.7	29.35	465	69
200M	8.22	81.0	0.69	0.03	38.43	0.42	0.03	0.01	0.03	40.82	15.16	729	36.7	86.1	7.7	6.2	23.42	450	61
800M	7.24	56.3	1.82	0.09	46.2	0.32	0.04	0.02	0.02	22.64	12.4	910	29.2	88.3	5.8	5.9	29.55	478	68
1KM	7.39	68.0	0.31	0.02	42.4	0.39	0.05	0.01	0.01	38.8	14.13	830	26.2	87.1	6.3	6.6	27.58	463	66
Mean	7.46	57.3	0.86	0.04	40.98	0.38	0.04	0.02	0.02	32.70	13.96	816.33	33.08						

*: CSA: Cylinder Storage Area; NBH: Near Borehole; OUF: Outside the Fence; OG = Oil and Grease

Table 3: Correlation coefficients of 2000 soil samples

	pH	Ec	TOC	N	NO3	PO4	Ni	Cr	Pb	Zn	Mn	Fe	OG	Sand	Silt	Clay	Cu	Ca	Mg
pH	1.000																		
Ec	-0.204	1.000																	
TOC	-0.160	0.968	1.000																
N	-0.218	0.972	0.997	1.000															
NO3	-0.470	0.070	0.005	-0.013	1.000														
PO4	-0.590	0.007	0.083	-0.012	0.286	1.000													
Ni	0.684	0.271	0.121	-0.196	0.300	0.828	1.000												
Cr	-0.250	0.282	0.056	0.093	0.388	0.571	0.698	1.000											
Pb	-0.513	0.777	0.659	0.710	0.311	0.557	0.811	0.648	1.000										
Zn	-0.537	0.521	0.499	0.549	0.184	0.793	0.656	0.483	0.766	1.000									
Mn	-0.376	0.164	0.004	0.071	0.587	0.676	0.913	0.645	0.705	0.420	1.000								
Fe	0.268	0.096	0.113	-0.130	0.198	0.176	0.053	0.680	0.103	0.234	0.140	1.000							
OG	-0.731	0.707	0.723	0.745	0.509	0.239	0.338	0.128	0.604	0.636	-0.008	0.231	1.000						
Sand	-0.212	0.482	0.323	0.373	0.668	0.685	0.799	0.840	0.853	0.708	0.806	0.310	0.180	1.000					
Silt	-0.477	0.357	0.302	0.313	0.353	0.418	0.252	0.507	0.377	0.652	-0.105	0.200	0.671	0.304	1.000				
Clay	-0.298	0.715	0.825	0.831	0.139	0.202	0.089	0.085	0.496	0.727	-0.151	0.468	0.779	0.213	0.511	1.000			
Cu	-0.278	0.822	0.787	0.772	0.383	0.153	0.027	0.261	0.489	0.368	-0.218	0.266	0.797	0.171	0.675	0.628	1.000		
Ca	0.522	0.515	0.651	-0.649	0.664	0.095	0.070	0.411	-0.215	0.329	0.357	0.564	0.851	0.275	0.350	-0.771	0.606	1.000	
Mg	0.520	0.187	0.367	-0.384	0.472	0.095	0.027	0.601	-0.089	0.290	0.166	0.898	0.582	0.311	0.004	-0.611	0.107	0.845	1.000

*: OG: Oil and Grease

Table 4: Correlation coefficients of 2004 soil samples

	pH	Ec	TOC	N	NO_3	PO_3	Ni	Cr	Pb	Zn	Mn	Fe	OG	Sand	Silt	Clay	Cu	Ca	Mg
pH	1.000																		
Ec	0.749	1.000																	
TOC	0.133	-0.102	1.000																
N	0.219	-0.201	0.995	1.000															
NO_3	0.553	-0.054	0.640	0.652	1.000														
PO_3	0.757	0.638	-0.214	0.288	-0.379	1.000													
Ni	0.883	-0.609	-0.263	0.181	0.322	-0.765	1.000												
Cr	0.502	0.120	0.415	0.385	-0.081	0.593	0.734	1.000											
Pb	0.814	0.814	0.335	0.238	-0.073	0.622	0.897	0.455	1.000										
Zn	0.715	0.724	-0.687	0.756	-0.576	0.783	0.438	0.057	0.418	1.000									
Mn	0.833	0.389	-0.488	0.532	-0.842	0.563	0.573	0.365	0.365	0.691	1.000								
Fe	0.121	0.032	0.589	0.579	0.438	0.265	0.366	0.822	0.227	0.238	0.051	1.000							
OG	0.291	0.321	0.248	0.200	0.102	0.759	0.584	0.583	0.487	0.285	0.054	0.415	1.000						
Sand	0.097	-0.321	0.506	0.537	0.296	-0.363	0.017	0.443	0.125	0.568	0.003	0.680	-0.352	1.000					
Silt	0.186	0.368	-0.432	0.463	-0.354	-0.103	0.069	0.718	0.183	0.383	0.156	0.892	-0.335	-0.653	1.000				
Clay	0.095	-0.027	-0.128	0.130	0.042	0.568	-0.101	0.281	0.056	0.261	0.183	0.189	0.822	-0.484	0.346	1.000			
Cu	0.059	0.381	0.507	0.469	0.770	0.298	0.188	0.308	0.350	0.052	0.495	0.612	0.640	0.026	0.418	0.451	1.000		
Ca	0.641	0.293	0.197	0.160	-0.182	0.368	0.603	0.757	0.430	0.165	0.630	0.674	0.020	0.675	0.467	-0.297	0.034	1.000	
Mg	0.124	-0.396	0.145	0.178	-0.204	0.070	0.185	0.706	0.177	0.214	0.382	0.647	-0.056	0.762	0.764	-0.061	0.188	0.734	1.000

OG: Oil and Grease

sand >silt >clay. Mean pH was 7.46 and Ec was 57.3 (Table 2).

From all variables analyses, mean concentrations were higher in 2000 than in 2004. This trend may not be unconnected with dissolution, diffusion and dispersion over time (Navarro *et al*., 2008). Apart from this, sand constitutes over 80% of soil body and as such very low retentive capacity. This means significant vertical infiltration and dispersion processes are the dominant factors (Navarro *et al*., 2008). Expectedly, the pH values increases during this period due to increased oxidation from surface environment (Chakravarty and Patgiri). From the filling station outwards, variables did not show a distinctive order of concentrations. The significantly higher Fe concentrations could be due to tropical climatic conditions, pyrites and marcasites associated with local sale found in the study area (Nganje *et al*., 2010; Adaikpoh *et al*., 2005).

From Table 3 and 4, the correlation coefficients were significant (r>0.7 or -0.7) and this indicates that variables have same source related to anthropogenic inputs (Reghunath *et al*., 2002; Ji-Hoon *et al*., 2003; Praveena *et al*., 2007).

The varimax rotated factor analysis yielded four factors in 2000. Factor 1 is a high factor loading of association of TOC, N, Ec, Cu, clay, OG, Pb, Ca and Zn. Factor 1 has eigenvalue of 5.881 and variance of 30.952%. Factor 2 has eigenvalue of 5.600 and % variance of 29.475. This factor consists of Ni, PO_4, Mn, sand, Pb, Zn, Cr, pH and NO_3. Ni is inversely

Table 5: Varimax rotated factor analysis of 2000 soil

Variables	Factor 1	2	3	4	Communalitis
pH	-0.059	-0.555	0.342	-0.684	0.897
Ec	0.969	0.176	0.084	0.046	0.979
TOC	0.990	0.047	-0.114	0.025	0.997
N	0.980	0.122	-0.134	0.034	0.995
NO3	-0.039	-0.454	-0.275	0.817	0.951
PO4	-0.131	0.924	-0.127	0.190	0.923
Ni	-0.061	-0.960	-0.022	-0.109	0.938
Cr	0.101	0.691	0.699	0.153	1.000
Pb	0.628	0.750	0.090	0.046	0.966
Zn	0.467	0.731	-0.165	0.255	0.844
Mn	-0.039	0.897	0.110	-0.274	0.892
Fe	-0.011	-0.014	0.985	0.036	0.973
OG	0.666	0.214	-0.265	0.655	0.989
Sand	0.336	0.848	0.354	-0.186	0.991
Silt	0.325	0.251	0.249	0.779	0.838
Clay	0.796	0.119	-0.413	0.232	0.872
Cu	0.811	-0.104	0.248	0.515	0.996
Ca	-0.577	0.179	0.604	-0.510	0.990
Mg	-0.252	0.016	0.932	-0.246	0.993

Eigen value: 5.881, 5.600, 3.477, 3.065; % Variance: 30.952, 29.475, 18.299, 16.134; % Cumulative: 30.952, 60.427, 78.726, 94.860

Table 6: Varimax rotated factor analysis of 2004 soil

Variables	Factor 1	2	3	4
pH	0.918	0.180	-0.352	-0.014
Ec	0.879	-0.284	-0.015	0.112
TOC	0.128	0.304	0.895	-0.088
N	0.028	0.323	0.892	-0.104
NO_3	-0.231	-0.070	0.896	0.110
PO_4	0.682	0.158	-0.321	0.638
Ni	-0.889	-0.308	0.013	-0.175
Cr	0.427	0.821	0.106	0.328
Pb	0.968	-0.023	0.209	0.055
Zn	0.586	-0.226	-0.656	0.320
Mn	0.555	0.318	-0.750	-0.167
Fe	0.168	0.791	0.467	0.269
OG	0.382	0.095	0.204	0.867
Sand	-0.131	0.786	0.335	-0.461
Silt	0.240	-0.839	-0.306	-0.360
Clay	-0.115	-0.004	-0.062	0.986
Cu	0.225	0.010	0.704	0.567
Ca	0.520	0.791	-0.072	-0.217
Mg	-0.121	0.975	-0.166	-0.084

Eigen value: 5.310, 4.795, 4.671, 3.236; % Variance: 27.950, 25.238, 24.582, 17.031; % Cumulative: 27.950, 53.188, 77.770, 94.801

related to heavy metals Factor 3 consists of high factor loadings of Fe, Mg and moderate loadings of Cr, Ca and weak clay loading. Factor 3 has eigenvalue of 3.477 and variance of 18.299 %. Factor 4 is made up of high factor loadings of NO_3, silt and moderate loadings of pH, OG and finally weak loadings of Cu and Ca (Table 5).

In 2004, the varimax rotated factor analysis generated four factors. Factor 1 has eigenvalue of 5.310 and variance of 27.950%. Factor 1 consists of high factor loadings of Pb, pH, Ni, Ec and moderate loadings of PO_4, Zn, Mn, Ca and Cr. Ni has inverse relation with other variables. Factor 2 is an association of high factor loadings of Mg, silt, Cr, Fe, Ca and sand. Factor 2 has eigenvalue of 4.795 and variance of 25.238%. Factor 3 recorded high factor loadings of NO_3, TOC, N, Mn and Cu; moderate loading of Zn and weak loading of Fe. It recorded eigenvalue 000000of 4.671 and variance of 24.582 %. Factor 4 yielded high loadings of clay, OG; moderate loading of PO_4 and weak loadings of Cu and sand. Factor 4 has eigenvalue of 3.236 and total variance of 17.031% (Table 6).

R-mode cluster analysis of 2000 soils yielded four clusters. Cluster 1 is an association of TOC, N, Ec, clay, OG, Cu and silt. Maximum similarities were observed between TOC, N and Ec in cluster 1. Cluster 2 consists of PO_4, Zn, Pb, sand, Mn and Cr. Attached to cluster 2 at a farther distance is cluster 3, which consists uniquely of NO_3. This uniqueness could imply different factor from factors affecting other variables. Cluster 4

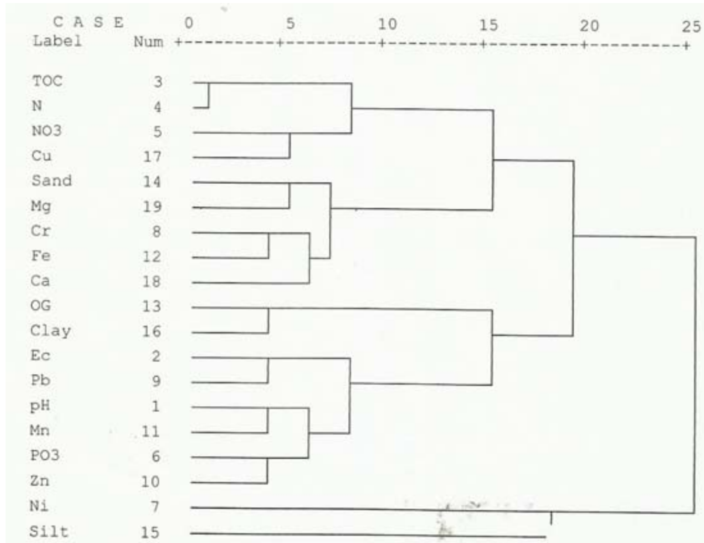

Fig. 3: R-mode cluster results of 2004 soil samples

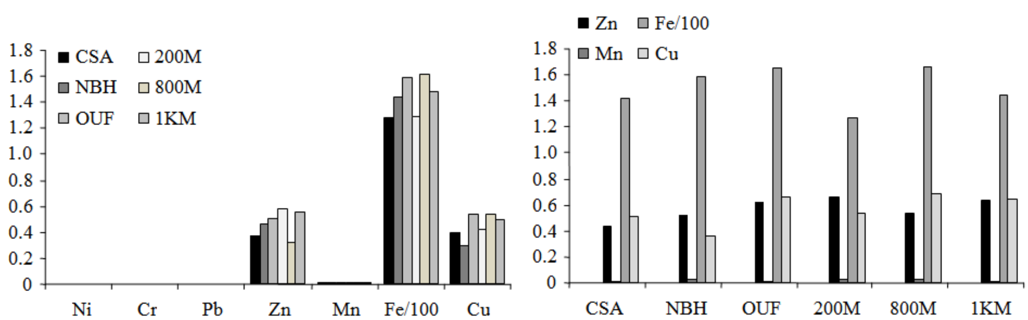

Fig. 4: CF result of 2000 soil

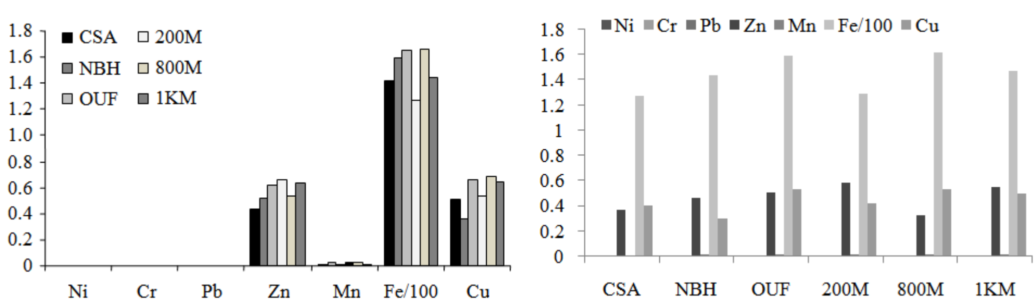

Fig. 5: CF results of 2004 soil

consists of Fe, Mg, Ca, pH and Ni. Maximum similarity was observed between Fe and Mg (Fig. 2).

In 2004, three clusters were obtained from R-mode analysis. Cluster 1 consists of TOC, N, NO_3, Cu, sand, Mg, Cr, Fe and Ca with maximum similarities observed between TOC and N followed by Cr and Fe. Cluster 2 revealed maximum similarities between OG and clay; Ec and Pb; pH and Mn and PO_4 and Zn. This cluster consists of OG, clay, Ec, Pb, pH, Mn, PO_4 and Zn. Cluster 3 consists of Ni and silt at the farthest Euclidean distance. Though Ni and silt in the same cluster, greatest dissimilarity was observed between them (Fig. 3).

In 2000, CF values for Ni, Cr, Pb, Zn, Mn and Cu were <1 in all locations. This means low contamination (Hakanson, 1980; Mohiuddin *et al*., 2010). Fe on the

Table 7: CF of heavy metals in 2000 soils

Variables						
Ni	Cr	Pb	Zn	Mn	Fe/100	Cu
0.0009333	0.0000	0.0000	0.44029	0.0137895	1.4133215	0.51018
0.0006667	0.0003	0.0016	0.52	0.0209053	1.5872114	0.35745
0.0006667	0.0004	0.0024	0.61657	0.0180105	1.6543517	0.664
0.0005333	0.0002	0.0032	0.65429	0.0209789	1.2722913	0.52982
0.0006667	0.0003	0.0032	0.53	0.0197474	1.6639432	0.68836
0.0008	0.0002	0.0024	0.63171	0.0163684	1.4442274	0.64218

Contamination Factor (CF) indices: CF<1, 1≥CF≥3, 3≥CF≥6, CF>6; Degree of contamination: low contamination, moderate contamination, considerable contamination, very high contamination

Table 8: CF of heavy metals in 2004 soils

Variables						
Ni	Cr	Pb	Zn	Mn	Fe/100	Cu
0.0008	0.0000	0.0000	0.37043	0.0123684	1.2788632	0.40255
0.0005333	0.0002	0.0008	0.46443	0.0170737	1.4422735	0.29727
0.0004	0.0003	0.0016	0.50743	0.0148421	1.5932504	0.53364
0.0004	0.0001	0.0024	0.58314	0.0159579	1.294849	0.42582
0.0005333	0.0002	0.0016	0.32343	0.0130526	1.616341	0.53727
0.0006667	0.0001	0.0008	0.55429	0.0148737	1.4742451	0.50145

other hand recorded moderate contamination (1≥CF≥3) in all sampled points (Table 7 and Fig. 4).

In 2004, Ni, Cr, Pb, Zn, Mn and Cu revealed low contamination in all locations (CF<1) while only Fe recorded moderate contamination (1≥CF≥3). When compared, 2000 CF values were higher in all sampled points than 2004 and particularly with respect to Fe, Zn, Cu and Mn (Fig. 5 and Table 8).

DISCUSSION

Between the period under study, mean concentrations of the variables were higher in year 2000 than 2004 (Table 1 and 2; Fig. 4 and 5). This may be due to dissolution, diffusion and dispersion from the source over time (Navarro *et al*., 2008). The composition of the soil is significantly made up of sand. This means low retentive capacity of soil and more of infiltration and lateral dispersion (Chakravarty and Patgiri, 2009).

In 2000, R-mode factor analysis yielded four factors. Factor 1 which consists of high factor loadings of TOC, N, Ec, Cu, clay, OG and Pb are directly related to activities arising from the fuel station and hence anthropogenic (Yang *et al*., 2009). The OG, TOC and N are plants matter related to fuel station. Ca, Zn have weak loadings and are not directly linked to the fuel station. The Ec high loading could be attributed to other variables which were retained by the presence of clay. Factor 2 is also anthropogenic. While Ni, Pb, Mn and Cr may be due to fuel station, NO_3 and PO4 may have arisen from chemical fertilizer/or phosphate mineral dissolution. The pH was influenced by the presence of PO_4 and NO_3 (Tauhid *et al*., 2008; Armah *et al*., 2010). Factor 3 on the other hand was naturally influenced given the high prevalence/association of Fe, Mg, Ca and clay in the area. Factor 4 was also anthropogenic in nature. While NO_3 could be due to fertilizer/manure applications, which is associated with pH, OG is linked directly to the fuel station. The Cu and Ca may or may not be associated with the fuel station, the presence of silt helps to absorbed/and retain these ions (Yang *et al*., 2009). In 2004, factor 1 may be due to anthropogenic activities within the study area while PO_4 could be agricultural/domestic effects (Afshin and Moore, 2007). Factor 2 was due significantly to natural processes. Factor 3 and 4 in 2004 were related directly to “petrochemical source” station (Yang *et al*., 2009). Fe is naturally high in the tropics and given its negative loading, natural influences may be more significant (Nganje *et al*., 2010; Adaikpoh *et al*., 2005). The clay in factor 4 is significant in its retentive capacity over sand hence the very high loading. Factor 4 is anthropogenic in origin and results from oil, gas, domestic and agricultural influences.

Cluster 4 in 2000 suggests influences arisen from natural processes operating in the soil. Cluster 3 consists of only NO_3 attached at a farther distance to cluster 1 and 2. This cluster suggests unique factor such as fertilizer application on farmland where NH_4^+, the main components of chemical fertilizer is easily oxidised to NO_3 due to nitrification process (Afshin and Moore, 2007). Clusters 1 and 2 were due to anthropogenic factors. While cluster 2 implies a mixture of agrochemical products, cluster 1 is related wholly to anthropogenic input from the oil and gas activities in the area (Ji-Hoon *et al*., 2003; Afshin and Moore, 2007). In 2004, clusters 1 and 2 were both anthropogenic and natural activities. This is because in cluster 1, Cu, Mg, Fe and Ca and in cluster 2, Zn cannot be easily be said to be associated with the human activity in the area. The rest variables in clusters 1 and 2 were easily related to anthropogenic influences (Armah *et al*., 2010).

Of the 7 heavy metals, Zn, Mn, Fe and Cu showed some level of contamination. During this period of study also, the CF were higher in 2000 than in 2004. While factors earlier suggested maybe responsible for these variations, low activity within the station around 2004 could have also contributed to this observation. Also note worthy is the fact that these heavy metals which shows some level of contamination cannot be directly linked to oil and gas related activities.

CONCLUSION

The activities around the fuel station were responsible for the presence of TOC, N, OG, Ni and Pb. The presence of NO_3 and PO_4 may have been due to agricultural/domestic wastes on the soil. The clay and silt were also responsible for the high retention of the relatively enhanced variables.

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