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 groundwater 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° 40’N and 6° 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; 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 gravelly 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 Akpoje, 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= Cm/Bm

where Cm is the measured concentration in soil, Bm 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 Borehole 1 | 2004 | 2000 and Borehole 2 | 2004 | 2000 and 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  | 5                   | 60   | 10                  | 5    | 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 | Alkalinity | TSS | OG |
|-----------|-----------|----|------|----------|-----|----|--------|--------|--------|----|----|----|----|-----------|------------|-----|-----|
| Turbidity | 1.00      | -0.93 | 1.000 | 1.000 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH        |           | 1.000 | -0.093 | -0.543 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Temp      |           |       | 1.000 | -0.431 | -0.288 | 0.957 | 0.014 | 0.072 | 0.127 | 0.198 | 0.198 | 0.198 | 0.198 | 0.198 | 0.198 | 0.198 | 0.198 |
| Salinity  |           |       |       | 1.000 | -0.358 | -0.162 | -0.269 | -0.046 | -0.253 | -0.227 | -0.227 | -0.227 | -0.227 | -0.227 | -0.227 | -0.227 | -0.227 |
| TDS       |           |       |       |        | 1.000 | -0.117 | -0.257 | 0.332 | 0.282 | 0.332 | 0.332 | 0.332 | 0.332 | 0.332 | 0.332 | 0.332 | 0.332 |
| Ec        |           |       |       |        |        | 1.000 | -0.543 | -0.337 | -0.373 | -0.373 | -0.373 | -0.373 | -0.373 | -0.373 | -0.373 | -0.373 | -0.373 |
| NO\(_3\)  |           |       |       |        |        |        | 1.000 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 |
| PO\(_4\)  |           |       |       |        |        |        |        | 1.000 | -0.909 | -0.909 | -0.909 | -0.909 | -0.909 | -0.909 | -0.909 | -0.909 | -0.909 |
| SO\(_4\)  |           |       |       |        |        |        |        |        | 1.000 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 |
| Cl        |           |       |       |        |        |        |        |        |        | 1.000 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 |
| Mn        |           |       |       |        |        |        |        |        |        |        | 1.000 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 |
| Zn        |           |       |       |        |        |        |        |        |        |        |        | 1.000 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 |
| Fe        |           |       |       |        |        |        |        |        |        |        |        |        | 1.000 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 |
| Hardness  |           |       |       |        |        |        |        |        |        |        |        |        |        | 1.000 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 |
| Alkalinity|           |       |       |        |        |        |        |        |        |        |        |        |        |        | 1.000 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 |
| TSS       |           |       |       |        |        |        |        |        |        |        |        |        |        |        |        | 1.000 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 |
| OG        |           |       |       |        |        |        |        |        |        |        |        |        |        |        |        |        | 1.000 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 | -0.938 |

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<sub>3</sub> | -.956 | -.197 | -.159 | .032 | .083 | .087 |
| PO<sub>4</sub> | .230 | -.464 | .776 | -.285 | -.154 | .106 |
| SO<sub>4</sub> | -.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 |
| Alkalinity | .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<sub>3</sub>, Fe, salinity and OG. Factor 2 was an association of TSS, hardness, turbidity, Cl and PO<sub>4</sub> 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<sub>4</sub>, 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<sub>4</sub>, OG and pH (Table 3).
From the rotated factor plot (Fig. 2), factors 3 and 2 were the dominant. 

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
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 | Factor 2 | Factor 3 | Factor 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).
Component Plot in Rotated Space

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).

![Component Plot in Rotated Space](image)

| Label | Num |
|-------|-----|
| Ec    | 6   |
| TDS   | 8   |
| Salinity | 4   |
| Alkalinity | 10  |
| Fe    | 12  |
| Mn    | 13  |
| pH    | 2   |
| OG    | 15  |
| Zn    | 14  |
| Turbidity | 1   |
| Cl    | 7   |
| NO3   | 5   |
| Hardness | 11  |
| Temp  | 3   |
| PO4   | 9   |

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 NO3, hardness and temperature while cluster 3 was made up of only PO4 (Fig. 5).

![Dendrogram for 2004 borehole samples](image)

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 processes rather than anthropogenic inputs (Fig.6).
DISCUSSION

In 2000, the correlation (Table 2) relationships were generally weak. This observation could suggest diverse origin for the variables measured (Tijani et al., 2004; Abimbola et al., 2005). Factor 1 (Table 3) may be 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 (Lokhande et al., 2009). 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 may be 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 evident over the period under study. Based on these observations, proper monitoring and control measures are recommended.

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