SPATIAL VARIATION IN GROUNDWATER GEOCHEMISTRY AND WATER QUALITY INDEX IN PORT HARCOURT

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ABSTRACT

The aim of this work is to convert the complex chemical quality data of groundwater in Port Harcourt area into a Water Quality Index, WQI, determine the Operating geochemical processes and produce a map reflecting the spatial distribution of the water quality. Results of the physicochemical analysis of the groundwater from 71 boreholes show that 21% of the boreholes are low in pH indicating acidic water. Elevated electrical conductivity values in some of the water samples suggest pollution by sea water. Iron concentration is above the World Health Organization guide value in 9% of the boreholes studied, with maximum value up to 0.62mg/L. A high Coliform count in 9% of the wells poses a potential health risk. The water is generally classified as soft and fresh water based on its hardness and TDS. Concentrations of major ions are: $Ca > Mg > Na > K = HCO_3 > Cl > SO_4 > NO_3$ in the order of abundance. Ca-Mg- HCO_3 and Ca-Mg-SO₄-Cl are the dominant hydrogeochemical facies. Interpretation of the hydrochemical data suggests that ion exchange; reverse ion exchange and silicate weathering are the prevailing hydrochemical processes responsible for the groundwater chemistry. Hydrochemical indices (Mg/Ca, Cl/HCO₃, and Cation Exchange Value, (CEV) generally indicate low-salt inland water, with minimal marine influence. Using the weighted arithmetic mean method of the Water Quality Index Scheme, the groundwater is classified into five groups: Excellent (59%), Good (30%), Poor (11%), Very poor (4%) and Unsuitable (6%) with respect to human consumption. The general trend on the WQI map reveals that water quality decreases southwestwards suggesting a possible influence of the sea water.

INTRODUCTION

Since the commencement of oil exploitation in the Niger Delta in 1958, the population of Port Harcourt has grown from 179, 563 according to the 1963 population census through 213, 443 (1991 Census) to an estimate of 1.3 million in 2008. These figures show that the city and its region have witnessed an unprecedented growth. This rapid growth has several implications on the carrying capacity of the environment and has resulted in poor sanitary conditions across the city, which portends danger to the availability of safe

drinking water arising from increasing sources of private water supply, solid waste generation and poor disposal system from various anthropogenic activities. With the present pace of industrialization and infrastructural development, groundwater resource contamination has become a matter of deep concern. However little or no efforts have been expended in combating these problems. For example, there is no policy regulating the development of private water supply via boreholes, and construction of household sewage disposal systems by septic tanks,

which can be found in every residential plot. This is against the backdrop of reported water quality problems, including the ingress of saline water in boreholes due to over pumping. Several groundwater quality investigations carried out in Port Harcourt metropolis consider the traditional physical, chemical and bacteriological constituents in line with the World Health Organization (WHO's) guide values. These studies have widely reported that iron and chloride concentrations in the Port Harcourt area and indeed, the Niger Delta region are above acceptable limits (Etu-Efeotor, 1981; Etu-Efeotor and Odigi, 1983; Amajor, 1986, 1989; Udom et al, 1999). However, most of these studies emphasize location-specific water quality with respect to individual chemical parameters without an attempt to give a picture of the local or regional water quality and its spatial distribution. This work is an attempt to use the physicochemical results of groundwater analysis to derive the water quality index, identify the chemical processes that control the hydrogeochemistry of the groundwater and produce a map showing the spatial variation of water quality in the study area.

Study area Description

Port Harcourt and its environs, the study area is the capital of Rivers State in the Niger Delta Sedimentary Basin of Southern Nigeria with an area of 924,000 km². Port Harcourt is located within latitudes 04°43'N and 05°00'N and Longitudes 06⁰45'E and 07⁰06'E (Fig.1) within the subequatorial region north of the Bight of Biafra. Its geomorphological features consist mainly of fresh water swamp, mangrove swamps, beaches, bars and estuaries (Etu-Efeotor and Odigi, 1983). The closeness of the area to the sea is marked by the localized Saltwater/Mangrove swamp to the extreme South of Port Harcourt, and

Northwest of Okrika. The tributaries and creeks of the main Bonny River constitutes the local anatomizing drainage pattern. Generally, elevations ranging between 7 and 16 above sea level were recorded during the field studies, which reveals that the Port Harcourt area is low-lying. A 55 year rainfall data (1950-2006) obtained from the Nigerian Metrological Agency, Lagos, shows that rainfall in the area exhibits a double maxima regime with peaks in July and September and a little dry season in August.

Geologically, the study area lies within the Niger Delta basin which covers an area of over 70,000km² and is composed of an overall regressive clastic sequence reaching a thickness of 10,000 to 12,000m composed of Quatenary and Tertiary sedimentary deposits (Table 1). The Tertiary Formations are made up of three principal lithostratigraphic units based on the dominant environment of deposition (Short and Stauble, 1967). The oldest stratigraphic unit is the Akata Formation which is a deep marine pro-delta unit composed of mainly shales deposited during the Paleocence. Shales of the Akata Formation are generally regarded as the hydrocarbon source rocks of the Niger Delta. Overlying the Akata Formation is the paralic Agbada Formation, Eocene to Recent in age and consisting mainly of sequences of sandstones and shales. The sand units constitute the hydrocarbon reservoir while the shales form the seal. The topmost unit is the Benin Formation, Eocene to Recent in age, deposited in continental fluviatile conditions. It consists mainly of over 90% massive porous sand with localized clay/shale interbeds and constitutes the regional aquifer. These subsurface lithostratigraphic units are overlain by various types of Quaternary deposits) which consist of either a relatively uniform lithology or rapidly alternating sequences of Recent deltaic sand, silt, claypeat or sand - silt - clay mixtures with the latter becoming increasingly more prominent

towards the sea.

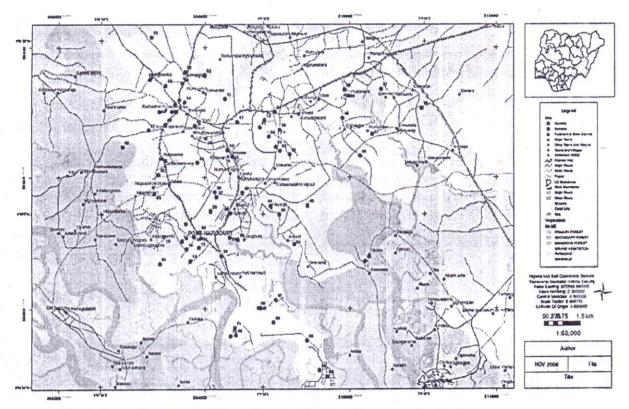


Fig.1: Location map of Port Harcourt, showing sampling points

Table 1.: Geologic units of the Niger Delta (after Short and Stauble, 1967).

Geologic Unit	Lithology	Age
Alluvium (General)	Gravel, sand, clay, silt	
Freshwater Backswamp, Meander belt	Sand, clay, some silt, gravel	
Saltwater Mangrove swamp and backswamp	Medium-fine sands, clay and some silt	Quaternary
Active/abandoned beach ridges	Sand, clay, and some silt	
Sombreiro-Warri deltaic plain	Sand, clay, and some silt	
Benin Formation (Coastal	Coarse to medium sand; subordinate silt and	Miocene -
Plain sand)	clay lenses	Recent
Agbada Formation	Mixture of sand, clay and silt	Eocene – Recent
Akata Formation	Clay	Paleocene

Using lithologic and geophysical logs, Etu-Efeotor and Akpokodje (1990) and Etu Efeotor (1996) delineated five regional levels of aquifers in the Niger Delta, including Port Harcourt. The first aquifer occurs under phreatic conditions between depths of 0 and 45m. It supplies water to small private boreholes and is the most extensively exploited causing water table decline, pollution and saline water intrusion. The second and third aguifers (45 to 130m and 130 - 212m deep respectively) are semi-confined and are usually penetrated by medium sized industrial, community and boreholes. Its exploitation is moderate, and it experiences limited saline water intrusion. The 4th aguifer is 219 to 300m deep and is tapped by few large scale deep boreholes for municipal and industrial water schemes. The 5th level of aquifer is more than 300m deep. It supplies water to very few community/ industrial boreholes in coastal mangroves swamp area. Majority of boreholes usually penetrate only the first and second aquifers. The regional groundwater problems include saltwater intrusion and pollution in upper aquifers of coastal areas and swamp due to over pumping; high iron content in some horizons/ areas causing encrustation and contamination and pollution by sewage, industrial activities and municipal waste.

METHODOLOGY

Data from 71 boreholes were obtained from the Niger Delta River Basin Development Authority (a federal agency charged with the development of groundwater resources in the area) In addition, the researchers collected

water samples directly from 24 boreholes to serve as a check against the secondary data Niger Delta Basin Development from Authority (NDBDA) which contain partial analyses with respect to the total ionic constituents. Samples were collected in 300ml screw cap plastic bottles. Before sample collection, the bottles were properly rinsed with the borehole water to be sampled, filled to the brim, tightly covered to retain the CO2 that was in the water when the sample was taken and to avoid contamination. appropriately labelled at the points of collection and transported to the laboratory in an ice box for further analyses. A Global Positioning System (GPS), GPSMap76 model was used for recording coordinates and elevation readings. Because the chemistry of groundwater is sensitive to environmental changes. the following parameters were measured and recorded insitu: Colour, pH, conductivity temperature. In the laboratory, the following parameters were analyzed: Magnesium, Sodium, Potassium, Chloride, Bicarbonate, Nitrate, Sulphate, Phosphate, Iron, Manganese, Carbonate and Total Dissolved Solids. Sulphate, Nitrate Phosphate were determined using the HACH 2400 Spectrophometer, while Magnesium, Potassium, Iron, Manganese, Calcium and Sodium were determined using the GBC Avanta AAS Version 2.2. The analytical methods used in the determination of water chemistry were in accordance with ASTM and APHA Standard procedures as summarized in Table 2. These data were compared with the WHO (1998) standards for potability.

Table 2: Methods used for the physicochemical analysis of groundwater samples.

Parameters	Measurement Method	Standard
Temperature	Mercury - in - glass thermometer	. •
Colour	Lovibond Nessleriser Comparator Electrical Resistivity Tester,	APHA 2510 B
EC pH and Eh	Hanna HI 8314 Membrane Metre	APHA 4500 H
Turbidity	HACH 2100AN Turbidimeter	APHA 2130 B
Total Hardness	Titration Method	APHA 2340-B
Chloride	Silver Nitrate Titration	ASTM 512B
Bicarbonate	Phenolphthalein Alkalinity Method	APHA 2320-B
Nitrate	Ultraviolet Spectrophotometer Screening Method	APHA 4500-NO ₃ B
Sulphate	Turbidimetric Method	ASTM D-516
Phosphate	Ascorbic acid Method	APHA 4500-PE
Magnesium	Direct Atomic Absorption	ASTM D 511-93
Calcium	Direct Atomic Absorption	ASTM D 511-93
Manganese	Direct Atomic Absorption	ASTM D 858
Iron	Direct Atomic Absorption	ASTM D 1068
Potassium	Direct Atomic Absorption	ASTM D 4192-97

Table 3: Water Quality parameters with their WHO (1998) standards and unit weights

WHO Standard (Si)	Unit weight (Wi)
6.5-8.5	0.004
500 <i>μs/cm</i>	0.002
500mg/L	0.002
500mg/L	0.002
250mg/L	0.004
250mg/L	0.004
0.3mg/L	3.333
50 <i>mg/L</i>	0.020
	6.5-8.5 500µs/cm 500mg/L 500mg/L 250mg/L 250mg/L 0.3mg/L

 $\Sigma wi = 3.371$

WATER QUALITY INDEX DETERMINATION

Water Quality Index (WQI) is a commonly methodology for summarizing quantitative water data. It was developed to provide standardized method for categorizing the water quality of various water bodies. It is a rating reflecting the composite influence of a number of water quality parameters on the overall water quality. It is aimed at improving the understanding of water quality issues by turning complex water quality data into information that is understandable by the public and policymakers. It is a simple, objective, consistent and reproducible numeric scale on which to represent water quality information. Indices are useful aids in quantification. simplification and communication of complex environmental data and also serve as tools for monitoring the state of the environment

The use of indices to condense and summarize large volumes of water quality data has increasingly gained acceptance because it is a quick guide to the overall water quality at different locations. Although more than 20 different water quality indexes have been published in different literatures since mid 1960's by various researchers including Horton, (1965); Dunnette, (1979); Dojlido et al., (1994); Cude, (2001), the most often used ones are the Solway modified unweighted and weighted sum, and the arithmetic unweighted and weighted mean methods. A common factor is that these methodologies use a set of composite factors, integrating physical, chemical, and bacteriological variables in their procedures. The importance of the various water quality parameters considered in the formulation of a WQI is largely dependent on the intended use of the water. Hence this study evaluated the water quality indices for potability. The formulation of the Water Quality Index in this study was based on the

modified Arithmetic weighted mean method as explained by Shankar and Sanjeev (2008). By this method, the basic steps involved in the development of most water quality indices include:

Selecting the set of water quality variables (indicators) of concern.

> Eight physicochemical parameters were considered in the calculation of WQI in this study. They are: pH, Electrical conductivity, Dissolved Solids, Total Hardness, Chloride, Sulphate, Iron and Nitrate.

2. Weighting the indicators based on their relative importance to overall water quality. The WHO recommended guide values (Si) for each parameter (Table 3) is used in calculating the unit weights (W_i). $W_i = \frac{K}{Si} \dots 1$

$$W_i = \frac{K}{S_i} \dots 1$$

Where K is proportionality constant and has been assumed to be equal to unity, i.e. 1.0 for the sake of simplicity.

- 3. Transformation of the raw analytical results for selected water quality variable with different units into unitless sub-index values the WHO recommended guide values (Si) for each parameter in calculating the unit weights (Wi).
- Aggregation of the sub-indices into the 4 overall quality index to give a water quality index value.

The quality rating, q_i for the *i*th parameter P_i for all other parameter except pH is given by:

 $q_i 100*(V_i/S_i)$..(2)

where V_i is the observed value of the ith parameter, and S_i is the WHO Standard recommendation for drinking water. However, the quality rating for

pH, $q_{\rm pH}$ can be computed from the equation:

 $q_{\rm pH}$ =100*[(V_{pH}~7.0)/1.5] (3) where, V_{pH} is the observed pH value and '~' is the algebraic difference between V_{pH} and 7.0.

5. Formulating and computing the overall water quality index.

The Water Quality Index (WQI) is calculated by aggregating the weighted arithmetic mean of the water quality rating q_i , together to form the overall index by the following equation:

WQI = $[\sum (q_i W_i)/\sum W_i]$ (4) where $q_i W_i$ is the sub-index stated earlier, and both summations are taken from i = 1 to i = n, where n is the number of parameters to be considered in the WQI calculation.

To potray the spatial variation in the potability of the water, the water quality data with their respective coordinates were imputed into the Environmental Systems Research Institute (ESRI) 2006 ArcGIS 9.0, Version 9.2.0.1324 software application to produce the water quality map of the study area.

RESULTS AND DISCUSSIONS

The chemical composition of the water is presented in Table 4. A summary of the result was compared with the WHO guidelines (1998) for drinking water and is presented in Table 5. Most of the water wells studied whose depth range is 19 - 77metres are tapping from the 1st and 2nd aquifers of the Benin Formation. However a few wells within the depth range of 165 to 255 metres, tap water from the deeper aquifers. 5 Hazen units are recorded in all the groundwater samples collected indicating that the colour is the WHO compared with acceptable Standards. Turbidity values ranged from 0.1 -WHO 0.3NTU, which is below

recommended 5NTU guideline for drinking water and is equally below the 1NTU median turbidity recommended in order to achieve adequate terminal disinfection. The hydrogen ion concentration (pH) and Redox potential (Eh) of the groundwater in the study area ranges from 3.80 - 7.80 and $124 - 195 \ mV$ respectively. Generally, the standard for healthy water is a pH between 6.5 and 8.5 (WHO, 1998). The groundwater of the area is acidic to slightly alkaline and is comparable to the results obtainede by Udom et al (1999). Slightly alkaline values are observed in wells in Elekahia, Elelenwo, Rumuibekwe, Trans-Amadi, Ogbunabali, Rumuolumeni, Churchill and Reclamation area. It was observed that the Eh increase as pH values decreases (Fig.3). between Electrical conductivity ranges $8.62\mu S/cm$ and $1250\mu S/cm$, far below the WHO guide values. TDS values are generally below 180mg/L which is within the WHO range for potable waters (Sawyer et al., 2003) except in some wells in Ogbunabali and Marine Base with concentrations of 298 and 468mg/L respectively.

Total suspended solids (TSS) are generally below 14mg/L, with maximum concentration of 35mg/L in wells located in Diobu and Rumuigbo respectively. Generally, salinity ranges between 0 and 10mg/L with anomalously high values of 4.8 and 10mg/L found in Reclamation and Borokiri areas respectively. There is an indication of saline water in the study area as evident from EC and Cl concentrations for which 4% of the samples showing values higher than their permissible limits. Groundwater hardness ranges from 0mg/L - 450mg/L. Based on the classification of groundwater hardness by Sawyer & McCarthy, 1967 (Table 3.), about 96% of the groundwater samples are soft. An extremely high value (450mg/L) was obtained in Reclamation area, which signifies very hard water. Only two wells located at Trans-Amadi

and Churchill out of the 71 wells studied fall within the moderately hard category, with

concentration values of 76mg/L and 82mg/L respectively.

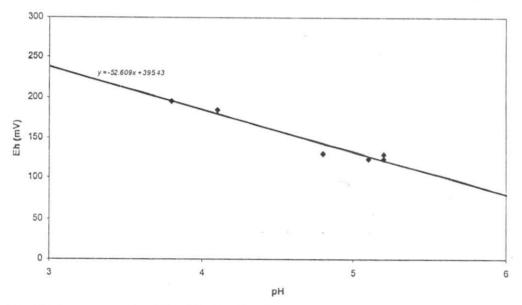


Fig. 2: Representative Eh-pH plot for the groundwater.

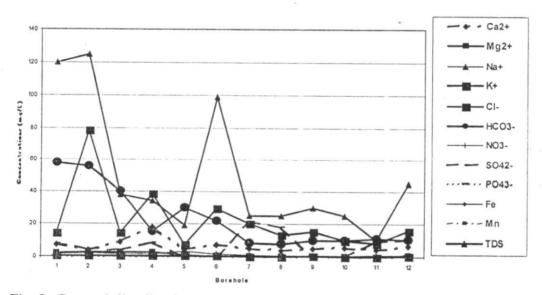


Fig. 3: General distribution pattern of the major ions in the groundwater.

Table 4: Major ion concentration in the groundwater samples PO43-Mn Mg2+ K HCO3 Ca2+ Na T.Coli NO. SO42-Fe Salinity Hard TSS Temp pH EC TDS S/N Location mg/Lmg/L mVmg/Lmg/Lmg/L mg/Lmg/L mg/L Cfw/ml µS/cm mg/L mg/L°C mg/L mg/Lmg/L 0.420 58.050 0.023 1.400 7.130 2.090 0.000 0.290 13.87 7.60 4.00 5.80 19.00 120.00 Amadi-ama 27.6 0.010 2.050 0.540 56.030 4.060 2.980 0.010 4.25 0.620 78.34 3.00 6.10 20.00 125.00 273 Abuloma 0.010 36.1 0.650 40.250 8.570 2,950 1.850 0.000 10.00 14.00 3.78 0.080 38.00 6.20 22.00 3 Elekahia 72 0.021 0.650 15.200 2.570 1.760 18.120 0.001 8.25 0.120 38.50 16.00 72.00 34.00 Diobu 28.8 6.50 30.000 0.150 45. 0.500 4.400 1.000 3,300 0.010 0.06 0.001 8.00 7.10 6.80 10.00 19.00 26.5 5 Rumuokwuta 0.800 21.800 0.000 0.180 1.500 7.100 0.001 0.010 0.08 58.00 99.00 8.00 29.50 5.90 Rumuigbo 26.8 0.000 0.004 165 8.080 0.144 4.920 0.348 0.827 0.010 20.00 21.00 0.001 4.00 25.00 4.80 50.00 Moscow Rd 1 255 0.000 0.001 7.470 124.00 3.940 0.445 0.310 0.004 0.010 0.001 4.00 13.00 18.00 50.00 25.00 5.10 Moscow Rd 2 26.3 8 183 0.461 0.311 10,000 0,000 0.311 0.571 124.00 5.000 0.020 0.01 0.001 10,00 15.00 30,00 60.00 9 Borokiri 26.9 5.20 0.000 0.083 0.083 9.600 5.496 0.366 0.799 0.070 10,00 0.01 0.029 15.00 NDDC 5.20 50.00 25.00 10 0.000 0.031 77 0,031 10.820 4.171 0.235 0.899 185.00 9.00 0.012 0.030 8.00 0.00 27.2 4.10 20.00 10.00 Rumuola 0.830 0.401 54 10.340 0.401 1.03 0.190 6.541 0.824 16.00 10.00 0.001 6.00 45.00 3.80 90.00 Rumuomasi 12 0.05 ND 8.00 71.04 0.080 1.00 12.00 16.00 35.82 10.00 5.39 13 Diobu 27.5 54 0.00 0.00 0.200 10.00 24.00 69.12 0.100 0.00 6.70 22.40 11.20 Diobu 26.9 14 763 0.140 0.00 4.600 0.00 ND 35.00 2.00 ND 25.10 11.50 5.90 15 Diobu 28.8 76. 0.00 6.400 ND 0.020 0.00 ND 73.00 34.60 12.00 16.00 26.8 Diobu 16 60) ND 0.00 ND 0.100 0.10 10.00 2.50 66.60 10.00 4.00 139.50 Diobu 26.8 17 0.00 5.500 0.00 3.20 ND 0.100 0.00 1.00 5.80 24.20 11.20 18 Diobu 26.9 76 ND 0.00 ND 0.120 0.00 7.00 16.00 38.00 72,30 33.70 6.50 19 Diobu 28.8 0.00 ND 0.00 38.00 49.92 0.200 16.00 1.00 4.14 86.00 10.00 NDBDA 27.0 20 0.00 ND 0.00 30.00 ND 0.100 86.00 10.00 1.00 18.00 4.28 26.7 21 Mile 1 45 ND 0.00 0.00 0.100 1.00 8.00 ND ND 25.00 27.2 6.70 53.20 Mile 4 22 0.00 0.090 0.05 ND 60.00 53,76 3.00 1.00 10.00 4.72 56.80 Amadi flats 27.3 23 0.05 ND 0.00 0.090 1.00 36.00 96.00 10.00 48.80 8.60 GRA II 26.6 5.64 24 0.00 ND 17.00 13.44 0.100 50.00 24.00 121.20 59.00 1.00 Amadi flats 28.3 3.89 25 24 ND 2.00 0.00 0 100 18.00 ND 2.00 12.00 38.90 6.40 82.50 **GRAII** 27.3 26 54 0.00 ND 0.00 14.00 0.050 16.00 16.20 0.00 40 00 32.40 6.80 27 D-Line 28.2 39 0.400 0.00 26.00 82.56 0.050 0.10 0.00 14.00 68.00 D-Line 28.2 6.20 137.40 28 453 0.00 ND 0.00 ND 0.070 10.00 6.40 32.10 14.90 5.00 6.00 27.2 29 D-Line 36.5 0.300 0.00 67.20 0.080 0.00 10.00 14.00 10.00 21.60 11.20 28.6 6.20 30 Elekahia 0.10 3.300 0.00 12.00 ND 0 600 2.00 32.00 26.6 6.70 124.80 61.50 Rumuomasi 31 0.00 0.00 ND 0.060 ND 18.90 8.00 14.00 Rumuomasi 28.7 40.80 6.80 32 60.3 0.00 ND 0.00 20.00 ND 0.050 24.00 3.00 14 00 28.00 7.10 33 Elekahia 26.9 ND 0.00 0.050 0.00 ND 20.00 40.20 8.00 12.00 5.70 82.40 Rumuomasi 28.8 34 453 4.00 0.00 0.600 40.00 6.00 72.96 0.160 6.00 4.60 Rumuomasi 27.9 6.10 89.70 35 453 0.170 0.00 6.400 0.00 84.48 18.00 14.00 15.60 12.00 7.80 31.40 26.7 36 Elelenwo 48.00 0.050 0.00 14,000 0.00 20.00 20.50 1.00 8 00 40.90 27.0 5.80 Elelenwo 37 Rumuibekw 17.00 0.100 82.56 0.050 0.00 12.00 12.00 80.20 4.10 1.00 7.20 38 Rumuibekw ND 0.00 18.00 20.00 72.78 0.001 0.00 0.00 8 00 6.10 64.60 28.5 39 48.7 ND 0.00 0.00 18.00 38.00 ND 0.150 32.30 0.00 64.60 Rumuola 26.8 6.40 40 0.00 34.000 10.00 ND ND 0.030 0.00 1.00 49.10 103.20 41 Rumuola 27.7 6.60 0.00 0.00 18.400 82,56 0.250 12.00 ND 62.50 29.50 0.00 6.30 Aba Rd 27.8 42

43	Trans Amadi	28.6	4.43	160	00 15	90 1	00	20.00	60.00	10.20	0.000	0.00	NID	1.00										
	Trans			160.		.80 1.		20.00	60,00	19.20	0.060	0.00	ND	4.00	•	•		•	•			•	5	
44	Amadi Trans	29.0	7.34	86.0	50 10	.60 1.0	00	76.00	18.00	90.24	0.140	0.10	ND	0.00	•	•	٠			5.5	•	•	42.67	A.
45	Amadi	29.0	6.80	49.		.60 4.0		8.00	16.00	ND	0.050	0.00	ND	0.00			•						-	
46	Ogbunabali		7.30	612.		3.00 2.0		32.00	76.00	24.96	0.010	0.30	ND	0.00		-	•	•	•	-		•	37.00	
47	Woji	28.8	5.66	68.				20.00	32.00	69.12	0.001	0.20	ND	0.00	•			•	•	-		•	*	1
48	Elijiji-Woji		6.40	23.1		.90 4.0		10.00	36.00	82.56	0.210	0.00	0.400	0.00			•		•	•	-	•	49.00	
49	Woji	28.6	6.50	74.0				10.00	ND	40.40	0.010	0.00	ND	0.00		•	•		•		•	•	43.00	h
50	Mgbuoba	29.0	5.91	58.6				4.00	12.00	96.00	0.300	0.05	ND	8.00				•		•	*		*	H
51	Rumuigbo		4.30	22.4				22.00	24.00	38.40	0.060	0.00		350.00	1	^		*		7.50	*	-	45.72	
52	Rumuigbo		4.90	67.5				26.00	14.00	58.60	0.100	0.00	14.100	79.00		* .	•	*	•		•	•		
53	Rumuigbo		6.80	359.		.80 35.		60.00	40.00	ND	0.040	0.20	ND	0.00		•					*		43.89	
54	Rumuokwuta		6.70	68.5				20.00	20.00	88.32	0.040	0.00	ND	21.00	•		•		•	•			61.10	
55	Mgbuoba Ada George	26.9						24.00	16.00	76.80	0.080	0.00	19.200	0.00		/ 5 c	*		•	•	•		45.72	Ľ
56	Rumuepirikom	26.9	6.40	6.70	14.93	6.80	3.00	8.00	18.00 ND	ND ND	0.050	0.00	0.400	0.00		-	•	•		-	-	-	54.86 48.80	
58	Ada George																	-	•	-	•	•		
59	Rumueme		17.0	6.80	21.90	6.90	4.00	10.00	12.00	ND 78.72	0.050	0.00	9.400	0.00	•	•		*	•	•	•	*	39.62	
60	Ada George Rd		6.8	6.50	21.60	10.80	0.00	18.00	20.00	24.20	0.210	0.00	ND	0.00							•		39.02	
61	Eagle Island		6.5	4.69	68.70	40.50	3.00	4.00	16.00	96.00	0.050	0.05	ND	2.00							•			
62	Rumuolumeni		6.9	7.20	55.80	54.70	2.00	30.00	12.00	65.28	0.060	0.00	ND	0.00									45.70	
63	Rumuagholu	2	16.8	5.61	120.80	10.00	3.00	28.00	12.00	23.04	0.070	0.00	ND	0.00									40.00	H
64	Abuloma	2	6.7	6.70	28.00	10.00	4.00	36.00	12.00	230.00	0.100	ND	ND	0.00		-							73.15	
65	Churchill Borokiri	2	6.5	7.40	48.60	10.60	1.00	82.00	94.00	24.96	0.170	0.10	ND	0.00	•				-				40.20	
66	sandfill	2	7.0	6,33	1250.00	ND	7.00	60.00	464.00	9.60	0.600	10.00	ND	64.00									25.91	
67	Marine Base Reclamation	2	8.8	6.80	937.00	468.00	8.00	60.00	280.00	76.00	0.520	0.50	ND	2.00						-			* :	
68	Rd	2	8.5	6.60	34.90	17.30	4.00	10.00	26.00	ND	0.050	0.00	0.100	0.00					٠.				19.81	
69	Aggrey Rd	2	8.1	6.50	75.90	38.00	0.00	16.00	24.00	78.72	0.130	0.00	ND	0.00		-			*	١,			36.58	
70	Reclamation Reclamation	2	8.5	7.60	8.62	4.31	14.00	450.00	282.20	327.04	0.200	4.80	13,000	0.00		-				*	-		36.60	
71	Rd	2	8.0	7.60	116.50	55.40	2.00	20.00 1779.8	120.00	ND	0.050	0.00	ND	0.00		7	14.66		-		•		37.00	
	Total	19	59.1	1	6227.60	2426.69		3	2595.21	2760.58	8.184	18.18	179.161	625.0	889.00	79.448	14.55	16.187	4.534	277.640	1.044	0.831		ļ
	Mean	27	7.59	6.08	87.71	34.67	4.68	25.07	40.55	56.34	0.12	0.31	5.27	10.58	148.17	6.62	1.21	1.35	0.38	23.14	0.09	0.14		
	Standard Deviation	0	86	0.98	190.65	67.48	6.89	53.83	70.49	56.9	0.135	1.43	6.526	47.04	32.69	3.91	1.105	0.825	0.266	18.706	0.238	0.173	5	

Table 5: Range in values of Chemical Parameters.

Parameter	Range	WHO Guideline
Temperature (°C)	26.5 - 29.0	No guide value
EC (µS/cm)	8.62 - 1250	500
рН	3.80 - 7.80	6.5 - 8.5
Eh(mV)	124 - 195	No guide value
Hardness (mg/L)	0 - 450	500
TDS (mg/L)	3 - 468	500
$\operatorname{Ca}^{2+}(mg/L)$	3.94 - 18.12	7.5
Mg^{2+} (mg/L)	0.18 - 2.98	50
Na^+ (mg/L)	0.31 - 3.30	200
K^+ (mg/L)	0.004 - 0.650	200
Fe (mg/L)	0.001 - 0.620	0.3
Mn (mg/L)	0.001 - 0.401	0.1
Cl' (mg/L)	2.50 - 464.00	250
HCO_3 (mg/L)	8.08 - 58.05	No guide value
SO_4^{2-} (mg/L)	0.06 - 327.00	250
PO_4^{3-} (mg/L)	0.00 - 0.83	10
NO_3 (mg/L)	0.00 - 34.00	50

HYDROGEOCHEMISTRY

Major ion distribution

Major ions constitute a significant part of the dissolved solids present in groundwater and the concentration of these depend on groundwater in hydrochemical processes that take place in the aquifer system (Lakshmanan, et al. 2003). The distribution of the ionic components of the groundwater in the study area is depicted in Figs.4 and 5.The concentration levels of the cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) and anions (HCO₃⁻, NO₃⁻, SO₄²⁻, and Cl⁻) in the groundwater given in Table 4 and 5 are generally less than the recommended limits for domestic purposes (WHO, 1998) with exceptions in SO₄² and Cl concentrations, with maximum values 327mg/L and 464mg/L in wells at Reclamation Borokiri sandfill areas respectively. Results from the author

derived borehole data show the abundance of these ions in the following order: Ca > Mg > $Na > K = HCO_3 > Cl > SO_4 > NO_3$. The concentration of calcium is generally below 20mg/L. Magnesium is also found in considerable amounts (0.18 - 2.98) mg/L, next to Calcium. Bicarbonate, with a mean value of 23.14mg/L dominates the anionic components of the groundwater, followed by Chloride, with 21.94mg/L. Manganese and Phosphate ions occur in concentrations less than the respective maximum permissible ranging from 0.001 - 0.401 and 0.000 while respectively, Iron 0.830mg/L concentrations are observed to be at the highest in Abuloma, (0.620mg/L). Wells in Rumuomasi, Borokiri sandfill and Marine base also have records of high iron concentrations 0.600, 0.600 and 0.520mg/L respectively

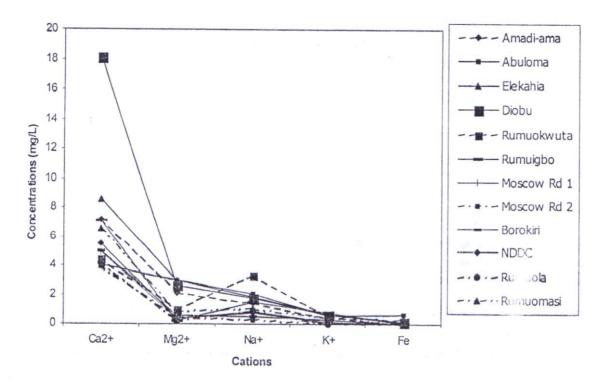


Fig. 4: Distribution of Cations in the groundwater.

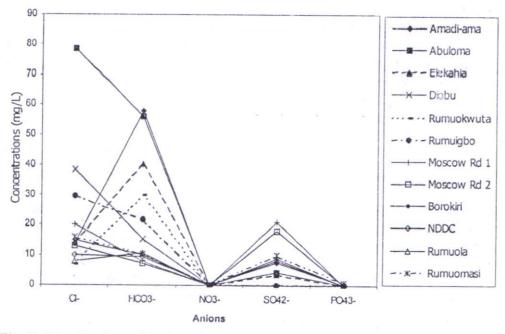


Fig. 5: Distribution of Anions in the groundwater.

Iron concentrations in 95.4% of the waters samples falls within the WHO permissible limit while 5.6% have high iron values above the WHO guide value of 0.3mg/L. It is generally observed that high iron is mostly associated with relatively shallower wells (<40m deep) as concentrations in relatively deeper wells (>40m deep) are very low. The highest Nitrate level of 34mg/L recorded in a 61m deep well at Rumuola is less than the maximum permissible level of 50mg/L (WHO, 1998), thus reducing the potential formation of harzardous nitrosamine from the influx of high nitrate contamination of the groundwater. 79% of the nitrate values fall within the range of 0 - 27.8mg/L. Relatively concentration observed in phosphate, manganese and iron (with few exceptions) indicates that there are no direct impacts from leachates associated with sewage, phosphate fertilizer, domestic and industrial wastes

Hydrochemical Evolution

The results of the chemical analyses were used to identify the geochemical processes taking place in the groundwater system. In the present study, the molar ratio of Na/Cl for groundwater generally ranges from 0.039 to 0.750 (Fig.6). All the samples have Na/Cl molar ratio below 1, which indicates that ion exchange is the major process, which is prevalent in the study area (Lakshmanan, et al., 2003). In general, when halite dissolution is prominent, it implies a 1:1 relationship between Na and Cl. The scatter diagram of Na against Cl (Fig. 7) shows most of the sample points above the 1:1 equiline, suggesting no halite dissolution (Lakshmanan, et al., 2003). and Cl do not increase simultaneously, instead, sodium is found comparatively less than Cl

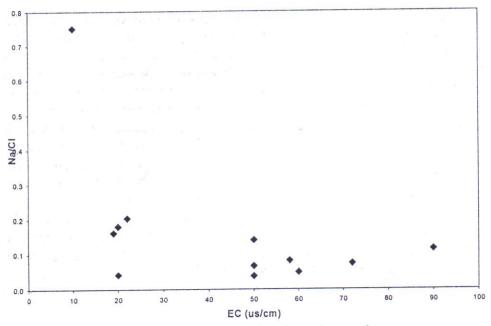


Fig. 6: Plot of Na/Cl ratio versus EC.

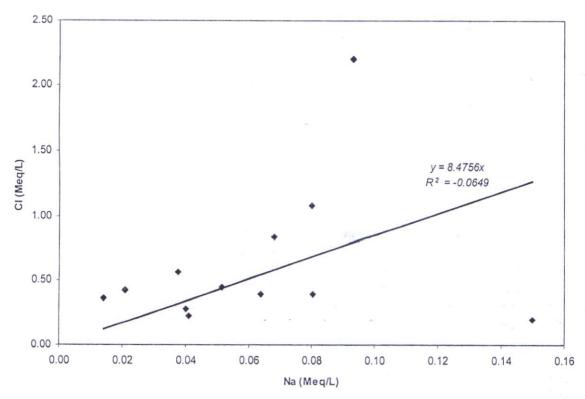


Fig. 7: Na vs. Cl scatter diagram.

This reduction in Na concentration is attributed to ion exchange. High chloride concentration may be attributed to the ingress of brackish water into the shallow aguifers in response to high pumping rates which give rise to increased salinity. The Ca/Mg ratio of groundwater from this area ranges from 0.82 -23.67 (Fig. 8). Overall it is generally greater than 2, indicating the dissolution of silicate minerals, which contributes calcium and magnesium to the groundwater (Maya and Loucks, 1995). The chemical composition of the groundwater is thus of Ca and Mg in the study area and has resulted from silicate weathering. The plot of Ca+Mg versus SO₄+HCO₃ (Fig. 9) shows that both ion

exchange and reverse ion exchange processes are taking place simultaneously in the groundwater system. Datta and Tyagi (1996) explained that in the Ca+Mg versus SO₄+HCO₃ scatter diagram, the ionic concentrations falling above the equiline result from carbonate weathering, whereas those falling below the equiline are caused by silicate weathering. The local geology of the area would definitely exclude the possibility of carbonate weathering in view of the absence of calcareous rocks in the area. Thus ion exchange and silicate weathering considered to be the main geochemical processes influencing the hydrochemical evolution of the waters.

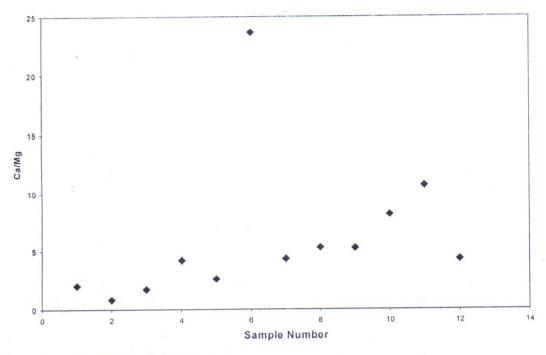


Fig. 8: Plot of Ca/Mg molar ratio

Hydrochemical indices

The ionic relationships of Mg/Ca, Cl/HCO₃, and the Cationic Exchange Value (CEV= [Cl-(Na+K)]/Cl) were studied in an attempt to check the salinity and origin of the groundwater in the study area. Mg/Ca values measured were all less than 1.0 (Table 6) ranging from 0.03 - 0.73. According to the interpretation of this index, the water in the study area appears to be of inland origin, because waters under marine influence would have values of about 5 (Morell et al., 1986) except where other processes such as cationic exchange intervene, when the values could be 4 or less.

The Cl/HCO₃ values ranged from 0.24 to 2.53. Values of this hydrogeochemical index given for inland waters are between 0.1

and 5 and for seawater between 20 and 50 (Custodio, 1987). In general, the CEV for seawater ranges from +1.2 to +1.3 whereas low-salt inland waters give values of close to zero, either positive or negative. The CEV values for groundwater of Port Harcourt are generally below 1.0, ranging from 0.47 to 0.98 indicating that the groundwater is inland with respect to provenance. This observation is consistent with the position of Port Harcourt where fresh water conditions are prevalent, although saline water intrusion is occasionally encountered in boreholes sited in the south of the area. This indicates that the freshwatersaltwater interface is very dynamic and over pumping of aquifers often push landward its frontiers.

Table 6: Hydrogeochemical indices Mg/Ca, Cl/HCO3, and Cationic Exchange Value (CEV) value

in water samples.

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S/N	Mg/Ca	CI/HCO ₃	CEV
w01	0.29	0.24	0.87
w02	0.73	1.39	0.97
w03	0.34	0.35	0.82
w04	0.14	2.53	0.94
w05	0.22	0.24	0.47
w06	0.03	1.35	0.92
w07	0.07	2.48	0.95
w08	0.11	1.74	0.98
w09	0.11	1.50	0.95
w10	0.07	1.04	0.91
wII	0.06	0.74	0.88
w12	0.13	1.55	0.91

Hydrogeochemical facies

Statistical distribution diagrams of Schoeller (1965) and Piper (1944) were used to gain insight into the hydrochemical better processes operating in the groundwater system. Water quality data plotted using the Schoeller scheme (Fig.10) fingerprints two distinct water types based on the Mg concentration. One type has low Mg content in the range 0.0150 - 0.0833 Meg/L and the other high Mg concentration in the range 0.1742 - 0.2458 Meq/L. The high Mg is of two types - the high Ca and low Ca varieties, designated as Ca-HCO3-Cl and Ca-Mg-HCO3-Cl-SO₄² types respectively, indicating a close proximity to the recharge area. Equally, two distinct water types are recognised based on SO42- concentration. They are low sulphate (0.0002 - 0.0015) and the high sulphate type (0.0788 - 0.4375) respectively. Also, the major cations and anions for the analyzed water were plotted on a Piper diagram (Fig.11). This method proposed by Piper (1944), is applied to show the relative concentrations of the major cations (Ca2+, Mg2+, Na+ and K+) and anions (HCO3, Cl, and SO_4^2). Two principal hydrogeochemical water types have been delineated. These are Calcium Magnesium

Bicarbonate (Ca-Mg-HCO₃) type water where the chemical properties of the water are dominated by alkaline earths and weak acids (Karanth, 1994). The Calcium Magnesium Sulphate Chloride (Ca-Mg-SO₄-Cl) is the second type identified. Thus, on the basis of the dominant cations and anions, the groundwater can be classified as Calcium Chloride (CaCl₂) and Calcium Bicarbonate (Ca(HCO₃)₂) types.

A non parametric, 2 tailed correlation analysis at 5 % alpha level of significance was carried out according to the procedure described by Akujieze and Oteze (2007) to understand the relationship and variation of ionic content of water and some pollution indicators. The correlation coefficient matrix is presented in Table 7. The highest correlation has been found to exist between manganese and EC, which is of the order of 0.792. A strong negative correlation is observed between pH and Eh (-0.976). A good correlation existed between EC and Mn (0.792); Na with pH (0.734) and Eh (0.754); Mn with Ca (0.762), Mg (0.893), PO₄ (0.742), TDS (0.792) and NO₃ (0.719); Fe with Mg (0.714), Cl (0.822), HCO₃ (0.795); and TDS (0.761); K and Mn (0.945); Eh and PO₄ (0.702); Mg and HCO3 (0.746); HCO3 and

TDS (0.775) and NO₃ and PO₄ (0.908) suggesting a common origin or a progressive enrichment of both parameters. Correlations

are generally weak with little or no association in about 35% of the data points.

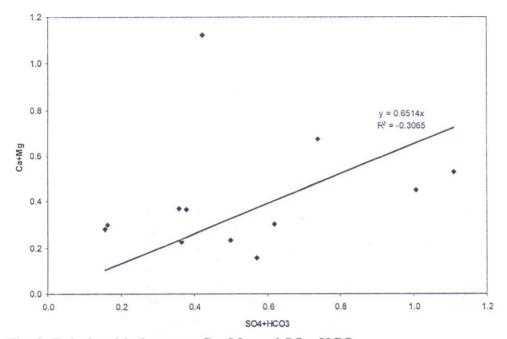


Fig. 9: Relationship between Ca+Mg and SO₄+HCO₃.

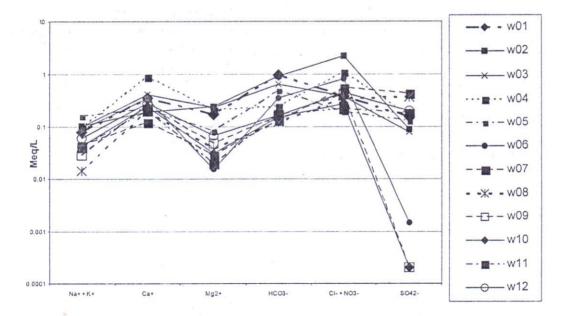


Fig. 10: Chemical Analyses of water represented on a Schoeller (1965) diagram.

Table 7: Correlation coefficient matrix of the hydrochemical data

	EC	hHd	T.H	Eh	Ca^{2+}	Mg2+	Na ⁺	\mathbf{K}^{\dagger}	CI	HCO3.	NO3.	SO ₂ -	PO43-	Fe	Mn	TDS
EC		1	î.	1	1		t	ī	1	1	1	1	,	1	1	1
Hd		1.000	Ē	ı	t	ī	ı	1	1	1	1	1	1	1	ı	i
T.H	0.393	0.430	1.000	ı	ı	1	,	1	1	Ĩ	1	1	1	1	ı	ı
Eh		0.976	-0.462	1.000	1	,	1	-1	1	1	1	i	ı	1	i	ì
Ca^{2+}		0.387	0.640	0.387	1.000	1	ı	1	1	1	1	Í	t	ı	Ĭ	i
Mg^{2+}		0.585	0.169	0.296	0.481	1.000	1	1	1	1	1	í	ŗ	r	Ē	1
Nat		0.734	0.124	0.754	0.184	0.497	1.000	1	1	1	1	ī	1	ī	ı	ı
K ⁺		0.653	0.333	0.319	0.515	0.562	0.642	1.000	1	1	1	ı	Ü	ı	i	ı
CI		0.327	-0.060	-0.223	0.175	0.560	0.251	0.430	1.000	1	1	- 1	1	ï	ı	1
HCO3.		0.558	-0.209	0.682	900.0-	0.746	0.567	0.509	0.455	1.000	1	Ţ	ı	ı	Ī	1
NO3		0.662	0.010	0.687	-0.119	-0.283	-0.240	-0.170	-0.180	-0.356	1.000	I,	ı	ī	i	1
SO42-		0.450	-0.459	0.003	-0.039	-0.151	-0.441	-0.497	990.0-	-0.299	0.035	1.000	ı	i	į	į
PO43-		0.467	-0.073	0.702	-0.015	-0.094	0.023	0.070	-0.125	-0.173	0.908	0.087	1.000	ř	į	1
Fe		0.347	-0.230	-0.055	0.003	0.714	0.307	0.285	0.822	0.795	-0.235	-0.113	-0.172	1.000	1	1
Mn		0.346	0.301	0.381	0.762	0.893	0.231	0.945	0.239	0.548	0.719	-0.479	0.742	-0.277	1.000	1
TDS	- 1	0.304	-0.229	0.143	-0.002	0.452	0.218	0.522	0.631	0.775	-0.155	-0.215	-0.061	0.761	0.792	1.000
												-				

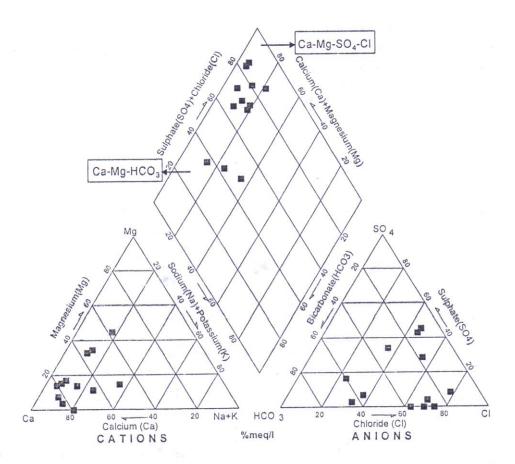


Fig. 11: Chemical analysis of water represented as percentages of total equivalents per litre on the trilinear diagram developed by Piper (1944).

Bacteriological Quality

The total coliform in the studied groundwater data ranges from 0 - 350mg/L. Maximum coliform count (350Cfu/ml) is found in a well in Rumuigbo. Wells in Amadi Flats a Rumuibekwe recorded a concentration of 17Cfu/ml, while concentrations of 79, 21 and Rumuokwuta and 64Cfu/ml are found in Borokiri sandfill ares respectively. Coliform counts of groundwater in these areas exceed the WHO guide value of 0 Cfu/ml and are generally unsafe for drinking. The source of this high coliform concentration is generally faecal contamination from nearby soak-away pits and this poses high risk of cholera and stomach disorder upon consumption.

Water Quality Index, WQI

The WQI values in the study area ranges from 0.11 - 204 (Fig.12). Water is considered fit for human consumption if its WQI ≤ 50, poor/very poor when WQI > 50 and is unfit for drinking without treatment if its WQI>100. A rule of the thumb is that the larger the value of WQI, the more polluted the water concerned. This classification scheme was applied to the calculated WQI and it was found that 797% of the boreholes studied have good quality drinking water, i.e. ranking between 0 and 50 on the WQI scale, while the rest are classified as are poor, very poor and unsuitable with respect to drinking water quality. The Water Quality index map of the study area in Fig. 13 shows that water quality decreases south-westwards towards the position of the major creeks where the transition between fresh and brackish water occurs with a dynamic boundary.

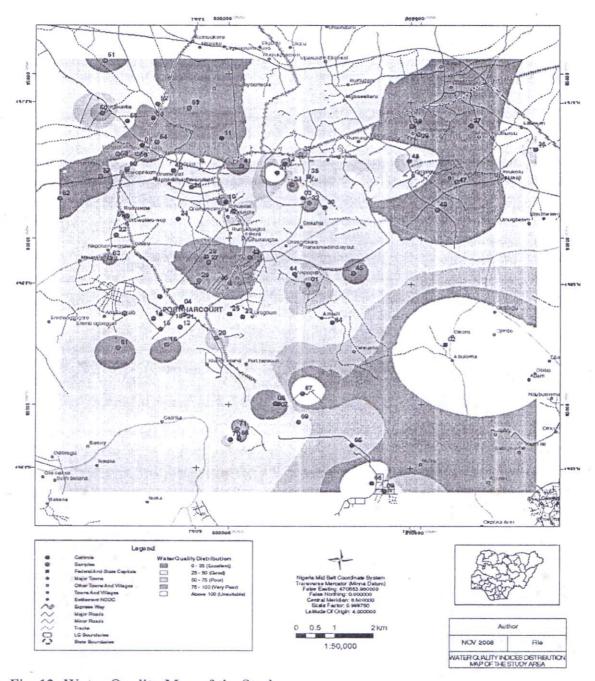


Fig. 12: Water Quality Map of the Study area.

CONCLUSION

Interpretation of the hydrochemical data suggests that ion exchange; reverse ion exchange and silicate weathering are the prevailing hydrochemical processes responsible for the groundwater chemistry of the study area. Hydrochemical indices (Mg/Ca, Cl/HCO₃, and CEV) generally indicate low-salt inland water, with minimal marine influence. The groundwaters of the area on the basis of the Water Quality Index Scheme are classified into five groups: Excellent (59%), Good (30%), Poor (11%), Very poor (4%) and Unsuitable (6%) with respect to human consumption. It is important that adequate long-term groundwater monitoring programmes be enshrined in government policies to ensure that reliable information is routinely available to serve as a guide to the public on the groundwater quality status within the area.

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