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Research Article

STATISTICAL AND SPATIAL ANALYSIS OF GROUNDWATER QUALITY IN WARRI AND ITS ENVIRONS, DELTA STATE, NIGERIA

Izeze O[1] and Adipere Konboye P[2]

Department Of Earth Sciences, Federal University of Petroleum Resources, Effurun, Delta State, Nigeria

ABSTRACT

Groundwater samples were taken from seventeen (17) sample points (cased and uncased boreholes) in Warri and its surrounding environs in Delta State, Nigeria. The ions analyzed are: Ca^{2+} Mg^{2+} Na^{+} K^{+} Cl^{-} SO_4^{2-} HCO_3^{-} NO_3^{-} NH_4^{-} and PO_4^{3-}. TDS, pH and EC were also analyzed in order to ascertain groundwater quality. Multivariate statistical analysis, Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA), was applied to standardized data sets. The result of HCA was tied to graphical methods, Stiff plot and Piper diagram, to obtain the water type as Ca^{2+}-Mg^{2+}-Cl^{-}- SO_4^{2-} and revealed the dominant ions. Durov plot was done to get an understanding of the TDS and pH. PCA revealed five factors that controlled the hydrochemistry of the study area. Ammonium, nitrate, phosphate and TDS dominated factor 1 which accounted for 28.98%; chloride, sulphate and EC are parameters in factor 2; factor 3 has calcium, magnesium and bicarbonate; factor 4 is dominated by pH and the fifth factor holds potassium and sodium accountable for hydrochemical variation. US EPA (EPA, 2012) and EU (EU, 1998) standards were compared with the parameters to ascertain the quality of the water for domestic use. Ammonium ion had a concentration above 0.5mg/L and pH had a value of less than 6.5 for most of the sampled locations, and these were out of the range of US EPA and EU DWD standards. The presence of ammonium indicates faecal contamination. This is as a result of contamination from leaking or compromised septic tanks.

INTRODUCTION

Groundwater is the main source of pure freshwater in the Niger Delta, for both domestic and industrial use. The groundwater quality in the region is variable, depending on the aquifer from which it was abstracted. Groundwater chemical composition is the result of the composition of water that enters the aquifers and the reactions with minerals present in the rocks forming the aquifer that may modify the composition. Groundwater, therefore, varies in composition from one well to another as a result of the varied aquifer characteristics.

The spatial variability in the concentration and/or composition of the chemical constituents can give insight into aquifer heterogeneity and connectivity, as well as the physical and chemical processes controlling water chemistry (Güler, et al., 2002), (Cloutier, et al., 2008). Graphical and statistical methods have been invented since the early 20th century in order to facilitate classification of water types and assess water quality using the concentration of chemical constituents, and these are the most commonly applied methods to study patterns in hydrologic and hydrogeochemical processes in both surface and groundwater systems. Graphical methods such as Piper diagram (classify water types), Stiff pattern diagram (making visual comparison of waters with different characteristics), and Durov diagram (to graphically illustrate cation/anion concentrations, relative to TDS and pH) are some of the commonly applied methods to analyze groundwater. Multivariate statistical methods like Hierarchical Cluster Analysis (HCA), a data classification technique most widely used in the Earth sciences, and Principal Component Analysis (PCA), a data transformation technique applied to unmask an underlying structure that is assumed to exist within a multivariate dataset (Guler and Thyne, 2002) are some of the most commonly used statistical methods.

Aim of the research work:

The aim of this paper is to determine the concentrations of the chemical constituents of groundwater and their spatial relationships within the study area using statistical methods.

Location and Accessibility:

The 1130.61km^2 study area lies between latitude 5°54´00´´N and 5°24´00´´N, and longitude 5°42´00´´E and 5°54´00´´E. The study area is located in the western part of the Niger Delta, and includes the area that covers the metropolitan city of Warri and Effurun in Warri South and Uvwie Local Government Area respectively, and Sapele Local Government Area. The area, located some 40km away from the Atlantic Ocean, has a population of over 300,000 people (Olobaniyi & Owoyemi, 2006). Warri is one of the prominent commercial cities in southern Nigeria as it has a port and a refinery, and the Sapele axis of the study area holds several oil fields and flowstations.

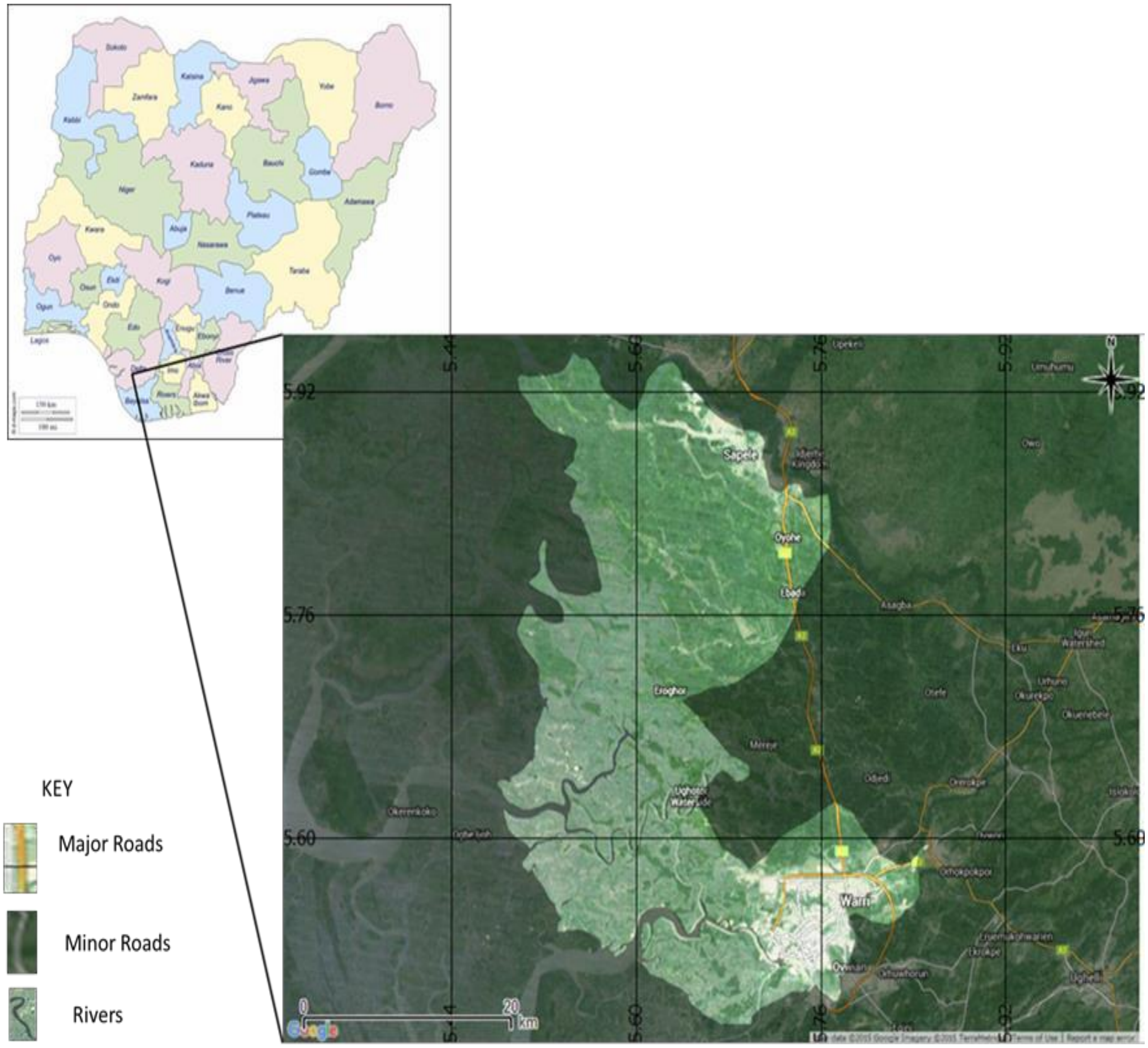

Figure 1: Map of the study area.

Climate and Vegetation:

Climate, in Warri and its surrounding area, is humid equatorial with a long wet season lasting from March to October that alternates with a shorter dry season that lasts from November to February. The climate is influenced by two prevailing air masses; the south-west monsoon wind and the north-east trade wind. The monsoon wind prevails during the wet season and the trade winds during the dry season. The south-west monsoon winds originate from the Atlantic Ocean and they are associated with the wet season, being warm and moisture-laden. In contrast, north-east trade winds originate from the Sahara desert and their prevalence is associated with the dry season. The effects of the dry north-east trade winds are most noticeable from December to February when they usher in the dry, dusty harmattan season. Annual rainfall is high, up to 3000 mm. The beginning and end of the wet season are usually marked by intense thunderstorms of short duration, often accompanied by strong winds which may blow off roofs of buildings and cause destruction of property. Prolonged and gentle showers, usually lasting several hours or a few days, are more characteristic of the middle of the wet season. The rainfall regime is double-peak, the two periods of peak rainfall being June/July and September which are separated by a relatively dry period in August. Annual temperature is between 23°C to 37°C (Adejuwon, 2012).

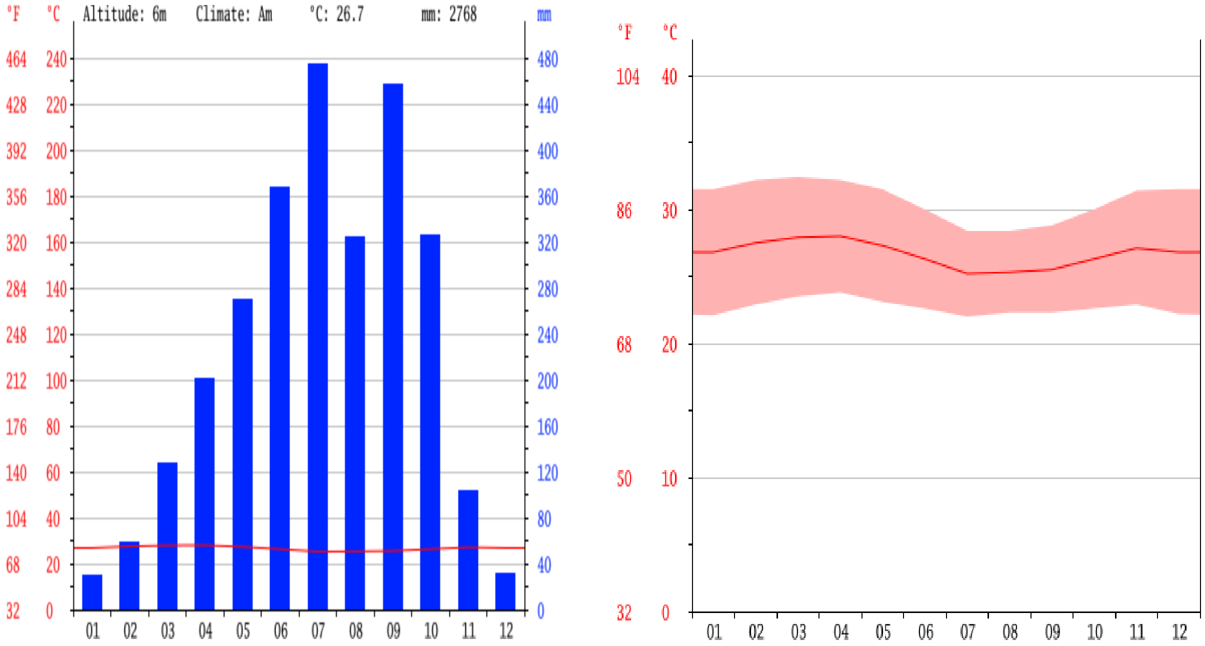

Figure 2 (a) and (b): Graph showing monthly distribution of rainfall and temperature for Warri (Climate-Data, 2015).

The natural vegetation of Warri is rain forest with swamp forest occurring in flat- floored valleys and adjoining low-lying areas that are seasonally or permanently waterlogged. The rain forest is floristically diverse and structurally complex, with several layers of trees. It was a major source of timber and the notable timber-producing species include Antiaris toxicaria, Milicia (Chlorophora) excelsa, Ceiba pentandra and Piptadeniastrum africanum. Other trees that feature in the rain forest include Pentaclethra macrophylla, Chrysophyllum albidum and Irvingia gabonenesis. The two last mentioned tree species are fruit trees which are important as sources of income and dietary supplement for rural people.

METHODOLOGY

Materials:

The materials used for this work are as follows:

1. Opaque polythene plastic cans (1 litre).
2. Global Positioning System (GPS).
3. Analogue Mercury-in-Glass thermometer (Graduated in degree centigrade).

4. Rope, tied to a float (wood) to measure the depth to water table head.
5. PH/EC/TDS high range meter (Model HANNA HI 991301).

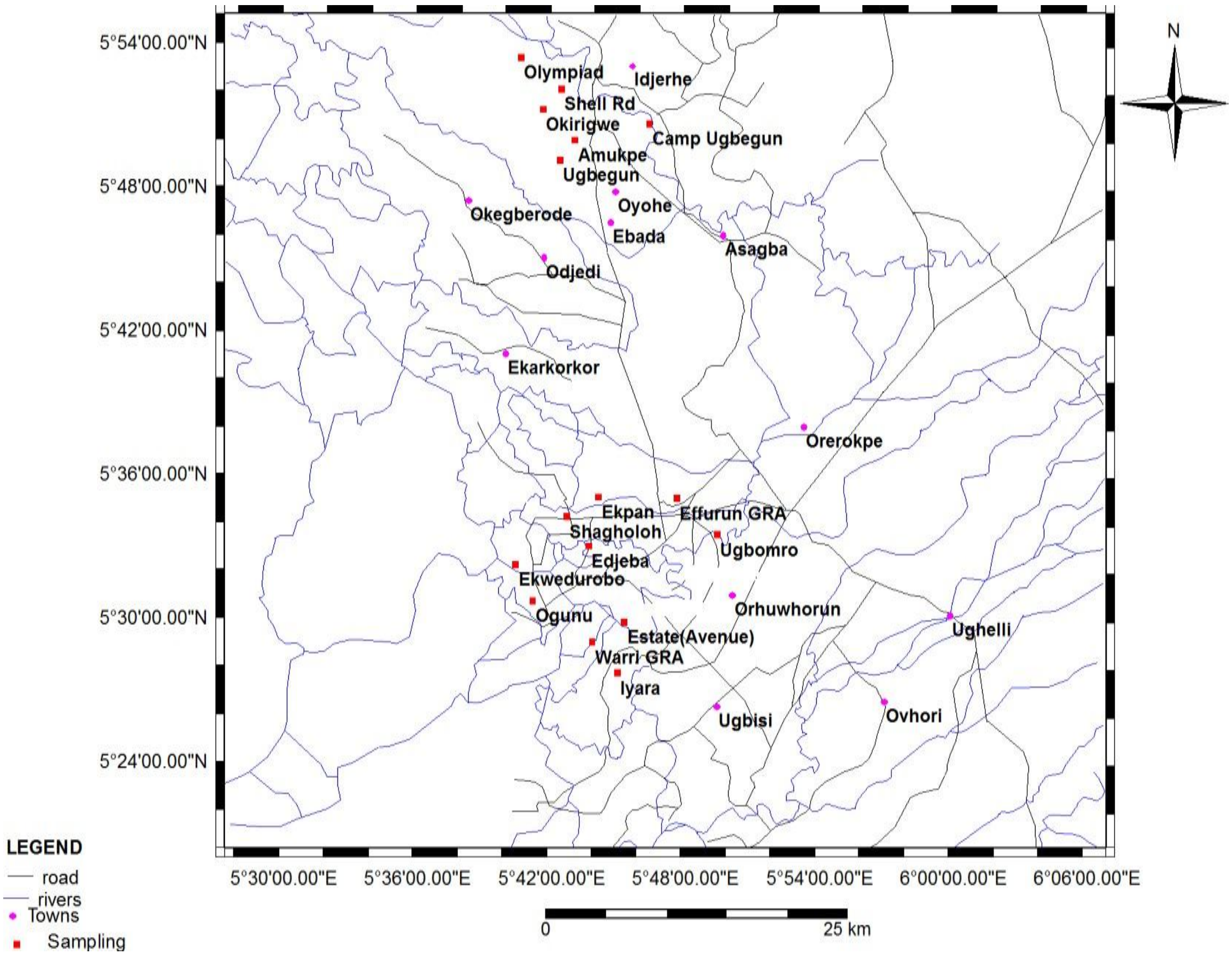

Figure 3: Geographical map of the study area indicating sample/borehole locations

Sampling:

Random sampling was done in the two major cities in the study area. Seventeen samples were collected. Eleven (11) samples were collected from Warri Axis, and six (6) samples from Sapele Axis. Sampling was carried out by collecting water samples in new 1litre opaque polythene plastic cans. The cans were rinsed thoroughly with water from the boreholes (Cased or uncased) being sampled. The temperature, pH and electrical conductivity of the water sample was taken in-situ using the thermometer, pH meter and electrical conductivity meter. The GPS took readings of the location's coordinates and elevation above sea level. The samples were then taken to the laboratory for analysis within retention time.

pH:

The samples collected were measured for pH value in the field, using a pH meter (Model Ecosense). Each sample was placed in a beaker, the electrode end of the meter was then rinsed with distilled water followed by the sample and inserted into the sample in the beaker. The read button on the pH meter was pressed, and the pH value at a stable pH reading was recorded.

Conductivity:

The water samples were measured for electrical conductivity (EC) using an Electrical Conductivity Meter (data logger). The EC meter electrode was rinsed-* with distilled water and the sample, the sample was poured into a beaker, and the electrode end of the meter was inserted in the sample. The READ button on the meter was pressed and the EC value was read and recorded at stable meter reading.

Temperature:

The temperature of samples was measure with the aid of Mercury-in-glass thermometer, the thermometer was rinse with distilled water and sample, and immersed in a beaker containing the sample. The temperature was then read at a stable value, and recorded.

FIELD MEASUREMENTS:

The following data were obtained using the aforementioned methods and instruments in the field.

UBH=Uncased borehole, BH=Cased borehole, Shagholoh=SHG, Ekpan=EKP, Edjeba=EJB, Ogunu=OGU, Effurun GRA=EFF GRA, Ugbegun=UGB, Iyara=IYA, Warri GRA=WRGRA, Estate=EST, Ekurede-urhobo=EKURB UBH, Amukpe=AMKP, Okirigwe=OKR, Olympiad=OLYM, Shell road=SHEL, Ugbegun=UGB, Camp=CMP

Warri Axis:

S/N	Location/ Borehole	Temp. (°C)	Longitude	Latitude	Elevation (ASL)(m)	Date
1	SHG UBH & BH	26.5	05°43′39.3′′	05°34′08.8′′	18	02.09.2015
2	EKP BH	26	05°44′43.4′′	05°34′14.2′′	23	02.09.2015
3	EJB UBH	27	05°44′13.9′′	05°32′35.04′′	19	02.09.2015
4	OGU UBH	28	05°42′46.7′′	05°31′51.2′′	10	02.09.2015
5	EFF GRA BH	27	05°47′34.5′′	05°34′16.4′′	16	04.09.2015
6	UGB BH	27.5	05°49′36.7′′	05°33′52.8′′	13	04.09.2015
7	IYA BH	29	05°45′28.0′′	05°30′33.8′′	14	04.09.2015
8	WRGRA BH	27	05°44′20.8′′	05°31′20.7′′	23	04.09.2015
9	EST BH	28	05°44′54.8′′	05°31′44.2′′	20	04.09.2015
10	EKURB UBH	27	05°43′46.6′′	05°31′53′′	21	04.09.2015

Table 1: Temperature, GPS coordinates and elevation data for Warri axis.

Sapele Axis:

S/N	Location/ Borehole	Temp. (°C)	Longitude	Latitude	Elevation (ASL)(m)	Date
1	AMKP UBH	28	05°43′17.0′′	05°51′27.4′′	18	03.09.2015
2	OKR BH	27.5	05°42′41.1′′	05°52′14.6′′	23	03.09.2015
3	OLYM BH	28	05°40′41.8′′	05°53′26.5′′	19	03.09.2015
4	SHEL BH	26	05°41′57.4′′	05°52′16.5′′	20	03.09.2015
5	UGB BH	26	05°43′17′′	05°50′37.0′′	6	03.09.2015
6	CMP BH	27	05°49′37.7′′	05°43′43′′	19	03.09.2015

Table 2: Temperature, GPS coordinates and elevation data for Sapele axis.

LABORATORY ANALYSIS:

The laboratory analysis was carried out at Tudaka Environmental Consultants Limited, Effurun, in Delta State, Nigeria. The analytical methods used in the determination of the water chemistry are in accordance with the American Standard for Testing Materials (ASTM) (1969) and American Public Health Association (APHA) (1989) Standard procedures. Analyses were carried out as soon as the water samples arrived at the laboratory, since it is usually not advisable to delay in order to accurately determine the water chemistry.

Phosphate Ion:

Determination of Phosphate (P) was in accordance with the American Public Health Association (APHA) 425C. 5ml of Antimony Molybdate solution was added to 40ml of Sample and 2ml of Ascorbic acid was added. The blank solution was to the same treatment as the sample. After about 10-20 minutes the absorbance of both sample and blank solution was measured with UV – visible spectrophotometer at a wavelength of 680nm.

Chloride Ion:

The salinity and chloride in water was determined in accordance with the American petroleum Institute (API-RP) 45. 100ml of sample was measure and put in a 250ml conical flask. A 1ml of k_2CrO4 was added and titrated with 0.014N $AgNO_3$. The end point for was marked by a colour change from yellow to reddish brown.

Nitrate Ion:

Nitrate in water was determined in accordance with the American Society for Testing and Materials. A number of reaction tubes in a wire rack containing 10ml of sample were set up, with blank and standard solution prepared from sodium nitrate, spacing them so that empty space surrounds each tube. The rack was set in a cool water bath, 2ml NaCl solution prepared from (300g of NaCl crystals in distilled water) was added to the sample, standard and blank solution. The set up was mixed thoroughly by swirling and then 10ml H2SO4 prepared from (500ml of conc.H_2SO_4 to 125ml distilled water) to each of the solution. The setup is was again swirl and mixed thoroughly and allow to cool. The rack of tube were replaced to mix thoroughly and placed in a well stirred boiling water bath, that maintain a temperature of not less than 95°C and left there for 20minute. The samples were then removed and immerse in a cool water bath. When thermal equilibrium was attained, the tubes were removed and dried with tissue paper. The standard and sample against the reagent blank at 410nm in the spectrometer was read.

Sulphate Ion:

The sulphate ion in water was determined in accordance with the American Public Health Association (APHA) 427C. A 70ml quantitative measure of each standard solution was added to the volumetric flask, 10ml of NaCl-HCl was then added and the content of the flask was shaken. A 10ml of Alcohol-Glycerol mixture was added and the content shaken again. 5.0g of finely divided BaCl2 was then added to make the volume mark. The absorbance of the reagent blank and standard was read and a calibration graph plotted using Microsoft Excel.

Calcium and Magnesium Ion:

The calcium hardness of sample was determined in accordance with the American Public Health Association 122B. 50ml of sample was measured into a conical flask, with 1ml of 8.0N KOH and 4-drops of calcon indicator. This was titrated with 0.01N EDTA, and at the end point, a colour change from wine to Blue was observed.

Ammonium Ion:

Ammonium was determined in accordance with the American Public Health Association (APHA 417). 1000mg/L Ammonium ion stock solution was prepared by dissolving 2.965g of NH4Cl salt in 500ml of distilled water in 1000ml capacity volumetric flask. After the dissolution, a volume was made to mark with distilled water. A working standard solution was prepared from the 1000mg/L standard stock solution, 0.50, 1.00, 1.50, 2.00 and 2.50mg/L into 100ml capacity volumetric flasks. Also a reagent blank was prepared. 20.0ml of each standard solution was placed in 50ml volumetric flask. 4.0ml tri-sodium phosphate solution was added. 10ml of phenate reagent 1 was added and shaken gently. 2.5ml of 3.5% alkaline bleach was added and shaken gently. The volume was made to mark. Colour development was allowed for about 25minutes. Same was carried out for the reagent blank. The absorbance of the standard and reagent blank on DR 2000 was read at 635nm. Then the calibration graph of absorbance vs. concentration in mg/l was plotted.

Data Analysis Procedure-Multivariate Statistical Analysis:

The data analysis procedure applied for this study is multivariate statistical analysis. Multivariate statistical analysis is a quantitative and independent approach applied to groundwater studies in order to group groundwater samples into hydrogeochemical facies, solve water quality problems and determine groundwater spatial associations (Cloutier et al., 2008), (Güler & Thyne, 2004). The parameters were first checked for normality using the Shapiro-wilk test and quantile plots, the latter revealed that the data were positively skewed. The parameters were log-transformed to normalize before standardization to their z-scores

Data standardization is a requirement in multivariate analysis. The results of multivariate statistical analysis are more unbiased and have a higher degree ofaccuracy when the parameters used in the analyses are of the same units and equally weighted. Data standardization is a process of achieving both objectives. The use of the raw data in multivariate statistical analysis, especially cluster analysis and factor analysis, where dissimilarity and similarity measures are determined tend to favor the parameters (variables) with the highest variances (Cloutier et al., 2008), (Yidana, 2008). Data standardization makes the dataset uniform so that the determination of similarity/dissimilarity measures and factors will be fairly distributed among all the variables used in the analyses.

Hierarchical cluster analysis (HCA) was then applied to the standardized dataset to classify the data into spatial associations. Squared Euclidean distance measures were chosen to measure similarity/dissimilarity among variables and the Ward's linkage method was chosen to link initial clusters resulting from the initial clustering steps. The combined use of squared Euclidean distance as a similarity/dissimilarity measure and the Ward's method as a linkage algorithm has been observed to produce very reliable clusters (Güler et al., 2002; Cloutier et al., 2008, Cloutier et al., 2006).

Principal component analysis (PCA) and Varimax rotation was also applied to the standardized dataset to determine the major sources of variation in the hydrochemistry within the study area. Components loadings greater than 0.3 are typically regarded as excellent and less than 0.3 very poor. Then, the Kaiser (1960) Criterion (The Kaiser Criterion suggests to retain those components with eigenvalues greater than or equal to 1) was applied to eliminate components which do not represent unique sources of variation in the hydrochemistry. The rationale behind the Kaiser (1960) criterion is that a factor which represents a unique process in the hydrochemistry should be able to account for the variance of at least one variable in the dataset. In reality, it is possible to obtain as many components as there are variables but a lot of the components will be very unnecessary. The resulting components loadings were in turn used to calculate components scores for the different parameters and sample locations. Durov, Piper, Stiff, and Schoeller diagrams are plotted using the Enviroinsite 9.2.0.44 software (HydroAnalysis, 2015) to establish a tie with the results of the multivariate statistical analyses.

RESULTS AND INTERPRETATION

BH	pH	TDS(mg/L)	EC(mg/L)	Ca(mg/L)	Mg(mg/L)	K(mg/L)	Na(mg/L)
EKP BH	4.48	52	110	2.23	0.97	0.24	4.92
EJB UBH	4.08	170	360	5.21	2.13	0.85	13.76
OGU UBH	6.51	280	570	8.18	3.37	1.14	19.42
SHG BH	5.51	250	510	6.91	1.92	0.53	14.56
SHG UBH	6.01	140	290	4.23	1.85	0.29	9.79
UGBO BH	6.45	30	39	8.83	2.46	0.62	4.13
EFFGRA BH	3.89	150	210	6.75	3.14	0.06	1.77
EST BH	5.29	280	380	11.42	3.87	1.13	6.19
IYA BH	5.7	230	310	7.25	2.22	0.87	11.25
WRGRA BH	4.23	140	200	6.98	4.73	0.14	2.96
EKURB UBH	5.76	360	490	5.25	2.27	1.25	8.19
OKR BH	4.01	330	450	9.26	5.15	0.46	3.04
UGBE BH	4.17	60	80	4.78	3.11	1.54	7.73
CMP BH	4.42	40	60	8.88	2.74	0.72	5.19
AMKP UBH	5.9	650	880	4.15	1.97	0.35	9.56
SHEL BH	4.24	80	110	12.48	4.51	0.83	6.15
OLYM UBH	6.38	190	250	17.83	3.79	1.25	8.53
Min.	3.89	30	39	2.23	0.97	0.06	1.77
Max.	6.51	650	880	17.83	5.15	1.54	19.42
Mean	5.119412	201.8824	311.7059	7.683529	2.952941	0.721765	8.067059
Median	5.29	170	290	6.98	2.74	0.72	7.73
S.D.	0.933409	149.9497	215.1322	3.615109	1.120282	0.424822	4.544003
Skewness	0.113089	1.380516	0.883453	1.134403	0.369984	0.179531	0.829242

Table 3: Laboratory results for groundwater analysis.

BH	Cl(mg/L)	SO_4(mg/L)	PO_4(mg/L)	NO_3 (mg/L)	NH4(mg/L)	HCO_3(mg/L)
EKP BH	20.02	0.18	0.02	0.07	1.35	0.1
EJB UBH	49.05	2.31	0.07	0.14	5.98	0.08
OGU UBH	67.57	4.03	0.11	0.35	7.77	0.35
SHG BH	91.1	3.96	0.04	0.67	3.72	0.18
SHG UBH	48.55	1.86	0.05	0.16	1.89	0.24
UGBO BH	21.72	0.79	0.01	0.18	1.34	0.75
EFFGRA BH	25.58	1.12	0.08	0.72	4.38	0.01
EST BH	32.83	2.95	0.03	1.09	2.75	0.11
IYA BH	31.38	5.18	0.06	0.54	5.11	0.18
WRGRA BH	33.8	1.28	0.01	0.08	0.79	0.04
EKURB UBH	65.66	4.12	0.04	0.83	7.19	0.21
OKR BH	28.17	1.95	0.07	0.31	4.72	0.02
UGBE BH	16.41	0.75	0.01	0.14	2.18	0.03
CMP BH	13.03	0.39	0.02	0.09	1.53	0.06
AMKP UBH	30.41	3.32	0.17	0.43	7.18	0.11
SHEL BH	25.19	0.93	0.01	0.14	2.15	0.05
OLYM UBH	19.31	1.24	0.05	0.19	3.24	0.18
Min.	13.03	0.18	0.01	0.07	0.79	0.01
Max.	91.1	5.18	0.17	1.09	7.77	0.75
Mean	36.45765	2.138824	0.05	0.360588	3.721765	0.158824
Median	30.41	1.86	0.04	0.19	3.24	0.11
S.D.	20.63703	1.474313	0.041016	0.297172	2.208396	0.172316
Skewness	1.235688	0.526546	1.421908	1.022034	0.478364	2.314617

Table 4: Laboratory results for groundwater analysis (continued).

The results of the raw laboratory analysis are presented in Table 3 and 4. These results show that most of the sample locations have alarmingly poor water quality. Most of the samples obtained from cased boreholes have pH values of less than 6.50 (less than United States Environmental Protection Agency (EPA, 2012) standards for drinking water) and are therefore acidic. The European Union Drinking Water Directive (1998) for ammonium in drinking water is 0.5mg/L, the mean value for ammonium is 3.72mg/L for all sampled boreholes, this extremely above the EU (EU, 1998) standards. The Amukpe uncased borehole has the highest TDS, 650, of all the sampled boreholes, this is also higher than the recommended level for drinking water by the US EPA (EPA, 2012).

	Min.	**Max.**	**Mean**	**Median**	**US EPA (2012)**	**EU DWD (1998)**
pH	3.89	6.51	5.119412	5.29	6.5-8.5	
TDS(mg/L)	30	650	201.8824	170	500	
EC(mg/L)	39	880	311.7059	290		
Ca(mg/L)	2.23	17.83	7.683529	6.98		
Mg(mg/L)	0.97	5.15	2.952941	2.74		
K(mg/L)	0.06	1.54	0.721765	0.72		
Na(mg/L)	1.77	19.42	8.067059	7.73		200
Cl(mg/L)	13.03	91.1	36.45765	30.41	250	
SO_4(mg/L)	0.18	5.18	2.138824	1.86		250
PO_4(mg/L)	0.01	0.17	0.05	0.04		
NO_3 (mg/L)	0.07	1.09	0.360588	0.19	10	50
NH4(mg/L)	0.79	7.77	3.721765	3.24		0.5
HCO_3(mg/L)	0.01	0.75	0.158824	0.11		

Table 5: Summary statistics of groundwater physical and chemical characteristics compared against US EPA (EPA, 2012) and EU DWD (EU, 1998).

Correlation Matrix:

	pH	**TDS**	**EC**	**Ca**	**Mg**	**K**	**Na**	**Cl**
pH	1	0.3133	0.3084	0.5703	0.3755	0.1425	0.0204	0.1730
TDS	0.2601	1	0.0000	**0.8441**	0.5941	0.8697	0.1926	0.0089
EC	0.2627	**0.9736**	1	**0.8130**	**0.9770**	**0.9554**	0.0822	0.0012
Ca	0.1482	0.0516	-0.0621	1	0.0002	0.1730	0.7705	0.6098
Mg	0.2295	0.1392	0.0076	0.7779	1	0.6323	0.2080	0.5848
K	0.3711	0.043	0.0147	0.3465	0.1251	1	0.0057	**0.8408**
Na	0.5562	0.3323	0.4334	-0.0765	-0.3217	0.6395	1	0.0250
Cl	0.3465	0.6132	0.7153	-0.1334	-0.1427	0.0527	0.5408	1
SO_4	0.4377	**0.8295**	**0.8057**	0.2005	0.1791	0.2597	0.5164	0.7518
PO_4	0.2799	0.77	**0.8054**	-0.0933	-0.1513	-0.0919	0.3459	0.4315
NO_3	0.3249	0.6835	0.6165	0.199	0.0929	0.1028	0.1496	0.4984
NH_4	0.2423	0.755	0.7496	0.0243	-0.0262	0.2783	0.4763	0.5031
HCO_3	**0.8925**	-0.0001	0.0546	0.0233	-0.3873	0.4497	0.6112	0.3621

Table 6: Pearson's correlation matrix for parameters analyzed.

	SO4	**PO4**	**NO3**	**NH4**	**HCO3**
pH	0.0789	0.2766	0.2032	0.3488	0.0000
TDS	0.0000	0.0003	0.0025	0.0005	**0.9997**
EC	0.0001	0.0001	0.0084	0.0005	**0.8351**
Ca	0.4402	0.7217	0.4439	**0.9263**	**0.9292**
Mg	0.4916	0.5621	0.7230	**0.9205**	0.1246
K	0.3142	0.7257	0.6945	0.2794	0.0701
Na	0.0338	0.1738	0.5666	0.0532	0.0091
Cl	0.0005	0.0837	0.0417	0.0395	0.1532
SO_4	1	0.0115	0.0006	0.0012	0.2849
PO_4	0.5966	1	0.0280	0.0000	**0.8638**
NO_3	0.7434	0.532	1	0.0027	0.7339
NH_4	0.7176	**0.8296**	0.6787	1	0.7967
HCO_3	0.2753	0.045	0.0891	0.0675	1

Table 7: Pearson's correlation matrix for parameters analyzed (continued).

Pearson's correlation matrix (Table 7) shows the relationship between the parameters. Only correlation coefficients above 0.8 were chosen since these indicates very high positive correlation. Correlations such as those indicated in the table suggests that the relationship between the parameters are very strong and that such relationships depend heavily on each other. For example, an increase in pH (increase towards basicity) would result in an increase in bicarbonate concentration and a decrease in pH will result in a decrease in bicarbonate concentration. Ammonium correlates highly with phosphate implying that their source may be the same and they increase and decrease together.

The classification of the samples into clusters is based on a visual observation of the dendogram. The phenon line was drawn across the dendogram at a linkage distance of about 31 . Thus, samples with a linkage distance lower than 31 are grouped into the same cluster. This position of the phenon line allows a division of the dendogram into three clusters of groundwater samples, named Group I, Group II (A and B) and Group III. As mentioned by Guler et al. (2002), fewer or greater number of clusters could be defined by moving the position of the phenon line up or down (down in this case) on the dendogram.

Using visual inspection, the Stiff plots were grouped under the dendogram. Group I has a relatively low concentration of chloride and moderate cation concentrations compared to Group IIA which has very high chloride concentration and low cation concentrations unlike Group IIB which favors higher calcium concentration and moderate chloride concentrations. Group III is dissimilar to Group II due to the relatively elevated concentration of sodium. Hierarchical Cluster Analysis (HCA), therefore, grouped the samples based on dominant concentration of chemical constituents. Chloride is the most dominant constituent in this case and has the highest linkage distance.

Components	Variance	Difference	Proportion	Cumulative
Comp1	3.76689	1.42363	0.2898	0.2898
Comp2	2.34326	.279267	0.1803	0.4700
Comp3	2.06399	.00861161	0.1588	0.6288
Comp4	2.05538	.367883	0.1581	0.7869
Comp5	1.6875	.	0.1298	0.9167

Table 8: Principal components with Varimax rotation applied.

The results of PCA shows that five factors account for the variation in the hydrochemistry within the study area. Factor 1 is dominated by TDS, nitrate, phosphate and ammonium, and accounts for 28.98% of the variation. Factor 2 is dependent on EC, chloride and sulphate, and responsible for 18.03% of the variation. Factor 3 is accountable for some 15.88% of the variation and dominated by calcium, magnesium and bicarbonate. Factor 4 is dominated by pH only but still responsible for some 15.81% of the hydrochemical variation. Factor 5 has only 12.98% of the variation but holds sodium and potassium accountable for that variation.

Variable	Comp1	Comp2	Comp3	Comp4	Comp5	Unexplained
pH				0.6942		.04333
TDS	0.3414					.08682
EC		0.3273				.06995
Ca			0.6492			.08623
Mg			0.6389			.06202
K					0.7427	.06193
Na					0.5760	.06362
Cl		0.7347				.06461
SO_4		0.4016				.07143
PO_4	0.5749					.0992
NO_3	0.3475					.2714
NH_4	0.5257					.07668
HCO_3			0.6212			.02572
Proportion %	28.98	18.03	15.88	15.81	12.98	
Cumulative %	28.98	47.00	62.88	78.69	91.67	

Table 9: Rotated Component loadings (pattern matrix) and unique variances.

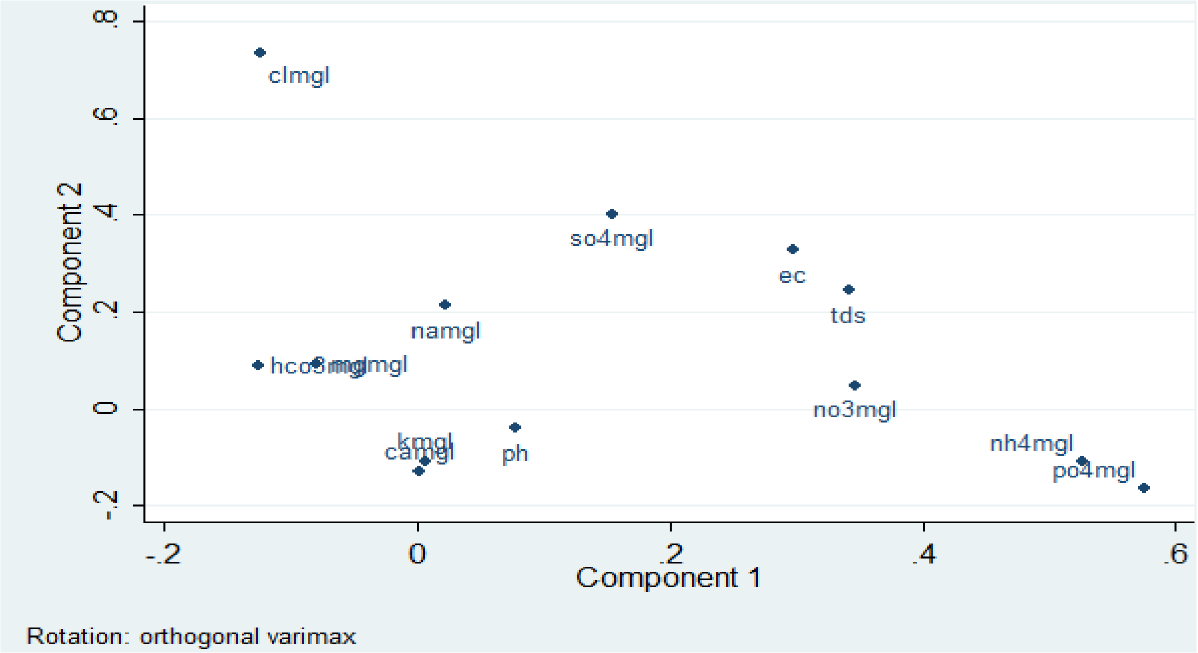

Figure 4: Graph of component loadings for components 1 and 2 showing parameters loading on components.

Chloride loads heavily on factor 2. Ammonium and phosphate loads heavily on factor 1 which accounts for the highest percentage of variation.

Score variables for the first two factors plotted against each other and the Amukpe uncased borehole is heavily linked to the first factor. The Ugbomro cased borehole is the least linked with factor 1. Shagholoh, Ekurede Urhobo and Ogunu are the most linked with factor 2.

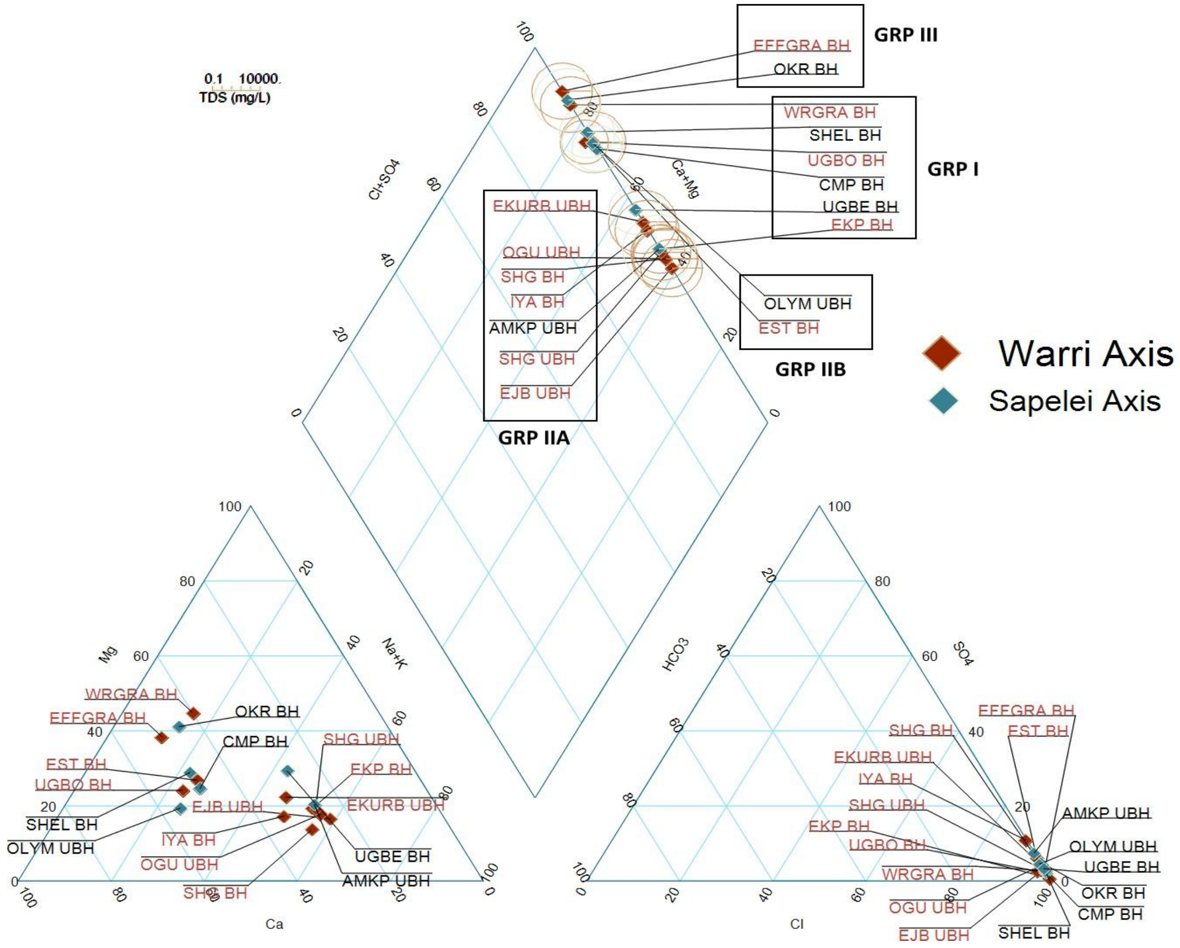

Figure 5: Piper plot for study area.

The Piper plot shows that the all the samples belong in the Ca^{2+}-Mg^{2+}-Cl^{-}- SO_4^{2-} hydrochemical facies. Chloride ion is the dominant parameter both in the anion and cation categories. Group I, Group IIB and Group III have the highest cation concentration compared to Group IIA. Group IIA is the most heavily Chloride-influenced group (Fig. 4.1). Only two samples, Ekpan and Ugbegun fall out of Group I into Group IIA. All samples are fall within the chloride ion type in terms of anions and the no dominant ion type in terms of cations.

Durov Plot:

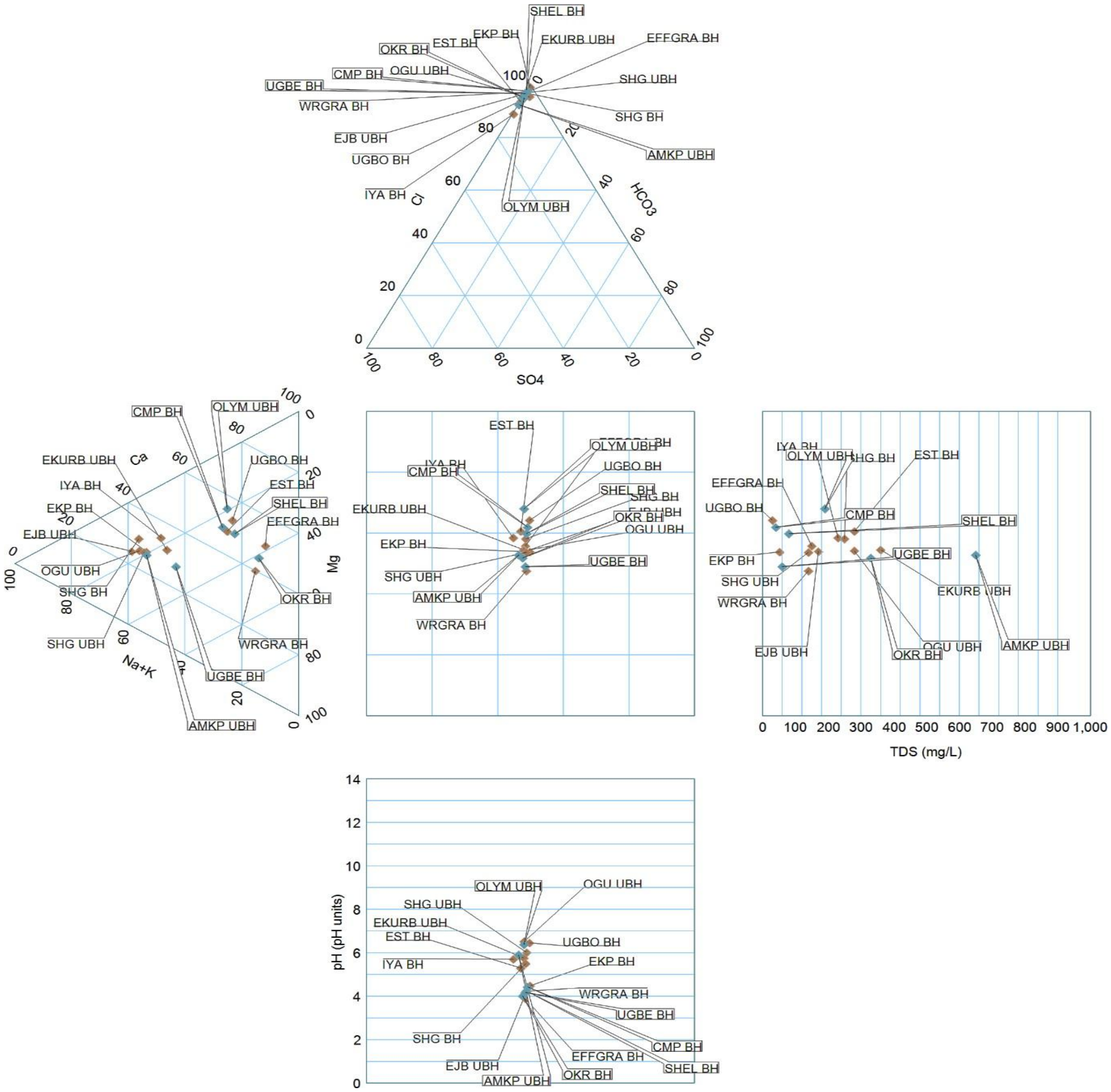

Figure 6: Durov plot for study area.

The Durov plot shows the TDS and pH values. Only Ogunu, Olympia and Ugbomro seem to have pH values in the region of the US EPA standards for drinking water, the rest sample locations have acidic waters. The TDS of the Amukpe uncased borehole is also out of the 500mg/L value for drinking water.

DISCUSSION

The presence of chloride ion as the dominant parameter and the fact that it doesn't correlate with any other parameter in the correlation matrix suggest that it has an external source. This source is from surface saline water close to those locations with high chloride concentrations since the presence of high chloride ion concentration is independent of the pH. The correlation matrix support this idea since chloride and pH have a weak relationship. And so in the Warri axis , areas close to water bodies with saline waters are dominated by groundwater with very high but safe levels of chloride ion concentration. This explains why Ugbomro and Effurun GRA load so weakly on Factor 2 and have very low chloride concentration. Both Shagholor borehole and Ogunu uncased boreholes have high chloride ion concentration. Chloride is a major parameter in factor 2 and its presence increases the EC and combines with factor 1 to have a 47% influence on the hydrochemistry. Also, the shallower uncased borehole have a lower chloride concentration compared with the deeper cased boreholes, this is explained by the depth. The ions in the groundwater in the shallow boreholes are able to mix easily at shallow depth, but at greater depth groundwater doesn't mix as easily (Todd and Mays, 2005).

The presence of ammonium in such high concentrations can only be indicative of pollution from sewage. The fact that ammonium along with phosphate load so heavily on factor 1 also supports this. The high concentrations of these parameters can be attributed to areas with poor waste management, old boreholes or uncased wells with groundwater from shallow water tables. The concentration of these parameters are highly localized. Nitrate and TDS increases along with ammonium and phosphate since the presence of contaminants from sewage increases the TDS. Factor 1, having a 28.98% influence on the hydrochemistry, will continue to increase if the pollution from sewages from septic tanks, and possibly leachates, are not checked.

Factor 3 is indicative of water hardness since calcium, magnesium and bicarbonates (in the absence of carbonates due to acidity of water samples, low pH) are involved. Bringing the percentage of variation to some 62.88%. Calcium ions react with bicarbonate ions to form insoluble calcium carbonate ($CaCO_3$) that is the marker for water hardness. Factor 4 and 5 are less significant compared to the aforementioned factors as the effects and variations are as a result of the first three factors.

The presence of ammonia at higher than geogenic (resulting from geologic processes) levels is an important indicator of faecal pollution. Taste and odour problems as well as decreased disinfection efficiency are to be expected if drinking-water containing more than 0.2 mg of ammonia per litre is chlorinated, as up to 68% of the chlorine may react with the ammonia and become unavailable for disinfection (EPA, 2012). Cement mortar used for coating the insides of water pipes may also release considerable amounts of ammonia into drinking-water and compromise disinfection with chlorine.

"The presence of the ammonium cation in raw water may result in drinking-water containing nitrite as the result of catalytic action or the accidental colonization of filters by ammonium-oxidizing bacteria. Ammonia has a toxic effect on healthy humans only if the intake becomes higher than the capacity to detoxify. If ammonia is administered in the form of its ammonium salts, the effects of the anion must also be taken into account. With ammonium chloride, the acidotic effects of the chloride ion seem to be of greater importance than those of the ammonium ion. At a dose of more than 100 mg/kg of body weight per day (33.7 mg of ammonium ion per kg of body weight per day), ammonium chloride influences metabolism by shifting the acid–base equilibrium, disturbing the glucose tolerance, and reducing the tissue sensitivity to insulin."-US EPA (EPA, 2012)

CONCLUSION

The groundwater within the study area is mostly acidic with high chloride concentrations. Contamination by anthropogenic sources is mainly from leaky septic tanks since the presence of ammonium in such high amounts indicates the presence of faecal contamination. The presence of chloride is from the proximity of areas that lie southward towards the Atlantic Ocean and the fact that water doesn't mix excessively at greater depths but the chloride levels are still within accepted standards for domestic use. Domestic wastes from septic tanks and improper waste disposal are the main sources of ammonium in the groundwater of the study area, and this reduces the groundwater quality in the area markedly.

HCA and PCA are very reliable statistical methods for water analysis in general. The graphical methods are essential in providing a visual guide to access dominant chemical constituents.

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