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Geoenvironmental Investigation of Some Physical and Chemical Constituents of Ground Waters in of Sapele and Environs, Western Niger Delta, Nigeria

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Abstract:
Hydrogeochemical studies have been carried out in parts of Sapele and Warri Local Government Areas of Delta State in order to determine the different hydrogeochemical facies and understand the groundwater flow regime and its effect on the chemical composition of the groundwater so as to evaluate the anthropogenic effects on groundwater quality in the study area. Twenty-five (25) water samples were taken from Sapele (18) and Warri (7) in one liter plastic cans with temperature, pH, electrical conductivity and Total Dissolved Solids (TDS) determined in-situ. The samples were then taken to the laboratory where the analyses were done using the Varian 220 flame atomic absorption spectrophotometer. Salinity and chloride in water was carried out in accordance with the American Petroleum Institute (API-RP) 45. Phosphate, Nitrate, Sulphate, Calcium, Potassium, Sodium, Magnesium and Ammonium were all determined in accordance with the American Public Health Association (APHA) 425C,427C and 417C.
The analyses carried out indicated the presence of chloride ion as the dominant parameter. Chloride shows a negative correlation with all other parameters thus indicating that its source is from surface saline waters close to those areas with high chloride concentrations. The presence of ammonia in such high concentrations and its strong positive correlation with phosphate supports that its source is as a result of pollution from sewage. The positive correlation of phosphate, sulphate, nitrate and TDS also indicate pollution from sewage. GPS readings and computation of several hydrogeological parameters showed a SW direction of groundwater flow for Sapele and a SE flow direction for Warri. The presence of ammonium at levels higher than geogenic (geologically related processes) levels is a strong indicator of fecal pollution. The groundwater in the area is mostly acidic with high chloride concentrations.
Contamination from anthropogenic sources is mainly as a result of waste waters from brines released as by-products of oil exploration activities and leaky septic tanks. 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.

Keywords: *Sapele, hydro geochemical facies, contamination, ammonia, chloride*

1. Introduction

Groundwater is the main source of 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 is extracted. 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. Within the aquifers, as groundwater flows through soil and rock particles by seepage, it dissolves substances (minerals present in the soil and rocks, contaminants such as improperly disposed industrial wastes, organic compounds, leachates from improperly disposed waste, etc.) in contact with it and becomes saturated with these dissolved substances. Dissolution of substances continues until chemical equilibrium is achieved between the water and the substances with which it is in contact, thereby altering the chemical composition of groundwater and hence the groundwater quality.

Land use, proximity to the coast, recharge source, soil type and resident time also influence the chemical composition of groundwater and susceptibility to pollution. In an area dominated by the petroleum industry, the quality of groundwater should be of some concern to the populace since the production of oil and gas is usually accompanied by substantial discharge of wastewater in the form of brines (composed of sodium, calcium, ammonia, sulphate, boron, chloride, trace metals and other dissolved solids) (Todd & Mays, 2005). Brine-polluted aquifers are common place in oil producing areas due to infiltration of improperly disposed wastewaters. Areas close to the coast are susceptible to pollution by saline waters that could increase dissolved salts concentration to some 10,000 mg/L making such water unusable domestically and to some extent industrially. Recharge source, soil type and resident time are other factors that have an influence on the chemical composition of groundwater as they determine the original chemical composition of groundwater, chemical reactions in the subsurface and the amount of time (varies from days for shallow aquifers to millions of years for deep aquifers) groundwater remains within a system.

The aim of this thesis is to determine the concentrations of some major trace elements in groundwater and their spatial relationships within the study area using statistical methods.

2. Study Area

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 Sapele, Warri South and Uvwie Local Government Area respectively. The area, located some 40km away from the Atlantic Ocean, has a population of over 300,000 people (Olobaniyi&Owoyemi, 2006).

Sapele is one of the prominent commercial cities in southern Nigeria as it has a port and several oil fields and flow stations. The Warri areas of the study area are home to a port and a refinery.

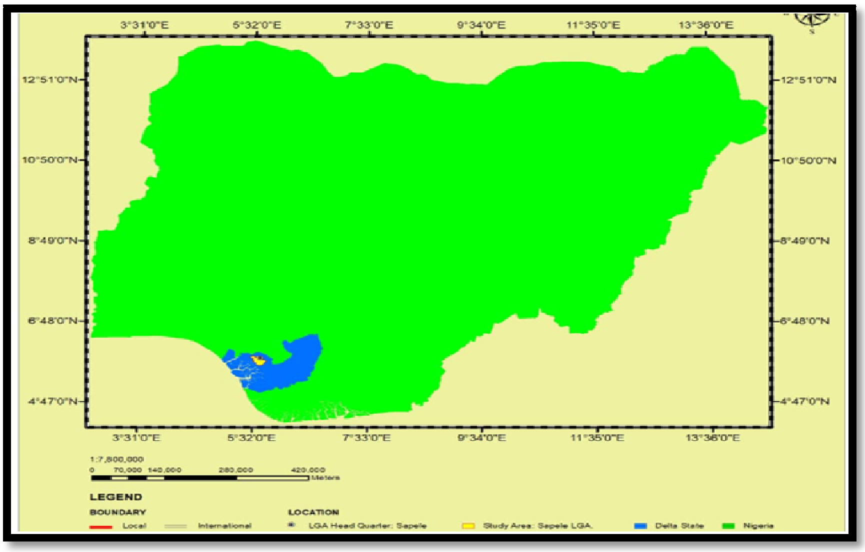

Figure 1: Ph, Total Dissolved Solids and Electrical Conductivity Data Obtained From the Field

S/NO	LOCATION	pH	TDS (ppm)	EC (mS/cm)
1	OKRD/BH	4.78	120	80
2	CRD/BH	6.05	150	120
3	UGB/BH	5.17	220	360
4	OGBRD/BH	3.96	260	570
5	MCF/BH	5.25	50	520
6	ADL/UBH	6.18	85	38
7	ASB/UBH	4.25	230	260
8	UGW/UBH	3.86	140	350
9	URA/BH	5.85	180	110
10	LBRD/BH	6.05	320	450
11	OKR/BH	6.38	300	420
12	OGR/BH	6.25	80	200
13	SHRD/BH	4.18	60	125
14	AKNT/BH	4.96	620	850
15	OGB/UBH	6.85	40	85
16	AMK/BH	6.38	150	320
17	AJM/BH	5.18	140	285
18	EBRD/BH	4.05	182	375

S/NO	LOCATION	pH	TDS (ppm)	EC (mS/cm)
19	SHG/UBH	4.85	150	350
20	EKP/BH	3.96	50	120
21	OGU/BH	6.85	80	185
22	IYA/UBH	6.45	230	500
23	EST/BH	6.25	190	270
24	WRGRA/BH	5.85	620	840
25	EFGRA/BH	6.65	270	450

Table 1: pH, Total Dissolved Solids and Electrical Conductivity Data Obtained from the Field

3. Results

BH	pH	TDS	EC	As	Cr	Pb
OKRD/BH	4.78	120	80	0.01	0.002	BDL
CRD/BH	6.05	150	120	BDL	0.003	0.002
UGB/BH	5.17	220	360	BDL	0.002	0.001
OGBRD/BH	3.96	260	570	0.003	BDL	0.004
MCF/BH	5.25	50	520	0.004	0.005	BDL
ADL/UBH	6.18	85	38	BDL	0.007	BDL
ASB/UBH	4.25	230	260	BDL	0.004	BDL
UGW/UBH	3.86	140	350	BDL	BDL	0.003
URA/BH	5.85	180	110	0.003	0.005	BDL
LBRD/BH	6.05	320	450	0.001	0.004	0.001
0KR/BH	6.38	300	420	0.004	0.007	0.004
OGR/BH	6.25	80	200	BDL	BDL	0.003
SHRD/BH	4.18	60	125	BDL	0.003	BDL
AKNT/BH	4.96	620	850	0.005	0.004	BDL
OGB/UBH	6.85	40	85	0.003	0.007	0.001
AMK/BH	6.38	150	320	0.001	0.005	0.003
AJM/BH	5.18	140	285	BDL	BDL	0.001
EBRD/BH	4.05	182	375	BDL	BDL	BDL
SHG/UBH	4.85	150	350	0.002	0.005	BDL
EKP/BH	3.96	50	120	0.003	0.004	0.01
OGU/BH	6.85	80	185	BDL	0.006	0.002
IYA/UBH	6.45	230	500	0.004	0.003	0.03
EST/BH	6.25	190	270	BDL	0.001	0.002
WRGRA/BH	5.85	620	840	BDL	0.002	BDL
EFGRA/BH	6.65	270	450	0.003	0.007	0.001
Min.	3.86	40	38	0.001	0.001	0.01
Max.	6.85	620	850	0.01	0.007	0.004
Mean	5.4596	196.68	329.32	0.00353846	0.0043	0.002133333
Median	5.85	150	-	0.003	0.004	0.002
S.D.	1.00336716	150.2461092	216.859924	0.00225889	0.001866604	0.001125463
Skewness	- 0.30210829	1.829697189	0.91732455	2.01700788	0.052871865	0.397240326

Table 2: Statistical Representation of Physical Parameters and Trace Elements

EST/BH	IYA/UBH	OGU/BH	EKP/BH	SHG/UBH	EBRD/BH	AJM/BH	AMK/BH	OGB/UBH	AKNT/BH	SHRD/BH	OGR/BH	0KR/BH	LBRD/BH	URA/BH	UGW/UBH	ASB/UBH	ADL/UBH	MCF/BH	OGBRD/BH	UGB/BH	CRD/BH	OKRD/BH	**BH**
30.6	27.2	25.2	19.1	18.4	60.27	25.5	40.2	30.9	19.2	35.21	12.9	28.1	65.41	27.4	28.3	80.5	47.3	90.4	65.4	40	38.35	25.16	**Cl**
0.85	0.19	1.28	0.75	3.12	4.07	3.03	2.15	2.32	4.01	3.25	1.85	0.45	0.39	1.98	2.85	1.96	1.35	1.85	0.85	4.25	3.81	0.25	**SO_4**
0.13	0.18	0.05	0.02	0.06	0.15	0.17	0.06	0.12	0.05	0.07	0.18	0.12	0.05	0.08	0.16	0.14	0.05	0.01	0.06	0.19	0.02	0.05	**PO_4**
0.03	0.18	0.15	1.03	0.09	0.12	0.43	0.18	0.07	0.65	0.07	0.09	0.82	0.15	0.82	0.19	0.06	0.72	0.18	0.67	0.31	0.12	0.08	**NO_3**
3.25	3.96	1.85	0.96	0.75	6.35	0.86	2.15	3.65	7.12	1.83	1.38	6.87	7.25	0.85	3.12	2.18	4.25	1.34	5.58	6.75	2.65	1.38	**NH_4**
0.15	0.02	0.05	0.01	0.04	0.18	0.15	0.17	0.18	0.07	0.05	0.35	0.05	0.58	0.08	0.06	0.11	0.05	0.02	0.51	0.45	0.28	0.05	**HCO_3**
8.85	6.95	4.81	3.36	7.21	6.38	5.37	12.5	17.3	8.33	12.42	8.8	4.32	5.32	9.71	5.25	11.5	9.27	6.85	8.03	5.35	4.08	2.35	**Ca**
3.25	1.93	3.65	1.95	2.25	1.93	1.85	3.11	1.98	3.72	3.65	5.32	3.13	5.13	4.32	2.38	2.35	2.46	1.36	1.95	3.25	2.25	1.35	**Mg**
0.18	3.12	5.25	0.95	0.08	3.75	1.32	2.38	0.08	0.33	0.65	0.38	1.32	1.87	0.19	1.58	0.08	0.58	0.45	0.62	1.31	0.88	0.35	**K**
3.82	8.57	8.25	12.3	15.2	16.5	3.38	7.95	8.3	5.18	6.28	8.25	3.45	8.5	2.85	6.35	1.85	4.12	6.85	14.3	17.4	13.2	5.9	**Na**

BH	Cl	SO_4	PO_4	NO_3	NH_4	HCO_3	Ca	Mg	K	Na
WRG RA/BH	19.3	0.88	0.15	0.05	5.81	0.17	5.72	4.78	1.14	13.3
EFG RA/BH	8.4	1.4	0.1	0.2	1.6	0.7	8.3	6.3	1.6	6.3
Min.	8.37	0.19	0.01	0.03	0.75	0.01	2.35	1.35	0.08	1.85
Max.	90.4	4.25	0.19	1.03	7.25	0.73	17.3	6.32	5.25	17.4
Mean	36.336	1.9636	0.0956	0.2968	3.3488	0.1824	7.5296	3.0248	1.2176	8.33
Median	28.3	1.85	0.07	0.16	2.65	0.11	6.95	2.46	0.88	7.95
S.D.	20.9665	1.28389	0.05687	0.29905	2.25877	0.19479	3.3561	1.32048	1.26656	4.4926
Skewness	1.20615	0.36846	0.26194	1.23679	0.5832	1.55676	1.06129	0.91985	1.80385	0.60169

Table 3: Statistical Representation of Anions and Cations

The results of the raw laboratory analysis are presented in Table 3. These results show that most of the sample locations have alarmingly poor water quality. Most of the samples obtained from both cased and uncased boreholes have pH values of less than 6.50 (less than the Nigerian Standard for Drinking water Quality (NSDWQ,2007) and the United States Environmental Protection Agency (EPA, 2012) standards for drinking water) and are therefore acidic. Theboreholes in Akintola, sapele and Warri GRA have TDS values of 620 mg/l which is above the Nigerian Standard for Drinking water Quality (NSDWQ,2007) and the United States Environmental Protection Agency (EPA, 2012) of 500 mg/l..The analysis of arsenic, chromium and lead show that their concentrations fall below the Nigerian Standard for Drinking water Quality (NSDWQ,2007) and the United States Environmental Protection Agency (EPA, 2012) standards for drinking water which are 0.01 mg/l, 0.05 mg/l and 0.01 mg/l respectively.EuropeanUnionDrinkingWaterDirective(1998)forammonium in drinking water is 0.5mg/l, the mean value for ammonium is 3.44 mg/l for all sampled boreholes which is well above the EU(EU,1998)standards

4. Summarized Statistics of Groundwater Physical and Chemical Characteristics

	Min.	Max.	Mean	Median	US EPA (2012)	EU DWD (1998)	NSDWQ(2007)
pH	3.86	6.85	5.4596	5.85	6.5-8.5		6.5-8.5
TDS	40	620	196.68	150	500		500
EC	38	650	329.32	320			1000
As	0.001	0.01	0.00354	0.003			0.01
Cr	0.001	0.007	0.0043	0.004			0.05
Pb	0.001	0.004	0.00213	0.002			0.01
Cl	8.37	90.38	36.334	28.25	250		250
SO_4	0.19	4.25	1.9636	1.85		250	100
PO_4	0.01	0.19	0.0956	0.07			5
NO_3	0.03	1.03	0.2968	0.16	10	50	50
NH_4	0.75	7.25	3.3488	2.65		0.5	
HCO_3	0.01	0.73	0.1824	0.11			
Ca	2.35	17.25	7.5296	6.95		200	
Mg	1.35	6.32	3.0248	2.46		200	
K	0.08	5.25	1.2176	0.88			
Na	1.85	17.35	8.33	7.95		200	200

Table 4: Compared against US EPA (EPA, 2012), EU DWD (EU, 1998) and NSDWQ

Degree of Hardness	Grains per Gallon (gpg)	Parts per Million (ppm) 1 gpg=17.1 ppm
Soft	<1.0	<17.0
Slightly Hard	1.0-3.5	17.1-60
Moderately Hard	3.5-7.0	60-120
Hard	7.0-10.5	120-180
Very Hard	10.5	>180

Table 5: Showing Standards for Hardness in Water
Source: American Society of Agricultural Engineers (S-339) and the Water Quality Association (WQA)

Tables show that the study area has very high mean TDS concentration. Using the equation to determine the hardness of water in the study area, we classified the water of the study area as very hard with mean hardness of 11.5. Akintola and Warri GRA boreholes have the highest hardness value of 47.

4.1. Correlation Matrix

	Ph	TDS	EC	As	Cr	Pb	Cl	SO_4
pH	1	0.204511	-0.01686	0.11112	0.024385	0.083518	0.275941	0.083518
TDS	0.19988	1	-0.09913	-0.29664	-0.01979	0.085964	0.127732	-0.10783
EC	0.210617	0.403846	1	0.181466	-0.20233	0.028296	0.279037	0.011487
As	-0.23805	-0.23805	-0.0347	1	-0.29664	0.081026	0.204511	-0.287
Cr	-0.26628	0.838278	-0.03887	0.12794	1	-0.04716	0.20048	-0.25852
Pb	0.408016	-0.12756	-0.2954	-0.01998	0.133479	1	0.043486	0.403846
Cl	-0.29539	0.41472	0.408016	-0.17602	0.046608	0.181466	1	-0.38871
SO_4	-0.31922	-0.00332	-0.01683	-0.10467	0.16816	-0.13938	0.053799	1
PO_4	-0.16089	0.134216	0.11112	-0.13189	-0.05042	0.135465	0.061927	0.108432
NO_3	0.18149	0.559458	-0.07488	-0.18708	0.021437	-0.1948	0.275941	-0.11144
NH_4	0.022411	0.232008	-0.02936	0.027155	0.134216	-0.14941	0.5588	-0.09844
HCO_3	-0.23777	0.204044	-0.10113	0.163411	-0.29236	0.014014	0.284765	0.5588
Ca	-0.13189	0.022411	0.30699	-0.17733	0.133476	0.559458	-0.1509	0.064799
Mg	-0.01979	-0.04381	0.148752	0.210201	-0.29236	-0.10113	-0.42931	-0.11679
K	0.139396	0.309058	-0.10415	0.053799	-0.25322	0.210201	-0.01998	-0.03327
Na	0.635746	-0.20233	0.41472	-0.37184	0.061927	0.224846	0.121394	-0.2954

Table 6: Correlation Table Showing Relationship between Analyzed Parameters

PO_4	NO_3	NH_4	HCO_3	Ca	Mg	K	Na
0.056242	0.12564	0.034267	0.034562	0.054637	0.045367	0.346789	0.045637
-0.05042	-0.08765	-0.01526	-0.10236	-0.03458	-0.03456	-0.03453	-0.03453
-0.14941	0.23459	0.034522	0.165637	0.034678	0.325678	0.034556	0.153663
0.02225	0.13865	0.016753	-0.26789	-0.03246	-0.03458	-0.02458	-0.02458
0.064799	0.034672	0.034568	0.236788	0.020345	0.023443	0.126746	0.023566
0.234304	-0.02548	-0.03452	-0.02355	-0.26759	0.043467	0.34629	-0.02358
0.061222	-0.02562	-0.01256	0.341267	0.045699	-0.03453	-0.02438	0.346798
-0.33307	-0.04533	0.01654	-0.03457	-0.03426	-0.03426	-0.02675	-0.02369
1	0.25639	0.235478	0.126788	0.235678	0.65378	0.564789	0.563875
-0.10467	1	-0.32675	-0.02564	-0.03453	-0.03456	-0.43528	-0.23417
0.300716	0.023347	1	0.034526	0.045327	0.023689	0.034527	-0.32418
-0.13256	0.023578	0.234577	1	-0.02346	-0.03426	-0.03453	-0.15339
0.279037	-0.03545	-0.21377	-0.02346	1	-0.03412	-0.02675	0.563452
-0.25852	-0.0654	-0.23415	-0.03453	-0.09368	1	-0.02347	-0.01568
0.234304	0.034627	0.023478	0.053676	-0.05345	0.025678	1	0.215786
-0.26579	0.143678	-0.02347	-0.04355	-0.02347	0.227834	0.156473	1

Table 7: Correlation Matrix Continued

Pearson's correlation matrix shows the relationship between the parameters .Only correlation coefficients above 0.5 were chosen since these indicate very highpositive correlation.

4.2. Hierarchical Cluster Analyses Results and Stiff Plots

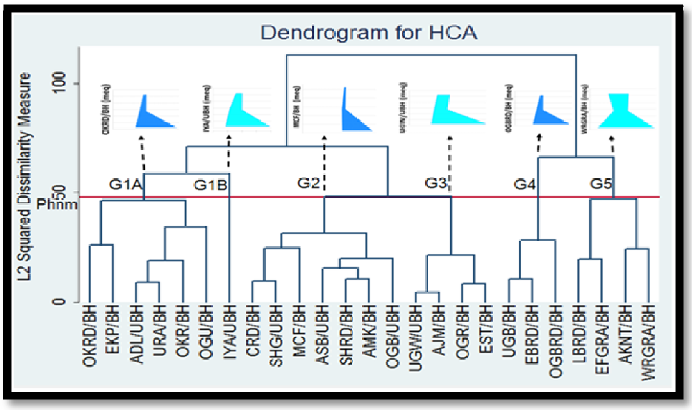

Figure 2: Cluster Analyses Dendogram Correlated with Stiff Diagrams of Sample Locations

The classification of the samples into clusters is based on a visual observation of the dendogram. Chloride is the most dominant constituent in this case and has the highest linkage distance.

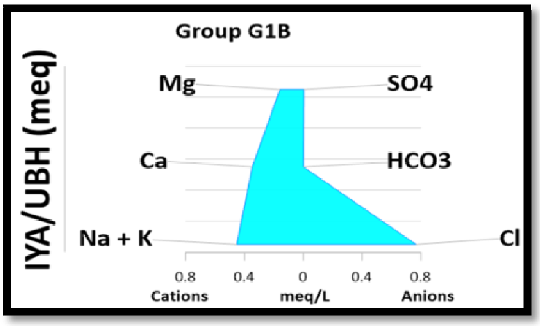

Figure 3: Stiff Diagram Indicating Parameters Used for Plotting

4.3. Principal Component Analyses Results

Component	Eigenvalue	Difference	Proportion	Cumulative
Comp1	2.46293	0.606188	0.1539	0.1539
Comp2	1.85674	0.0465308	0.116	0.27
Comp3	1.81021	0.0296736	0.1131	0.3831
Comp4	1.78054	0.0229129	0.1113	0.4944
Comp5	1.75762	0.181181	0.1099	0.6043
Comp6	1.57644	0.130455	0.0985	0.7028
Comp7	1.44599	.	0.0904	0.7932

Table 8: Principal Components with Varimax Applied

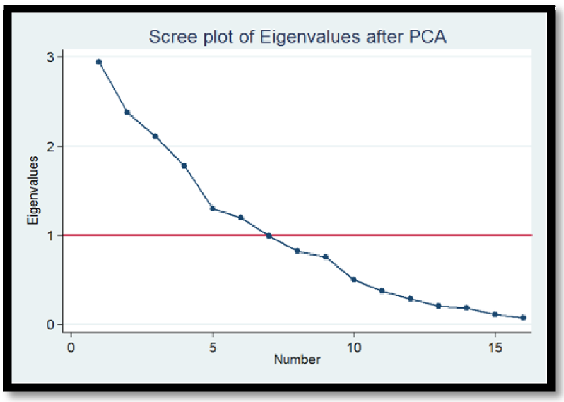

Figure 4: Scree Plot for Eigenvalues after Principal Component Analysis

From the graph, only Eigen values above 1 were retained which shows that seven (7) factors are responsible for the variation in hydro geochemistry of the samples.

Variable	Comp1	Comp2	Comp3	Comp4	Comp5	Comp6	Comp7	Unexplained
pH		0.4143				0.3205		0.1869
TDS	0.5881							0.08911
EC	0.5445							0.1951
Ca		0.6036						0.2498
Mg			0.4838				-0.3497	0.132
K						0.7125		0.2075
Na		-0.4405						0.321
Cl							0.8072	0.09337
SO4					0.6984			0.1834
HCO3			0.6756					0.2134
NO3			-0.3539	0.3754				0.4003
PO4				-0.6554				0.1583
NH4	0.5287							0.2154
As					-0.4638			0.3037
Cr		0.3779		0.5449				0.1181
Pb					-0.4025	0.3529		0.2421
Proportion (%	15.39	11.6	11.31	11.13	10.99	9.85	9.04	
Cumulative (%	15.39	27	38.31	49.44	60.43	70.28	79.32	

Table 9: Rotated Component Loadings (Pattern Matrix) and Unique Variances

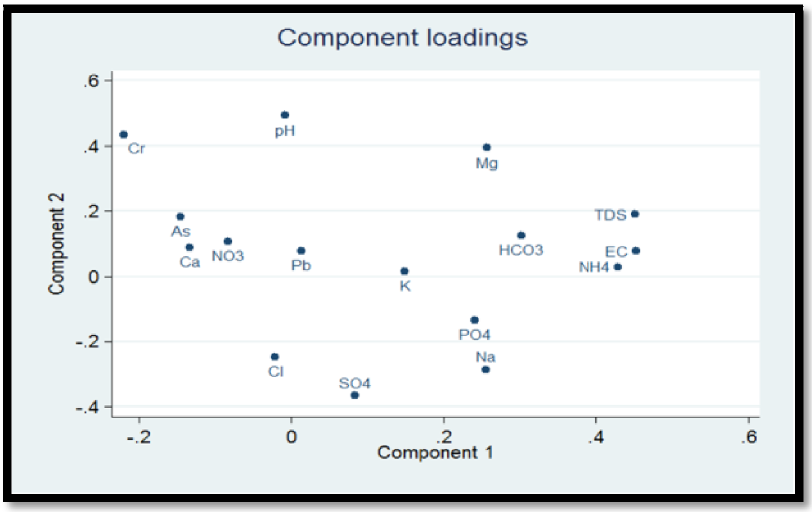

Figure 5: Graph of Component Loadings for Components 1 and 2 Showing Parameters Loading on Components

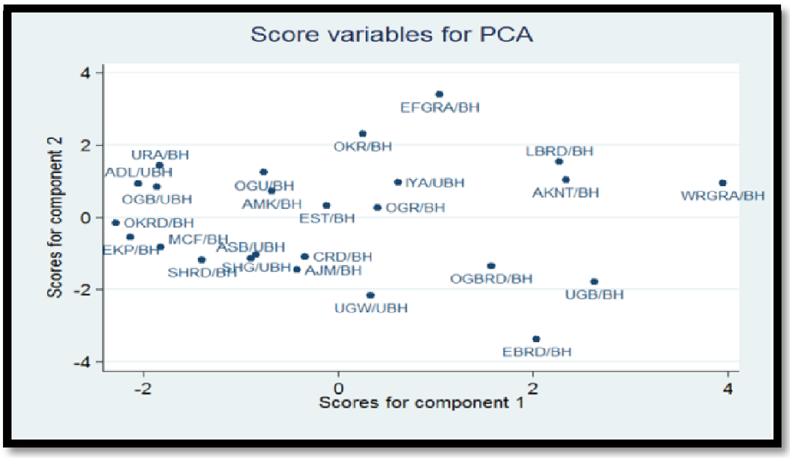

Figure 6: Graph of Score Variables For Component 1 And 2 Showing Sample Locations Loading On Components

Score variables for the first two factors plotted against each other. The Warri GRA borehole is heavily linked to the first factor. The Shell road borehole is the least linked with factor 1. Labored road, Akintola and Effurun GRA are the most linked with factor 2.

4.4. Piper Diagram

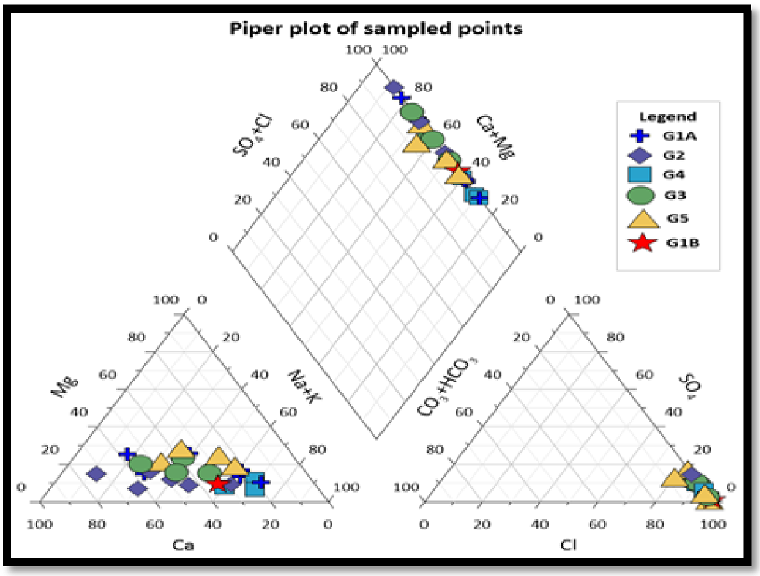

Figure 7: Piper Plot for Study Area

The Piper plot shows that the all the samples belong in the Ca^{2+}-Mg^{2+}-Cl^{-}- SO_4^{2-}hydrochemical facies. Calcium ion is the dominant parameter both in the anions and cations in the study area. The waters of the study area can therefore be classified as a Ca^{2+}- Cl^{-} waters.

4.5. Durov Plot

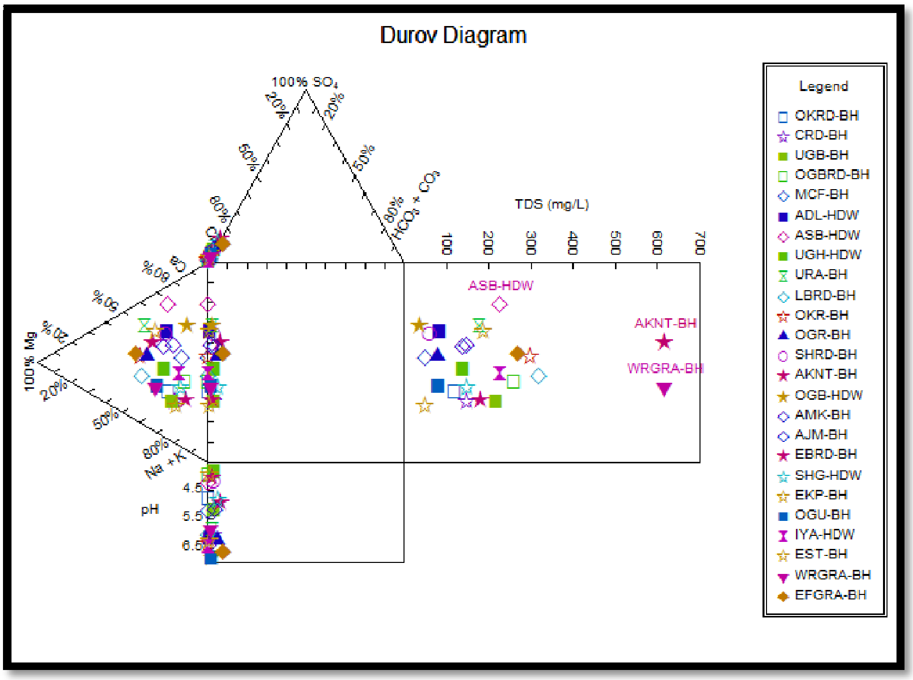

Figure 8: Durov Plot of the Study Area

ThDurov plot shows the relationship between physical parameters such as pH,EC and TDS with chemical parameters which include trace metals, anions and cations. The plot shows that areas with high TDS values equally have high concentration of Na,Ca and Mg.

4.6. Schoeller Diagram

The Schoeller diagram gives a graphical representation of the average composition of the major cations and anions present in the water samples of the study area. Warri GRA, Eboh road Akintola,Ogunu and Effurun GRA boreholes have the highest chloride concentrations which implies a susceptibility to saline intrusion and hence not suitable for drinking.

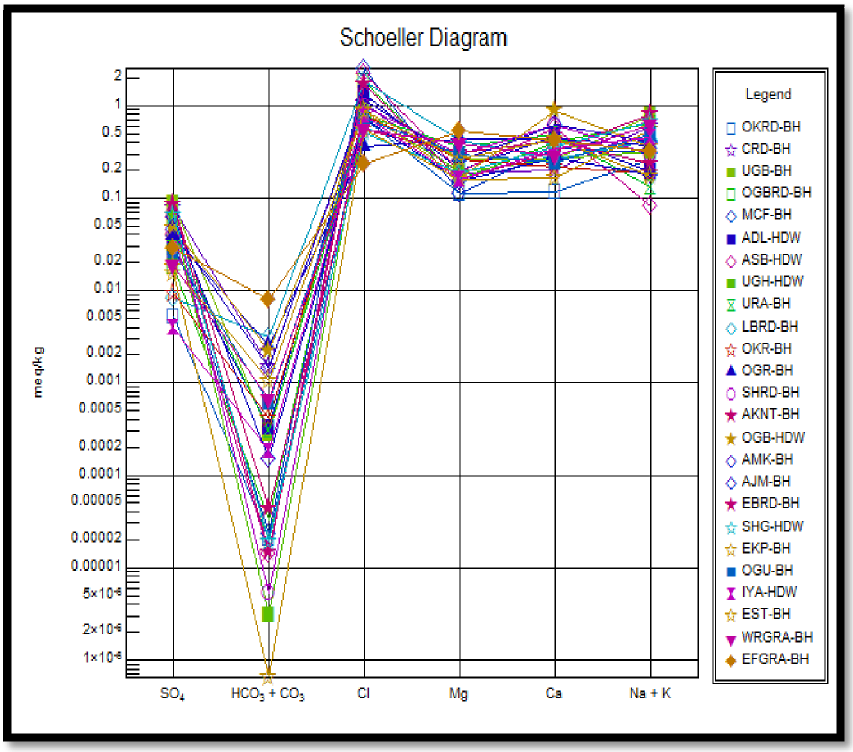

Figure 9: Schoeller Diagram of Study Area

5. Conclusion

The groundwater within the study area is mostly acidic with high chloride concentrations. Contamination by anthropogenic sources is mainly as a result of waste waters in the form of brines released as by-products from oil exploration activities and also from leaky septic tanks as can be seen by the relatively high concentration of chloride and ammonia. The presence of chloride is from the proximity of areas that lie south ward towards the Atlantic Oceanand 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.

The following findings were made:

- Chloride and calcium ions are the dominant ions and they have anthropogenic contribution. The groundwaters of the study area are thus classified in the Ca-Cl hydrogeochemical facies.
- The shallower uncased boreholes have a lower chloride concentration compared with the deeper cased boreholes; this is explained by the depth. (Todd and Mays, 2005).
- Using GPS readings and other hydrogeological parameters, we concluded for a SW trend for the direction of flow of groundwater for the study areas.
- The level of ammonium and nitrate ions at higher than geogenic (resulting from geologic processes) levels are an important indicator of pollution from sewage. Cement mortar used for coating the water well may also release considerable amounts of ammonia into drinking-water and compromise disinfection with chlorine.
- As, Cr and Pb show very strong positive correlation and their presence in the groundwater is most probably as a result of anthropogenic activities.
- The very high hardness of the ground waters in the study area is most probably as a result of equally high calcium and chloride concentrations.

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