JASEM ISSN 1119-8362

Full-text Available Online at www.ajol.info and www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage. *Sept*, 2011
Vol. 15 (3) 479 -488

Investigation of Hydro-Geochemical Characteristics of Groundwater In Port Harcourt City, Nigeria: Implication for Use and Vulnerability

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ABSTRACT: A hydrogeochemical evaluation of groundwater in Port Harcourt City, Southern Nigeria has been carried out. Thirty two (32) groundwater samples were analysed for their physical, chemical and microbiological properties. The average temperature of the groundwater samples is 29 ^oC, The water is slightly acidic with pH values between 4.28 – 7.72. Elevated Electrical Conductivity (EC) values in some coastal wells suggest possible pollution by seawater. The study also reveals saltwater contamination in the area as Chloride contents in some boreholes are up to 710.00mg/l. Besides of the major chemical compositions, ionic ratio (HCO_3/Cl, Na/Ca, Ca/Cl, Mg/Cl and Ca/SO_4) was used to delineate saline water intrusion. Iron and Manganese concentrations are above the World Health Organization guide value in majority of the boreholes studied, with maximum value up to 1.60mg/l in Abuloma area. Constituents of the heavy metals as shown in this study reveal that, in some locations, values are slightly higher than the permissible levels. Microbial analysis of the water samples to determine the presumptive coliform count of the water indicates the presence of coliform bacteria in majority of the analysed samples, indicating anthropogenic contamination of groundwater. The water is generally classified as soft and fresh based on its hardness and Total Dissolved Solids (TDS), which ranges from 2.50mg/l – 142mg/l and 2.60mg/l – 401mg/l, respectively. The analytical results present the abundance of the ions in the following order: Mg > Ca > Na > K = Cl > SO_4 > HCO_3 > NO_3. Chloride is the dominant anion found in the groundwater of the study area. Piper trilinear diagram for the study area shows that there is a mixture of two types of water with variable concentrations of major ions. These are Ca – Mg – Cl – SO_4 type and Na + K – Cl – SO_4 type water. The second water type is also influenced by NO_3. This means that groundwater in the area is mainly made up of mixtures of earth alkaline and alkaline metals and predominantly Cl^- - SO_4^{2-} water type. Most of the water samples are made up of mixtures of the two water types. The study provides the basic tool for sustainable groundwater management in the area in the context of quality assessment. @JASEM

The determination of the processes that control groundwater chemistry is essential for effective water resource management and protection (Tweed et al., 2004; Edmunds et al., 2002). This is especially important in groundwater systems where there is the presence of multiple aquifers.

The need to ascertain the quality of water used by humans has become very intense in the past decade (Olatunji, et al., 2005; Nwankwoala et al., 2007). It has also been established that geology has a role to play in the chemistry of subsurface water (Abimbola, et al., 2002; Olatunji, et al., 2001). More importantly, research has also shown that mineralogical composition of the underlying rock (s), secondary products and the nature of the surface run-offs are factors that affect quality of groundwater (Tijani, 1990).

The chemical constituents of groundwater is known to cause some health risks, so supply cannot be said to be safe if specific information on water quality which is needed for sustainable resource development and management is lacking (Amajor, 1986; Amadi et al., 1989).

The hydrochemical processes and characteristics of the aquifer systems in the area are generally not known due to an overall lack of hydrologic and hydrogeologic data, which complicates planning and management of groundwater abstraction. Large uncertainties also exist in the understanding of the main processes controlling the evolution of groundwater in the area.

The main objectives of this study are to assess and determine the chemical characteristics, the most relevant controls on the water quality, and the dominant chemical processes, which control the groundwater composition in the area. The study is also aimed at ascertaining the effect or otherwise of saline water in the groundwater system, their implications for use and vulnerability.

The Study Area: The study area is the capital of Rivers State (Fig.1). The area is approximately between latitudes $04^0 43'$N and $05^0 00'$N and longitudes $06^0 45'$E and $07^0 06'$E. Physiographically, it lies entirely within the saltwater or mangrove swamp geomorphic unit of the Niger Delta. The Niger Delta basin is situated on the margin of the Gulf of Guinea in the Equatorial West Africa, and extends from the Calabar flank and the Atlantic Ocean in the south (Reijers, 1996). The Niger Delta protrudes southwards into the Gulf of Guinea as an extension from the Benue Trough and Anambra Basin provinces. The Delta Complex merges westwards across the Okitipupa high into the Dahomey Embayment. To the southeast the most important line of volcanic rocks containing the Cameroon volcanic zone and Guinea ridge form a limit to the other margin. The Tertiary Niger Delta

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covers an area of about 75,000 square kilometers and the progradation which produced an overall regressive clastic sequence which is in the order of 9000m to 12,000m as its maximum thickness (Reijers, 1996).

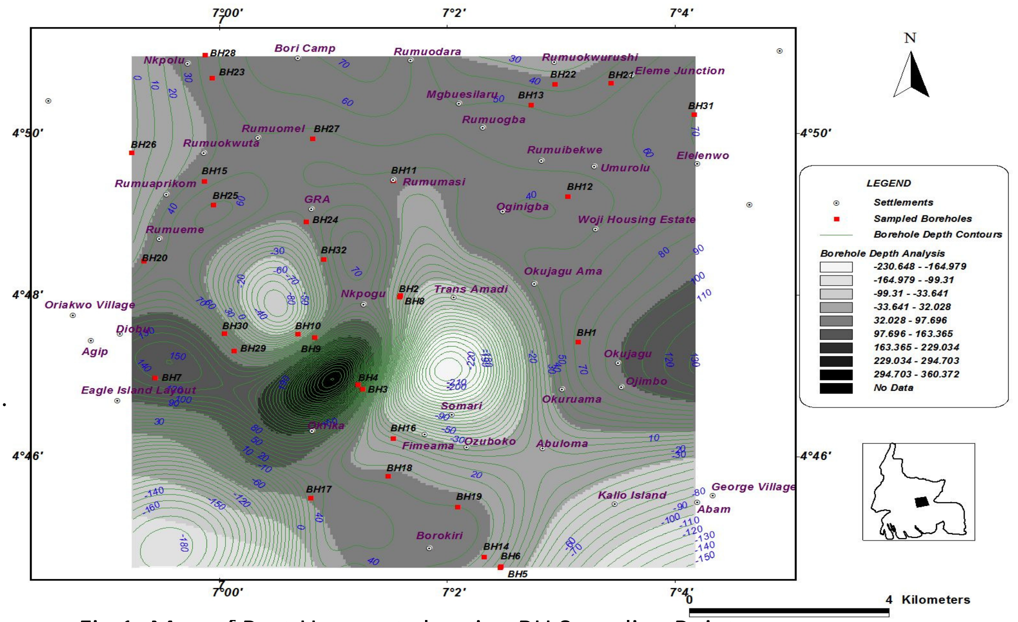

Fig.1: Map of Port Harcourt showing BH Sampling Points

Methods of Study: The ground water samles were collected near the well head of each of the sampled boreholes before the water went through tanks/treatment units. One (1) liter of water was collected from each borehole. Prior to all sample collection, the wells were pumped for about three to five minutes. This was to ensure collection of representative samples. 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 CO_2 that was in the water when the sample was taken and to avoid contamination, appropriately labeled at the points of collection and transported to the laboratory in an ice box for further analyses. Sampling was done only in good weather condition to avoid rainwater contamination, as this would affect the quality of the samples collected. The total depth penetrated by the boreholes was equally recorded where possible. A maximum of three samples were collected per visit to avoid possible deterioration, thus affecting the actual groundwater chemistry. A Global positioning System (GPS), Garmin 76, 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 *in-situ:* Colour, pH, Conductivity and Temperature. Field activities were mainly carried out during the raining season, between June and September, 2009.

Laboratory Evaluation Technique: 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 and are as presented in Table 2.

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. Table 1 shows the study locations and coordinates of the study area

Table 1: Study Locations and Coordinates

S/N	LOCATION (STATION)	LATITUDE	LONGITUDE	BH DEPTH (M)	SWL (M)
1.	Abuloma (GSS)	$04^0 47.025^1$	$007^0 03.485^1$	73.15	4.60
2.	Amadi-Ama	$04^0 47.989^1$	$007^0 01.565^1$	-	5.20
3.	Moscow Rd I	$04^0 46.050^1$	$007^0 01.151^1$	255	7.21
4.	Moscow Rd II	$04^0 46.053^1$	$007^0 01.107^1$	165	4.31
5.	UPE Primary Sch. Borokiri	$04^0 44.620^1$	$007^0 02.645^1$	-	3.82
6.	Comprehensive High Sch. Borokiri	$04^0 44.630^1$	$007^0 02.650^1$	183	4.72
7.	Eagle Island (NAOC Fence)	$04^0 46.967^1$	$006^0 58.913^1$	71	4.50
8.	Eastern Bye Pass (LNG)	$04^0 47.970^1$	$007^0 01.561^1$	-	4.00
9.	Harley Street (Old GRA)	$04^0 47.467^1$	$007^0 00.641^1$	43.05	
10.	Forces Avenue (Old GRA)	$04^0 47.511^1$	$007^0 00.457^1$	42.03	
11.	Elekahia	$04^0 49.409^1$	$007^0 01.485^1$	35.82	
12.	Woji	$04^0 49.217^1$	$007^0 03.370^1$	50.06	
13.	Elijiji Woji	$04^0 50.021^1$	$007^0 02.978^1$	43	
14.	Borokiri Sandfill	$04^0 44.750^1$	$007^0 02.467^1$	183	2.44
15.	Rumuolumeni	$04^0 49.400^1$	$006^0 58.087^1$	100	
16.	Marine Base	$04^0 46.217^1$	$007^0 01.489^1$	25.91	4.71
17.	Reclamation Rd	$04^0 45.478^1$	$007^0 00.598^1$	36.60	
18.	Aggrey Road	$04^0 45.750^1$	$007^0 01.435^1$	36.58	
19.	Churchill (Harold Wilson Drive)	$04^0 45.370^1$	$007^0 02.185^1$	40.20	
20.	Rumuagholu	$04^0 48.413^1$	$006^0 58.794^1$	45.72	7.00
21.	Elelenwo	$04^0 50.620^1$	$007^0 03.837^1$	70	6.80
22.	Rumuibekwe	$04^0 50.609$	$007^0 03.014^1$	38.46	7.57
23.	Mgbuoba (Okilton)	$04^0 50.685^1$	$006^0 59.032$	99.44	-
24.	D/Line (Okija street)	$04^0 48.054^1$	$007^0 00.033^1$	50	
25.	GRA III (Abacha Rd)	$04^0 49.109^1$	$006^0 59.033^1$	48.80	
26.	Mile 4 (Mkt. Junction)	$04^0 49.761^1$	$006^0 58.663^1$	39.62	
27.	Orazi	$04^0 49.935^1$	$007^0 00.619^1$	77	
28.	Rumuigbo	$04^0 50.967^1$	$006^0 59.457^1$	43.89	
29.	Diobu (Nanka Street)	$04^0 47.304^1$	$006^0 59.772^1$	72.20	
30.	UST(New VCs lodge)	$04^0 47.522^1$	$006^0 59.663^1$	76.15	
31.	Onne	$04^0 50.228^1$	$007^0 04.739^1$	264	
32.	Odili Rd (By GTC/200 Rd)	$04^0 48.435^1$	$007^0 00.739^1$	42.67	

Table 2: Methods used for the Physico-chemical analysis of groundwater samples.

Parameters	Measurement Method	Standard
Temperature	Mercury- in- glass thermometer	-
Colour	Lovibond Nessleriser Comparator	-
EC	Electrical Resistivity Tester,	APHA 2510B
PH and Eh	Hanna HI 8314 membrane Meter	APHA 4500 H
Turbidity	HACH 2100AN Turdidimetrer	APHA 2130B
Total Hardness	Titration Method	APHA 2340-B
Chloride	Silver Nitrate Titration	ASTM 512-B
Biocarbonate	Phenolphthalein Alkalinity Method	APHA 2320-B
Nitrate	Ultraviolet Spectrophotometer Screening Method	APHA 4500-NO_3B
Sulphate	Turbidimetric Method	ASTM S-516
Phosphate	Ascorbic acid Method	APHA 4500-PE
Magnesium	Direct Atomic Absorption	ASTM D511-93
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

RESULTS AND DISCUSSION

Groundwater Quality: The groundwater quality data for the study area is presented in Table 3. The hydrogen-ion concentration (pH) of the groundwater in the study area ranges from 3.84 – 7.72. This is the situation in most parts of the Niger Delta Region (Udom et al., 1998, 1999, 2002). Acidity in groundwater in the Niger Delta has been attributed partly to gas flaring in the area.

Total Dissolved Solids (TDS) is a quantitative measure of the sum of organic and inorganic solutes in water. The concentration of TDS ranges from12.60–401.00mg/ in sampled borehole waters in the study area. This shows that groundwater in the area is quite fresh in most locations (Table 4). The TDS values correlate well with conductivity values. The highest TDS value (401.00mg/l) recorded had a corresponding high conductivity of 560.00uS/cm in Marine Base (BH16).

The concentration of TSS range from BDL to 35.00mg/l in borehole waters in the study area. TSS is not stated in WHO (2004) guidelines. WHO (1996) stipulates 10mg/l as the desirable level of TSS and a maximum permissible limit of 25mg/l in drinking water. In the study area, the highest TSS value (35.00mg/l) was recorded in Borokiri Sandfill (BH 14).

Iron (Fe) concentrations are observed to be at its highest, well above the WHO (2004) guide value of 0.3mg/L in so many locations in the study area. Abuloma has value of 1.6oomg/l; Amadi-Ama 0.400mg/l; 0.300mg/l in Eastern- Bye Pass; 0.400mg/l in Forces Avenue; 0.500mg/l in Elekahia; 0.800mg/l in Woji; 0.820mg/l in Rumuolumeni; 0.400mg/l in Market Junction; 0.303mg/l in Diobu (Nanka Street); 0.400mg/l in UST; 0.361mg/l in Onne. It is generally observed that high iron is most associated with shallow wells, as values in deep wells are very low.

Table 3: Results of Hydrogeochemical Analyses in the Study Area

S/N	Location	Temp (^{0}C)	pH	EC (µS/cm)	TDS (mg/l)	TSS (mg/l)	Hardness (mg/l)	Cl^- (mg/l)	Eh (mV)	SO_4^{2-} (mg/l)	Fe (mg/l)	Salinity (mg/l)	NO_3^- (mg/l)	HCO_3^- (mg/L)
1.	Abuloma (GSS)	27.22	55.53	573.00	250.00	1.00	28.00	710.00	122.00	ND	1.600	116.00	0.230	18.401
2.	Amadi-Ama	26.91	6.81	421.60	370.50	5.00	8.43	250.00	131.00	ND	0.400	511.00	ND	21.800
3.	Moscow Rd 1 (Pumping Station)	27.02	4.50	522.00	230.60	10.0	14.50	330.00	170.00	ND	ND	355.00	0.201	6.701
4.	Moscow Rd 2(Post Office)	28.33	7.40	513.00	221.30	12.00	20.40	300.00	143.00	75.00	0.400	82.00	0.831	10.321
5.	Borokiri (UPE)	26.51	3.84	717.40	142.70	1.00	14.00	351.00	152.00	19.30	0.020	181.00	0.510	21.010
6.	Borokiri (Comprehensive Sec. Sch.)	29.03	7.72	618.20	297.20	0.00	36.00	410.00	191.00	90.10	ND	163.40	ND	54.011
7.	Eagle Island (NAOC Fence)	26.35	6.50	230.00	49.00	10.00	10.40	53.00	124.00	69.13	0.200	398.60	ND	11.000
8.	Eastern-Bye-P(LNG)	27.67	6.70	183.70	183.21	3.00	70.00	331.00	187.00	82.55	0.300	200.50	14.000	39.230
9.	Harley Street(Old GRA)	29.03	7.23	195.20	55.00	1.00	142.00	300.00	192.00	96.32	0.200	85.10	34.000	23.003
10.	Forces Avenue (Old GRA)	29.64	7.34	181.40	59.70	0.00	8.00	68.00	137.00	38.31	0.400	49.31	0.100	8.190
11.	Elekahia	28.28	7.30	33.50	21.00	2.00	6.00	18.00	123.00	87.15	0.500	240.11	6.500	12.110
12.	Woji	27.19	5.90	49.30	12.60	3.00	7.00	48.00	127.00	75.80	0.800	150.00	3.200	15.300
13.	Elijiji Woji	26.40	5.81	28.00	20.00	1.00	20.00	38.00	135.00	ND	0.200	50.00	0.310	58.040
14.	Borokiri Sandfill	27.92	6.23	429.30	241.00	35.00	13.5	250.00	196.00	48.00	0.020	113.21	6.300	3.171
15.	Rumuolumeni	27.51	5.90	350.60	122.70	3.00	2.50	115.00	193.00	72.96	0.820	210.32	0.600	30.000
16.	Marine Base	26.83	7.11	560.00	401.00	7.00	11.00	103.50	123.00	22.03	0.000	63.70	13.000	7.110
17.	Reclamation Rd	26.33	6.02	527.00	270.00	8.00	13.00	132.00	124.00	24.70	0.100	25.00	9.311	9.500
18.	Aggrey Rd	27.04	5.83	150.00	255.00	4.00	121.32	401.00	130.00	230.11	0.020	15.60	0.500	15.210
19.	Churchill (Harold Wilson Drive)	28.27	5.31	160.00	218.00	14.00	78.36	390.50	185.00	9.70	0.010	62.10	0.100	20.713
20.	Rumuagholu	29.47	5.44	50.00	25.00	2.00	135.00	12.00	131.00	78.00	0.200	95.30	0.200	8.080
21.	Elelenwo	28.03	5.93	35.00	25.00	3.00	132.10	35.00	192.00	65.10	0.100	26.40	0.500	10.345
22.	Rumuibekwe	28.17	6.01	56.00	59.00	4.00	12.34	38.00	194.00	74.71	0.010	62.10	0.010	11.000
23.	Mgbuoba (Okilton)	26.78	6.82	32.00	39.30	1.00	18.00	19.00	196.00	96.00	0.040	672.75	1.550	13.400
24.	D/Line (Okija Street)	28.51	6.76	49.42	65.60	3.00	48.00	23.00	197.00	ND	0.030	60.24	1.580	10.361
25.	GRA 111(Abacha Rd)	28.02	4.69	36.73	140.54	1.00	4.00	41.00	96.30	80.00	0.051	130.30	2.000	12.712
26.	Mile4(Mkt Junction)	27.30	7.71	30.21	33.60	2.00	13.13	30.80	26.44	70.00	0.400	220.50	5.320	15.170
27.	Orazi	28.03	6.50	74.01	36.00	1.00	12.00	50.51	27.78	78.00	0.210	120.12	0.400	12.121
28.	Rumuigbo	27.22	4.75	33.00	33.00	3.00	10.00	32.00	55.77	191.32	0.090	50.00	0.330	13.100
29.	Diobu (Nanka Street)	28.00	6.83	45.00	35.72	4.00	30.23	16.10	ND	126.00	0.303	10.33	0.624	29.100
30.	UST (New VCs Lodge)	27.11	5.73	250.13	150.10	1.00	19.31	28.00	39.22	100.00	0.400	15.11	0.666	12.000
31.	Onne	28.13	4.28	519.40	381.31	2.00	25.22	215.00	123.22	80.00	0.361	12.00	0.378	12.000
32.	Odili Rd (GTC/Zoo)	27.10	7.00	210.28	211.00	1.00	14.12	28.13	50.00	120.30	0.111	10.00	0.507	12.300
WHO (2004)	LOCATIONS	NS	6.5-8.5	500	500	NS	500	250	NS	250	0.3	NS	50	NS

Chloride (Cl^-): The Chloride ion concentrations from groundwater samples in the study area are generally high and ranges from 12.00 to 710.00mg/l. The highest recorded value of 710.00mg/l is BH 1. The chloride levels in the samples in most of the locations show that the water is not suitable for drinking. A highest desirable level limit of 250mg/l and maximum permissible level of 100mg/l have been recommended by WHO (2004) for this parameter in drinking water. Therefore, the sampled waters are not all safe for drinking and for some industrial processes.

The limit for chloride in drinking water is given primarily for reasons of taste. Chloride in excess of 100mg/l impacts a salty taste on drinking water and can cause physiological damage. The high Chloride concentration in most part of the study area suggests that there has been salt water encroachment into the aquifers at the depths where the water is exploited. Lusczynski & Swarzenski (1966) considered Chloride above 50mg/l as an indication of saltwater intrusion, while Todd (1980) has suggested that Chloride contents greater than 40mg/l in the coastal aquifers indicate saltwater contamination. It is interesting to observe from the results of this study, that 63% of the groundwater samples have Chloride concentrations greater than 40mg/l. Only 37% of the sampled groundwater shows Chloride concentrations below 40mg/l. This portends serious concern and calls for concerted studies.

Table 3: Results of Hydrogeochemical Analyses in the Study Area (Conti.)

S/N (BH)	S_r^{2+} (mg/l)	Ca^{2+} (mg/l)	Na^{+} (mg/l)	Mg^{2+} (mg/l)	K^{+} (mg/l)	PO_4^{3-} (mg/l)	Mn (mg/l)	F^{-} (mg/l)	SiO_2 (mg/l)	Zn^{2+} (mg/l)	Cu^{2+} (mg/l)	Pb (mg/l)	Br^{-} (mg/l)
1	4.00	3.460	2.756	2.222	0.540	0.010	0.002	1.900	2.64	0.21	0.01	0.01	20.00
2	3.90	4.444	3.000	2.981	0.810	0.221	0.041	2.200	4.30	0.30	0.03	0.02	76.10
3	3.80	7.633	1.022	0.826	0.505	0.030	0.033	2.310	0.94	0.60	0.05	0.01	18.30
4	4.50	4.111	0.834	4.500	0.300	0.732	0.780	0.800	0.60	0.33	0.03	0.02	29.11
5	1.99	2.000	0.666	2.757	0.891	0.010	0.101	1.300	5.50	0.03	0.63	0.28	11.00
6	2.00	6.123	3.400	0.445	0.431	0.233	0.011	0.411	4.94	0.48	0.01	0.02	12.50
7	2.40	8.100	1.400	0.233	0.733	0.131	0.004	0.330	5.86	0.30	0.00	0.07	63.50
8	2.11	11.23	1.776	2.080	0.144	0.001	0.001	0.500	6.80	0.36	0.05	0.04	80.30
9	2.33	5.000	1.822	1.000	0.656	0.233	0.041	0.510	6.00	0.15	0.01	0.03	93.01
10	2.50	4.121	0.310	3.221	0.444	0.000	0.033	1.631	1.49	0.30	0.00	0.09	16.13
11	2.70	5.395	0.433	0.310	0.500	0.231	0.003	0.010	5.40	1.30	0.01	0.06	18.00
12	4.10	7.523	1.777	0.277	0.401	0.088	0.334	2.100	3.10	0.26	0.05	0.03	7.90
13	0.91	12.21	2.433	0.823	0.300	0.001	0.100	2.333	4.44	0.52	0.03	0.00	71.00
14	3.99	4.223	2.321	1.789	0.424	0.232	0.230	2.000	0.80	0.15	0.02	0.01	79.70
15	4.00	3.000	1.443	5.677	0.555	0.221	0.727	1.520	4.55	0.14	0.03	0.04	31.72
16	3.78	8.234	2.320	2.111	0.678	0.781	0.030	0.910	6.70	0.43	0.01	0.03	15.00
17	3.21	9.200	1.000	4.577	0.341	0.210	0.004	0.701	9.13	0.21	0.05	0.02	63.31
18	4.37	6.322	2.303	8.900	0.231	0.200	0.003	0.322	5.00	0.77	0.06	0.03	17.93
19	2.52	18.30	1.820	7.000	0.322	0.020	0.010	0.410	0.56	0.28	0.06	0.03	9.34
20	0.92	4.245	2.211	2.821	0.788	0.231	0.782	0.335	0.75	0.21	0.01	0.10	81.33
21	4.30	2.478	0.213	0.332	0.133	0.777	0.605	0.441	0.38	0.36	0.06	0.03	18.22
22	4.22	13.78	0.241	4.300	0.567	0.200	0.200	0.210	4.13	0.18	0.06	0.04	61.00
23	3.72	5.333	1.444	2.781	0.044	0.000	0.210	0.222	9.00	0.15	0.09	0.03	88.33
24	2.33	6.781	2.300	4.000	0.781	0.233	0.002	0.800	2.15	0.65	0.02	0.01	19.20
25	1.01	5.340	1.000	8.721	0.233	0.440	0.033	0.788	10.89	0.70	0.02	0.01	11.90
26	2.30	6.000	3.445	3.010	0.457	0.788	0.450	0.011	4.08	0.45	0.75	1.09	83.00
27	3.77	7.586	2.111	2.111	0.543	0.421	0.333	0.310	2.64	0.43	0.03	0.04	93.00
28	4.10	2.300	0.333	6.200	0.789	0.210	0.210	0.210	60.02	0.35	0.02	0.06	66.00
29	0.93	5.777	2.113	5.833	0.233	0.780	0.200	0.227	2.75	10.09	0.01	0.01	75.76
30	2.00	4.234	0.631	4.050	0.540	0.788	0.021	0.233	0.57	0.40	0.05	0.06	14.00
31	3.78	8.000	1.376	2.341	0.220	0.220	0.030	0.734	0.55	0.24	0.30	0.06	19.78
32	4.00	6.333	0.311	3.000	0.567	0.221	0.456	0.400	0.57	1.0	0.08	0.02	12.75
W	NS	7.5	200	50	200	10	0.1	NS	NS	0.5	0.05	0.1	NS

ND = Not Determined NS = Not Stated, W = WHO

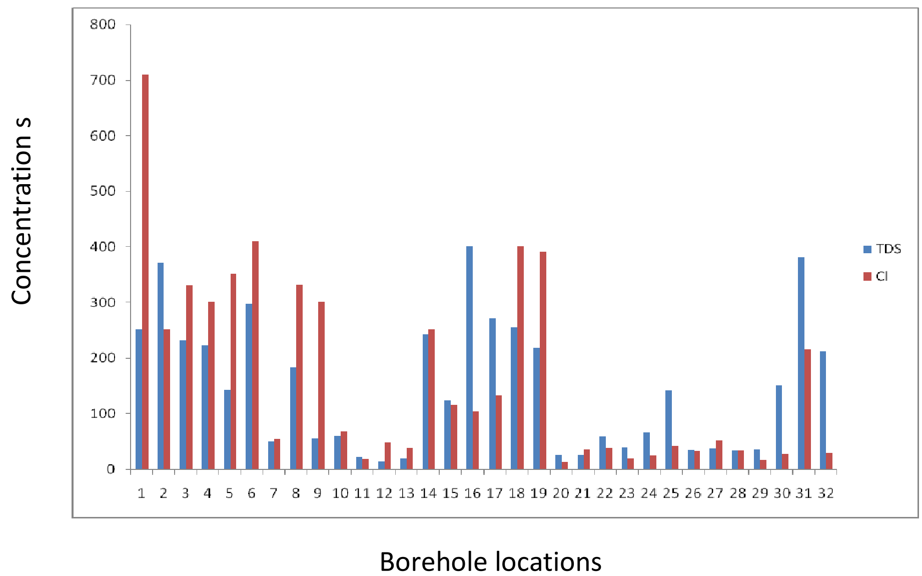

Fig 2: Relationship of TDS/Cl

Table 4 is the statistical summary of the hydrogeochemical parameters while Table 5 shows the range of values compared with the World Health Organization (WHO, 2004) guidelines.

Table 4: Statistical Summary of the Hydrogeochemical Parameters

Parameters	Minimum	Maximum	Mean	WHO 2004	SD
Temp 0C	26.33	29.64	27.67	NS	0.056
pH	3.84	7.72	7.73	6.5 – 8.5	0.44
EC (uS/cm)	28.00	717.40	245.76	500	22.53
TDS(mg/l)	12.60	401.00	145.49	500	10.84
TSS (mg/l)	0.00	14.00	4.63	NS	0.42
Hardness(mg/l)	2.50	142.00	34.31	500	6.71
Cl^- (mg/l)	12.00	710.00	161.49	250	35.27
Eh (Mv)	26.44	197.00	131.68	NS	3.53
SO_4^{2-}(mg/l)	9.70	230.11	68.76	250	9.04
Fe (mg/l)	0.00	1.600	0.26	0.3	0.095
Salinity (mg/l)	10.00	672.75	142.41	NS	35.17
NO^{3-}(mg/l)	0.010	34.000	3.24	50	2.43
HCO_3^-(mg/l)	3.003	58.040	16.68	NS	2.45
Sr^{2+} (mg/l)	0.91	4.370	6.53	NS	0.69
Ca^{2+}(mg/l)	2.300	18.300	3.02	7.5	0.07
Na^+(mg/l)	0.213	3.445	1.58	200	0.17
Mg^{2+}(mg/l)	0.233	8.721	3.16	50	0.22
K^+(mg/l)	0.044	0.891	0.47	200	3.54
PO_4^{3-}(mg/l)	0.001	0.788	0.28	10	0.02
Mn (mg/l)	0.002	0.782	0.19	0.1	0.04
F^-(mg/l)	0.010	2.310	0.85	NS	0.05
SiO_2(mg/l)	0.38	60.02	8.38	NS	3.86
Zn^{2+}(mg/l)	0.03	10.09	0.70	0.5	0.77
Cu^{2+}(mg/l)	0.00	0.75	0.08	0.05	0.05
Pb (mg/l)	0.00	0.28	0.08	0.1	0.01
Br^-(mg/l)	7.90	93.01	43.07	NS	1.31

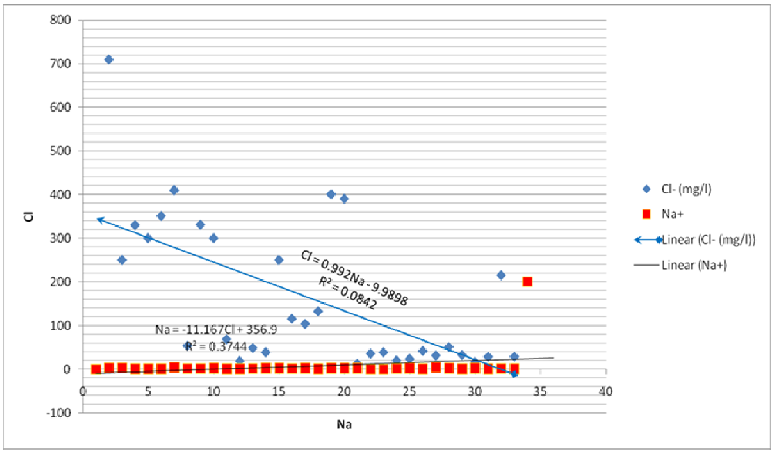

Fig. 5: Relationship between Cl^- and Na^+

Water Types and Classification: Hydrochemical facies are distinct zones having cation and anion concentrations describable within defined compositional categories. The diagonistic chemical character of water solutions in hydrologic systems has been determined with the application of the concept of hydrochemical facies (Back, 1966), which enables a convenient subdivision of water compositions by identifiable categories and reflects the effect of chemical processes occurring between the minerals within the subsurface rock units and the groundwater.

Statistical distribution diagrams, such as Piper and Schoeller are used to gain better insight into the hydrochemical processes operating in the groundwater system. The Piper diagram (1944) in Figure shows the relative concentrations of the different ions from the individual samples based on average values for each location. The Piper trilinear diagram (Fig. 2) was used for the purpose of characterizing the water types present in the area. It permits the cation and anion compositions of many samples to be represented on a single graph in which major groupings or trends in the data can be discerned visually (Freeze and Cherry, 1979).

Piper trilinear diagram for the study area shows that there is a mixture of two types of water with variable concentrations of major ions. These are Ca – Mg – Cl – SO_4 type and Na + K – Cl – SO_4 type water. The second water type is also influenced by NO_3. This means that groundwater in the area is mainly made up of mixtures of earth alkaline and alkaline metals and predominantly Cl^- - SO_4^{2-}water type. Chloride is the dominant anion followed by sulphate. Most of the water samples are made up of mixtures of the two water types.

The chloride and sulphate ions, as revealed in this study, are clearly the dominant anions and so there are practically no bicarbonate waters, as might be expected from the chemistry of the lateral groundwater recharge. Given the influence of the recharge in the aquifer systems of the area, the groundwater generally gives a SO_4/Cl (in meq/l) ratio that is higher than that corresponding to seawater in the sampled water. This reveals that only a part of the sulphate content can be attributed to seawater and that a significant proportion must come from other saline contributions that differentially enrich the water with the sulphate ion. This sulphate enrichment is accompanied by increases in calcium and magnesium, and this suggests a common, non-marine origin for these ions.

Since this is a coastal aquifer subject to marine intrusion, the ion exchange process assumes great significance in the salinized zones and is a very important factor regulating ion concentrations in the groundwater (Howard and Lloyd, 1983). The classic bibliography on ion exchange processes in coastal aquifers (Howard and Lloyd, 1983; Tellam and Lloyd, 1986; Lloyd and Tellam, 1988; Ikeda, 1989) all state that the appearance of Ca-Cl facies in a coastal aquifer reflects the operation of inverse ion exchange, whereas the Na-HCO_3 facies can indicate direct exchange, and the predominance of Ca-Cl or Ca-Cl, SO_4 facies over much of the aquifer clearly indicates the existence of inverse ion exchange.

The Schoeller semi-logarithmic plots of the data further confirmed this water type (Fig.3). The peaks indicate the dominant ions in the water samples while the trough indicates the less dominant ions. In this study, the dominant ions are Cl^-, Na with Ca^{2+} and HCO_3^- ions following. Generally, within the evolutionary trend, groundwater tends to acquire chemical compositions similar to that of seawater (that is more dissolved and relative increase in chloride ion) the longer it remains underground and the further it travels

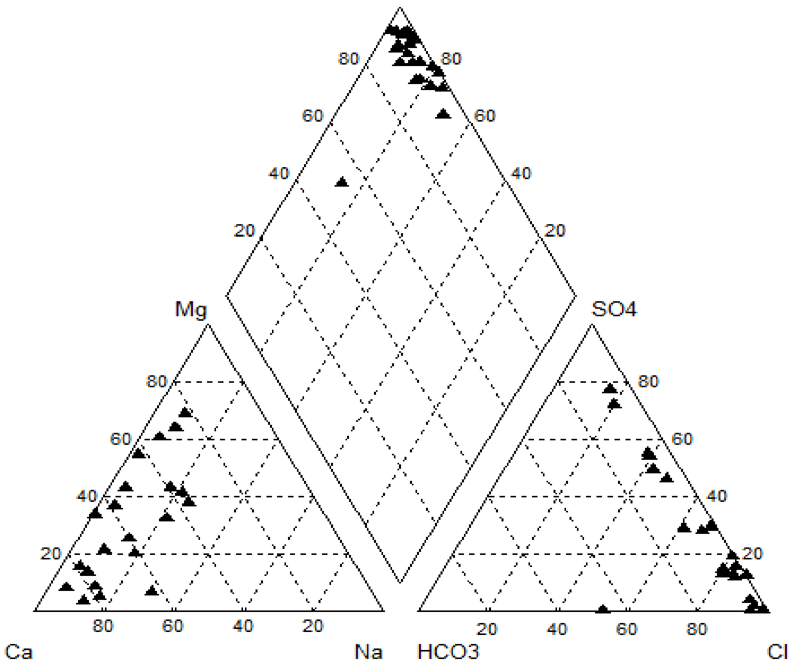

Fig. 2: Piper Trilinear Diagram of Groundwater Characterization in the Area

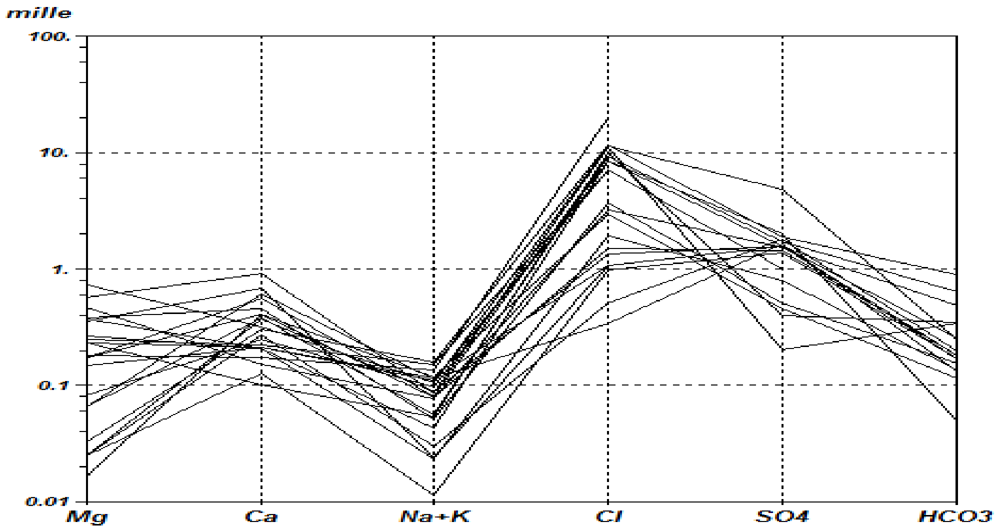

Fig. 3: Schoeller Diagram of Major Ionic Species

Microbial Abundance: The interpretation of the results of the groundwater quality studies must take into account the fact that the presence of a few pathogenic microorganisms (disease causing organisms) in water is more significant than that of many saprophytic bacteria (microbes that obtain food by absorbing dissolved organic matter). This is of course because of the human health implications. In fact, the World Health Organization (WHO, 2004) guidelines stipulated that all water intended for drinking must have zero coliform (Escherichia Coli, Salmonella species, Shigella species, etc) count in any 100ml sample of water. Generally, however, water of good quality is expected to give a low coliform count – less than 100 per ml (Pelczar et al., 1993).

Total coliform refers to a group of bacteria used to indicate the potential presence of harmful bacteria in water resulting from human and animal wastes. Bacteria standards (Coliform results) are reported as Colony Forming Units (CFU) of Total Coliform bacteria counted in 100 millilitres of water submitted. Tests for Faecal Coliforms provide a direct means of measuring human and animal waste inputs.

Of the groundwater samples analysed for microbial content, only four (4) locations have no coliform in them. The total coliform in the studied groundwater data in the area ranges from 0 – 260 cfu/ml. Maximum coliform counts (260cfu/ml) is found in BH29 (Diobu -Nanka Street). BH 24 (D/Line – Okija Street), BH 26 (Mile 4) and BH 15 (Rumuolumeni) recorded 138cfu/ml, 128cfu/ml, and 83cfu/ml, respectively. Coliform counts of groundwater in these areas exceed the WHO (2004) guide value of 0 cfu/ml and are generally unsafe for drinking. The source of this high coliform concentration is generally due to faecal contamination from nearby soak-away pits and this poses high risk of Cholera and stomach disorder upon consumption.

Generally, the presence of coliform in majority of the groundwater samples in the study area indicates pollution from sewage and pit latrines.

Groundwater Use and Vulnerabilty in the Area: Port Harcourt, the capital of the oil rich Rivers State is one of the coastal cities in the southern part of Nigeria. Population and economic activity in the area is increasing, as is the development of more intensive industrial sector. These activities, and the realization that surface water provides an unreliable supply means that groundwater will be in increasing demand.

Following the population explosion in the area in recent times as a result of oil exploration and production activities, there is continuous increase in demand for fresh groundwater, the major source of urban water supply for domestic and industrial uses. The increased rate of groundwater abstraction may pose severe pressure on groundwater resources. This is a very serious issue as almost every home in the city has a well. Added to this is the fact that most of the companies that generate chemical effluents discharge their waste directly into the sea or creeks, without regard to the effects of these effluents on coastal aquifers that surround the area.

The result of this study indicates that salt water intrusion as well as elevated iron and manganese are serious problems facing groundwater resource in the area. Also, the various ionic ratios indicate that secondary salinization is affecting the shallow groundwater as a consequence of rising water tables. This salinity source represents another potential threat to the underlying groundwater in the city.

The shallow sandy aquifers that underlie the area could be protected from the intrusion of seawater by controlled pumping of boreholes. However, little may be done at the present to control effectively the excessive pumping of groundwater in the area due to the continuous influx of people in search of better and improved living conditions associated with the huge oil and gas exploration and production activities.

Conclusion: Hydrochemical study show that groundwater in Port Harcourt City is fresh water but mostly acidic and will need to be treated to lower its acidity. The low pH of the water makes its use unsuitable, especially for household drinking purposes but it can be treated with little lime by users before usage. It is recommended that further monitoring of boreholes in the area be carried out to fully ascertain the cause(s) of the low pH. Besides of the major chemical compositions, ionic ratio (HCO_3/Cl, Na/Ca, Ca/Cl, Mg/Cl and Ca/SO_4) was used to delineate saline water intrusion. Iron and Manganese concentrations are above the World Health Organization (2004) guide value in majority of the boreholes studied, with maximum value up to 1.60mg/l in Abuloma area. Constituents of the heavy metals as shown in this study reveal that, in some locations, values are slightly higher than the permissible levels. Microbial analysis of the water samples to determine the presumptive coliform count of the water indicates the presence of coliform bacteria in majority of the analysed samples, indicating anthropogenic contamination of groundwater.

REFERENCES

Abimbola, AF; Odukoya, AM and Olatunji, AS (2002). Influence of bedrock on the hydrogeochemical characteristics of groundwater in Northern part of Ibadan metropolis, SW Nigeria. *Water Resources Journal*, Vol. 9, pp1-6.

Amadi, PA; Ofoegbu, CO & Morrison, T (1989). Hydrogeochemical Assessment of Groundwater Quality in parts of the Niger Delta, Nigeria. *Environmental Geol. Water Science*, Vol.14, No.3, pp 195 – 202.

Amajor, LC (1986). Geochemical Characteristics of Groundwater in Port Harcourt and its Environs. Proc. Int'l Symp. on Groundwater Resources of Nigeria, Lagos, pp 358 – 375.

American Public Health Association (APHA) (1989). Standard Methods for Examination of water and wastewater, 17th Edition: Washington DC, American Public Health Association.

American Society Testing Materials (1969). Manual on Water, 14th Edition. Hamilton D.E., Philadephia, pp171 -227

Back, W (1966). Hydrochemical facies and groundwater flow patterns in northern part of Atlantic Coastal Plain:US Geological Survey Professional Paper 498 – A, 42p

Edmunds, WM and Carrillo-Rivera, C (2002). Geochemical evolution of groundwater beneath Mexico City. J Hydrol. 258:1-24.

Freeze, RA and Cherry, JA (1979). Groundwater. Prentice-Hall Inc. Englewood Cliffs, NJ.

Howard, KWF and Lloyd, JW (1983). Major ion characterization of coastal saline groundwaters. Groundwater 21 (4):429-437

Ikeda,K (1989). Chemical evolution of groundwater quality in the southern foot of Mount Fuji. Bull Geol Surv Japan 40 (7):331- 404

Lloyd, JW and Tellam, JH (1988). Caraterizacion hidroquimica de las agues subterraneas en areas costeras (Hydrochemical characterization of groundwater in coastal areas). Proceedings of International Symposium TIAC'88 (Tecnologia de la Intrusion marina en Acuiferos Costeros), Vol 1, Almunnecar, Granada, Spain, June 1988, pp1-8

Luscznski, NJ and Swarzenski, WV (1966). Saltwater Encroachment in Southern Nassau and SE Queens County, Long Island, U.S Geological Survey Professional Paper 1613-F

Nwankwoala, HO; Okeke, EV & Okereke, SC (2007). Groundwater quality in parts of Port Harcourt, Nigeria: An overview, trends and concerns. *International Journal of Biotechnology and Allied Sciences*, Vol.2(3), pp 282 – 289.

Olatunji, AS., Abimbola, AF., Oloruntola, MO & Odewade, AA (2005). Hydrogeochemical evaluation of groundwater resources in shallow coastal aquifers around Ikorodu area, Southwestern Nigeria. *Water Resources,* Vol.16:65-71.

Olatunji, AS; Tijani, MN; Abimbola, AF and Oteri, AU (2001). Hydrogeochemical evaluation of water resources of Oke-Agbe Akoko, SW Nigeria. *Water Resources Journal*, Vol.12, pp 81-87.

Piper, AM (1944). A graphical interpretation of water analysis. Transactions of the American Geophysical Union, Vol.25, pp914 -928

Reijers, TJA (1996). Selected Chapters on Geology, Sedimentary Geology, Sequence Stratigraphy. Three Case Studies: A Field Guide. SPDC Reprographic Services, Warri, Nigeria, 197p.

Telford, WM; Geldert, LP; Ssherriff, RW; and Keys, PA (1976). Applied Geophysics, Cambridge University Press, London, 632p.

Tellam, JH and Lloyd, JW (1986). Problems in the recognition of seawater intrusion by chemical means: an example of apparent chemical equivalence. Q J Eng Geol 19:389-398

Tijani, MN (1994). Hydrogeochemical Assessment of Groundwater in Moro Area, Kwara State, Nigeria. Environmental Geology, 24(3):194-202.

Todd, DK (1980). Groundwater Hydrology, 2nd Edition. John Willey and Sons Inc., New York, pp267 – 315.

Udom, GJ, Etu-Efeotor, JO and Ekwere, SJ (1998). Quality Status of Groundwater in Calabar Municipality, Southeastern Nigeria. Global Journal of Pure and Applied Sciences, 4(2):163 – 169.

Udom, GJ, Etu-Efeotor, JO and Esu, EO (1999).Hydrochemical evaluation of groundwater in parts of Port Harcourt and Tai-Eleme Local Government Area, Rivers State., Global Journal of Pure and Applied Sciences, Vol.5,pp546-552.

Udom, GJ., Ushie, FA., and Esu, EO (2002).A geochemical survey of groundwater in Khana and Gokana Local Government Areas of Rivers State, Nigeria J. Appl. Sci.& Environ. Mgt., Vol.1,pp51-59.

World Health Organization (WHO) (2004). Guidelines for Drinking Water Quality: Incorporating 1st and 2nd Agenda, Vol. 1. Recommendations, Geneva.