Hydrogeochemical Assessment of Shallow Borehole Water Quality across Yenagoa, Bayelsa state, Niger Delta, Nigeria

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Abstract- The increasing dependence on shallow boreholes for potable water in Yenagoa and its environs necessitated a detailed investigation into the potential health implications associated with their use. This study integrates geological, and chemical analyses to evaluate groundwater quality. A total of nineteen groundwater samples were collected from both existing and freshly drilled boreholes and analyzed for physico-chemical parameters. Results revealed elevated levels of dissolved iron in boreholes capped by impermeable clay layers, likely due to anoxic conditions inhibiting oxygen infiltration. Conversely, boreholes without such confinement showed low iron concentrations. The groundwater was found to be fresh and mildly acidic, with pH values ranging from 5.78 to 6.93. Total hardness averaged 80.3 mg/L, well below the WHO permissible limit. Total dissolved solids (TDS) were also largely within safe limits, with 90% of samples below 1520 mg/L. Major cations and anions including Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, NO_3^-, SO_4^{2-}, and Cl^- remained within WHO standards. Hydrogeochemical facies analysis identified Na-HCO_3 and Ca-Cl as dominant water types. Multivariate and graphical analyses suggest that the water chemistry is influenced primarily by rock-water interaction, silicate mineral weathering, and oxidation of pyrite. The dominance of alkali metals over alkaline earth metals and the abundance of weak acids over strong acids further support this. Overall, the groundwater in Yenagoa and surrounding areas is considered suitable for consumption and other uses, with caution regarding iron level in some areas.

Indexed Terms- Groundwater Quality, Hydrogeo Chemistry, Shallow Boreholes, Rock-Water Interaction, Yenagoa Aquifer System

I. INTRODUCTION

Background to the study Clean water is an indispensable necessity of life and plays a fundamental role in the socio – economic growth of any nation. In the City of Yenagoa and environs, in Southern Nigeria, clean water is often a scarce commodity because there is no municipal water supply. The lack of municipal water supply accounts for why water borne diseases occur and sometimes to epidermic scale (Dawoud and Raouf 2009), compelling residence in the area to look for alternative sources of water such as streams and boreholes. Unfortunately noxious compounds and elements are on daily basis being discharged through leachates and effluent into the surface waters (Rivers, streams and lakes). More so, large-scale pollution from petroleum spills by the international companies and artisan refinery have rendered surface waters unusable. As a result, the groundwater of the quaternary shallow alluvial aquifer is the most important alternative source and it is been exploited widely in the area under study. The quality of shallow groundwater is affected by the characteristics of the media through which the water passes on its way to the groundwater zones of saturation (Raji and Alagbe, 1997). The mineralogical composition of the underlying rocks and secondary products such as clay are significant factors in this process. Consequently, shallow ground waters are mostly characterized by pollutant elements, and in the presence of secondary products by base exchanged reactions leading to dominance of normally subordinate cations. The quaternary sediments consist mainly sand, interspersed with clay, pyrite, marcasite etc. Okiongbo and Douglas (2013) reported that over 90% of private boreholes in the study area have elevated concentration of iron (> 0.3 mg/L). While Fe is essential for both plants and animal forms 2 (Hem,

1989), its presence in excessive amounts can result in metallic tasting water, staining of clothes and dishes . According to the report of Brown et al.,(1992), a high concentration of dissolved Fe (> 0.5 mg/L) in the groundwater can lead to reduction in water pressure and flow in pipes due to accumulation of Fe oxides, for which treatment and remediation are difficult and costly (Siegel et al., 1992). Additionally, high concentration of Fe is also considered harmful to human health if such water is consumed for a long time (Liap, 1992). According to the report by Rehema et al., (1998), exposure to long term alimentary iron overload can cause a positive serum iron (Fe) balance, which in turn , results in an increased oxidative stress . For individuals who suffer Fe storage diseases such as hemochromatosis, consumption of groundwater with Fe concentration of up to 2-3 mg/L in drinking water might pose a problem (Donohue et al., 2004; Franchini and Veneri, 2005). Since most of these private boreholes derive their water from shallow quaternary aquifers, the examination and determination of their chemical composition becomes very important for a proper understanding of potential health hazards that might result from continuous drinking of such contaminated water. Majority of the boreholes are less than 30 m deep, drilling is done manually, over 85% of households in Yenagoa depend either entirely on groundwater for domestic use or other purposes. A consideration of the widespread use of shallow boreholes in Yenagoa and environs, and an appreciation of the likelihood of health hazards they might pose has led to the present investigation involving geological, geoelectrical and hydrogeochemical studies. Nineteen (19) ground water samples were collected from existing and freshly drilled. boreholes for physiochemical test.

II. DESCRIPTION OF THE STUDY AREA

The study area lies between longitudes 0060 05'and 0060 040' East of the prime meridian and latitudes 040 23.3' and 040 38.2' North of the equator within the coastal region of the recent Niger Delta. It has an areal extent of about 100 km2 and has a tropical rain forest climate with two distinct seasons: wet (April- October) and dry (November – March). Akpokodje (1986) reported that mean annual rainfall is around 4500 mm with about 85% within the wet season serving as major source of the groundwater recharge. There are a

number of perennial streams, oxbow lakes and rivers in the area,(e.g Kolo Creek, Epie Creek, Yenagoa and Nun river etc.).They all form a network which empties to the atlantic ocean through Nun River Estuary. This area mostly is submerged during the wet season where flood waters range from 0.5 to 4 m deep (Akpokodje, 1986).
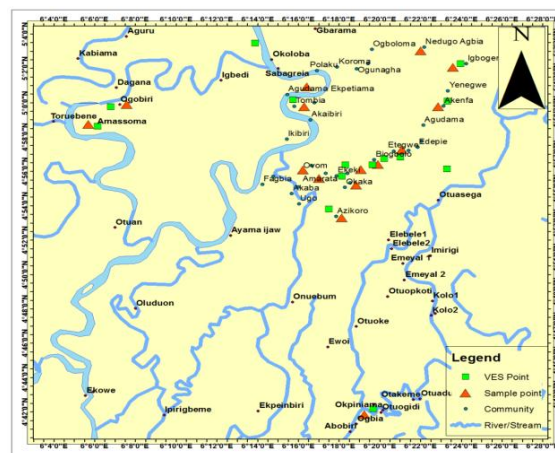

Fig 1.0 Map showing the study area

2.2 Geological Setting

The regional geology of the Niger Delta was obtained from the published works of Reyment (I965); Short and Stauble, (1967); Merk, (1970). The configuration of the Pro-to Niger Delta occurred during the second depositional sequence (Campanian-Maastrichtian) of the southern Nigerian basin. Meanwhile, the present Niger Delta was shaped during the third and last depositional sequence of the Southern Nigeria basin which started in the late Paleocene. The geology of the Niger Delta consist primarily of three lithostratigraphic units, which are overlain by the quaternary deposits. These quaternary deposits are considered generally to be the recent expressions of the Benin formation and consist of medium to coarse grained sands, sandy clays, silts and subordinate, lenstoid clay bands thought to have been deposited during quaternary interglacial marine transgressions (Durotoye 1989). It was also reported by Amajor (1991) that these sediment are an admixture of fluvial/tidal channel, tidal flats and mangrove swamp deposits. The sands are micaceous and feldspathic subrounded to angular in texture and constitute very good aquifers. However, depth to occurrence and

thickness is irregular and may not be predicted with accuracy within the study area due to rapid horizontal and vertical facie changes. The three lithostratigraphic units are: Benin Formation (Top), Oligocene to Recent, Agbada Formation (Eocene), and the Akata Formation.

2.2.1 Benin Formation

This is the topmost lithostratigraphic unit, which consist primarily of about 90% sands and few shale intercalations. Shale content increases towards the base, while sand and sandstones are coarse to fine grains, poorly sorted, typically unconsolidated and regularly sub angular to well rounded texture in shape. The colour of the sand and sandstones are white to yellowish brown because of the present of limonite coats. According to report from Onyeagocha (1980), rocks of this formation are made up of about 95-99% quartz grains, Na +K –Mica 1-2.5%, feldspar 0-1.0% and dark colored minerals 2.3%.These minerals are loosely bound by calcite and silica cement. The presence of clayey intercalations have given rise to multi-aquifer systems in the area. The Benin Formation was deposited in continentalfluviatile environment and back swamp deposits and the age of this Formation is given as Oligocene to Recent by Reyment (1965). This Formation is massively exploited for sand and ground water. The upper section of the Benin Formation is the quaternary deposits which is about 40-150m thick and comprise of sand and silt/clay with the later becoming increasingly more prominent seawards, Merki (1970). It consists of primarily freshwatercontinental friable sands and gravel that have exceptional aquifer properties with irregular intercalations of clay stone /shales.

2.2.2 Agbada Formation

Chronologically, the Agbada Formation is late Eocene to Recent as reported by Reyment (1965).
This Formation underlies the Benin Formation, with thickness of 300 to 4500 m (Short and Stauble 1967). It consists mainly of an intercalation of sand, sandstone and siltstone. It is broadly, divided into two sections, the upper and the lower units. The upper unit of this formation consist of an intercalation of sandstone and shale, predominantly sandstone, the lower unit is mostly of shale, which in some areas are thicker than that of the upper unit. This Formation was deposited in paralic, brackish to marine fluviatile, coastal and fluio- marine environment. This Formation serves as the core reservoir in the Niger Delta Petroleum system.

2.2.3 Akata Formation

The Akata Formation underlies the Agbada Formation. It was deposited in a typically marine environment with maximum thickness of about 6,000 m (Ofoegbu 1985). Chronologically, the age of this formation is late Paleocene to Recent. It is composed mainly of marine shale but consists of silt, turbidite sands and silt forming sinuous lenses which are thought to have been laid down as turbidite and continental slope channel fills. Based on organic matter content, type and maturity, both marine shale Akata and the shale interbedded within the Agbada Formation are the source rocks of the Niger Delta Petroleum System

2.3 Hydrogeology

The Benin Formation which is fluvial in origin is the main aquifer in the study area. Groundwater in this formation occurs mainly under unconfined conditions. Abam (1999) reported that the sediments of the Benin Formation were deposited during the late Tertiary-Early Quaternary period and is about 2100 m thick. The sediments are lenticular and unconsolidated and consists of coarse to medium – fine grained sands with localized intercalations of clay/shale. Gravel and pebbles are minor components. Mbonu et al., (1991) reported that the sands are moderately sorted and poorly cemented. The presence of thin clay beds creates discontinuities in the vertical and lateral 10 continuity of the aquifer, resulting in the presence of local perched aquifer (Amajor,1991). The aquifer is directly recharged through the infiltration of rainwater. Also the water table in many areas of the Niger Delta is close to the surface but subject to seasonal variations .In the dry season, the water table is about 3- 4 m in the study area (Ekine and Osobonye, 1996). During the rainy season, the water table rises considerably, in some cases; the surface of the ground is flooded.
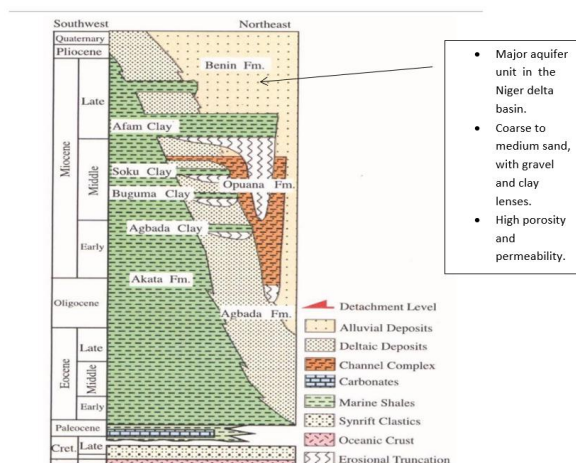
Fig 2.0 Depositional Sequence in The Niger Delta Basin after (Lawrence et al., 2002).

III. MATERIALS AND METHOD

3.1 Groundwater Sampling and Hydrogeochemical Analysis

Thirteen drilled boreholes (Table 2) were developed and groundwater samples were collected in clean 500 ml polyethylene bottles. The boreholes were handed over to the villagers soon after collecting the groundwater samples. Groundwater samples were also collected from six pre-existing boreholes in which aquifer sand color was known making a total of Nineteen groundwater samples. A global positioning system (GPS) was used for location and elevation reading. Prior to sample collection, the boreholes were pumped continuously for about 20 minutes. In these groundwater samples, in situ measurements of temperature, redox potential (Eh) and pH were carried out using precalibrated portable pH/ORP meter at the time of groundwater sampling. Major ions such as Na, K, Ca, Mg, Fe, HCO3, Cl, and SO4 were determined including total dissolved solids (TDS) in the laboratory using standard procedure. Major ions like sulphate (SO) were determined by spectrophotometric turbidimetry. Using EDTA, calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined titrimetrically; chloride (Cl^-) was determined by standard $AgNO_3$ titration and bicarbonate (HCO) was determined using titration with HCl. Sodium (Na^+) and potassium (K^+) was measured using flame photometry; nitrate (NO) was determined by colourimetry with a UV-visible spectrophotometer (brucine method) while iron was measured using colourimeter with a UV-visible spectrophotometer at 520 nm. The quality of the data was evaluated by computing the charge balance error (CBE),which is calculated by comparing the sum of the equivalents of the cations with the sum of the equivalent of the anions. If result is positive, it means that either an excess of cation or insufficient anion exists. while a negative result reflect the opposite. Charge balance error of 5% difference was confirmed and recorded, suggesting that HCO3 anion must have precipitated as calcite as when CO_2 escaped from the sample bottle owing to delay in laboratory analysis.

IV. RESULT

Table 1 Aquifer lithology, sediment colour, sediment iron (Fe) and groundwater iron conc

Borehole No	Screen Depth(m)	Aquifer Lithology	Aquifer Sediment Colour	pH	Redox Potential (mV)	Sediment Fe conc. (mg/L)	Ground Water Fe conc. (mg/L)
B-1	15.2	Fine-medium sand	Grey	6.3	118	0.75	12.6
B-2	30	Fine-medium sand	Grey	6.3	125	0.26	4.50
B-16	21	Fine-medium sand	Grey	6.2	128	0.30	0.86
B-9	12	Fine-medium sand	Off white	6.8	120	0.9	0.50
B-10	18	Fine-medium sand	Off white	5.6	126	0.79	4.80
B-6	8.0	Fine-medium sand	Brown	6.5	164	0.50	0.16
B-13	27.0	Fine-medium sand	Brown	6.0	157	0.75	0.14
B-15	24.0	Fine-medium sand	Brown	6.4	148	0.62	0.26
B-14	20.0	Fine-medium sand	Brown	6.4	115	0.59	0.29
B-7	15.0	Fine-medium sand	Brown	6.3	178	0.82	0.18
B-4	12.0	Fine-medium sand	Brown	6.4	163	n.d	0.02
B-5	12.0	Fine-medium sand	Brown	6.6	158	n.d	0.18

n.d is not determined..

Table2. Hydro geochemical Analysis of Groundwater Samples in Yenagoa and Its Environs.

S/N	Sample Location	Code	Ph	EC	TDS	TA	TH	Na⁺	K⁺	Ca⁺²	Mg³⁺	Fe	Cl -	SO₄⁻²	NO₃⁻²	HCO₃
1	Agudama Epie,Majors.	BW1	6.04	304	1520	70	290	95.4	48.88	70	15.6	0.65	88.4	5.2	0.31	382.2
2	Akenfa 3,NT.	BW2	6.16	338	169	15	48	14.2	6.8	2.4	0.5	0.02	2.85	0.5	0.11	50
3	Akenfa 3,T.	BW3	5.78	615	308	26	25	28.4	16.5	4	0.8	0.01	4.82	4.2	0.08	48.09
4	Agudama Ekpetiama NT.	BW4	6.38	708	354	30	48	28.4	9.5	6.75	3.4	0.12	17.3	2.8	0.03	77.41
5	Agbia Sprk. NT	BW5	6.2	2620	1310	48	254	60.4	28.5	36.4	8.5	0.02	81.95	5.65	0.13	163.85
6	Azikoro, Austine, NT	BW6	6.24	800	400	28	40	14.5	8.65	5.6	3.5	0.25	11.3	0.85	0.16	48.56
7	Igbogene,TownHall, NT	BW7	5.8	1091	546	33	120	42.2	17.6	5.5	2.3	0.18	21.2	4	0.09	118.22
8	OKaka,Housing Est,NT	BW8	6.25	963	482	22	98	19.96	10.3	8.5	2.6	0.18	9.5	2.6	0.15	56.3
9	Nedugo,Mrs Kate,NT	BW9	5.87	1098	549	40	48	15.4	9.75	10.7	6.2	0.31	21.60	10.6	0.11	38.37
10	Kpansia,NT.	BW10	6.34	2820	1410	65	265	48.7	15.2	20.92	6.85	0.18	39.09	6.48	0.42	146.1
11	Hon,Obedient, Kpansia,T	BW11	6.05	654	327	44	30	25.6	14.4	5.2	2.24	0.15	17	0.42	0.15	76.31
12	Ovom-Gwegwe NT	BW12	6.88	792	396	30	68	18.75	8.2	8	1.8	0.18	8.35	5.4	0.15	81.44
13	NDU Compus,NT	BW13	6.18	495	248	18	42	13.75	6.5	3.5	1.77	0.86	14.2	4.7	0.6	26.96
14	Amarata,Forcados.NT	BW14	6.7	591	296	26	24	7.8	12	5.7	4.2	0.2	5.3	3.3	0.28	43.6
15	Water Board, Ekeki.T	BW15	6.31	418	209	30	15	12.2	10.5	6.74	3.46	0.25	16	0.54	0.09	41.3
16	CHS,NDU.	BW16	6.93	593	297	10	15	6.4	7.4	2.8	6.9	12.1	1.5	0.54	3.7	34.28
17	Dr Christine's Premises	BW17	6.02	230	115	25	35	6.34	2	10.68	2.27	0.48	15	3.68	0.684	2
18	Reward's Compound,Igb	BW18	5.95	79	39.5	11	15	5.46	2.16	10.4	2.76	0.32	19	0.54	0.246	1
19	Akenfa 11.	BW19	5.91	228	114	18	38	5.63	2.44	12.83	3.18	0.42	22	0.75	0.317	1

All parameters have been expressed as mg/L, except pH and EC. The unit of EC is µs/cm

Table 3 Descriptive Statistics of Analyzed Groundwater Compared with WHO standard.

Parameter	Min	Max	Mean	S.D	Accept Limit	Max Limite	WHO Limit
		Range of samples			ISI standards		
PH	5.78	6.93	6.21	0.334	7.0 - 8.5	6.5 - 9.2	8.0 - 8.5
EC (µS/ cm)	79	2820	812	554.3	-	-	-
TDS (mg/L)	39.5	1520	478.4	932.5	500	1500	500
TA (mg/L)	10	70	31	15.95	200	600	-
TH (mg/L)	15	290	80.3	83.79	200	600	100
Na $^+$(mg/L)	5.46	95.4	25	23.41	50	-	-
K $^+$(mg/L)	2	48.88	12.1	10.53	-	-	-
Ca $^{2+}$(mg/L)	2.4	70	12.5	16.33	75	200	75
Mg $^{2+}$(mg/L)	0.5	15.45	4.14	3.39	200	400	50
Fe (mg/L)	0.01	12.1	0.88	2.64	-	-	-
Cl (mg/L)	2.85	88.4	23	22.7	200	1000	200
SO $_4^{2-}$ (mg/L)	0.42	10.6	3.5	3.2	200	400	200
HCO $_3$(mg/L)	1	382.2	75.63	81.7	-	-	-
NO $_3$-(mg/L)	0.08	3.7	0.423	0.813	-	-	-

WHO Limit- World Health Organisation (WHO).(2004).

Table 4. Pearson Correlation Coefficient Matrix for the various Hydro- geochemical Parameters of the Investigated Groundwater Samples

Sample	pH	EC	TDS	TA	TH	Na	K	Ca	Mg	Fe	Cl	SO$_4$	NO$_3$	HCO$_3$
PH	1.000													
EC	0.218	1.000												
TDS	0.277	0.638	1.000											
TA	0.529	0.504	0.798	1.000										
TH	0.224	0.600'	0.933	0.686	1.000									
Na	0.393	0.792	0.792	0.719	0.795	1.000								
K	0.436	0.178	0.665	0.671	0.592	0.889	1.000							
Ca	0.146	0.716	0.675	0.501	0.615	0.789	0.828	1.000						
Mg	0.065	0.512	0.512	0.721	0.221	0.413	0.411	0.761	1.000					
Fe	0.007	0.037	0.018	0.003	0.023	-0.612	-0.812	-0.5	0.017	1.00				
Cl	0.235	0.703	0.703	0.531	0.627	0.786	0.805	0.868	0.423	-0.5	1.000			
SO$_4$'	0.174	0.237	0.208	0.142	0.164	0.138	0.124	0.109	0.188	0.108	0.189	1.000		
NO$_3$	0.005	0.099	0.062	0.007	0.084	0.005	0.001	0.005	0.012	0.846	0.00'	0.077	1.000	
HCO$_3$	0.253	0.194	0.753	0.56	0.759	0.934	0.869	0.865	0.633	0.04	0.739	0.083	0.016	1.000

Table 5 Nature of Groundwater Based on TDS

TDS (Mg/L)	Nature of water	Bore holes	Total No. BH
< 1000	Fresh water	2-4, 6-9, 11-19	16
1000 - 10, 000	Brackish water	1, 5, and 10	3
10, 000 - 100, 000	Saline water	Nil	0
> 100, 000	Brine water	Nil	0

Table 6 Classification of Groundwater based on Hardness

Total hardness (Mg/L)	Water class	Bore holes	Total No. BH
	Very soft	2-4, 6	4
< 75	Soft	8, 9, 11-19	11
75 – 150	Moderately hard	7	1
150 – 300	Hard	1, 5, 10	3
> 300	very hard	Nil	0

Table 7 Quality of Irrigation water based on Electrical Conductivity.

EC (µ/cm)	Water class	Bore holes	Total No. boreholes
< 250	Excellent	17, 18 and 19	3
250 – 750	Good	1, 2, 3, 4, 11, 13, 14, 15, 16	9
750 – 2000	Permissible	6, 7, 8, 9, 12	5
2000 – 3000	Doubtful	5, 10	2
> 3000	Unsuitable	Nil	0

Table 8 Alkalinity Hazard classes of Groundwater.

SAR	Alkalinity Hazard	water class bore hole	Total No. of boreholes
< 10	S1	Excellent	19
10-18	S2	Good	Nil
18-26	S3	Doubtful	Nil
> 26	S4	Unsuitable	Nil

Table 9 Calculated ratio of SO4/Cl

Sample code	TDS	Na	Ca	Cl-	HCO3	Na/Na+Ca$_2$	Cl/(Cl+HCO$_3$)	SO$_4$	SO$_4$/Cl-
BW1	1520	95.4	70	88.4	382.2	0.577	0.1878	5.2	0.059
BW2	169	14.2	2.4	2.85	50	0.855	0.054	0.5	0.18
BW3	308	28.4	4	4.82	48.09	0.877	0.0911	4.2	0.87
BW4	354	28.4	6.75	17.3	77.41	0.808	0.1827	2.8	0.62
BW5	1310	60.4	36.4	81.95	163.85	0.620	0.3334	5.65	0.069
BW6	400	14.5	5.6	11.3	48.57	0.697	0.1809	0.85	0.075
BW7	546	42.2	5.5	7.2	118.22	0.885	0.1521	4	0.6
BW8	482	19.96	8.5	17.5	56.3	0.701	0.2371	8.5	0.5
BW9	549	15.4	10.7	21.6	38.37	0.575	0.3601	10.6	0.5
BW10	1410	48.7	20.92	39.09	146.1	0.700	0.1625	6.48	0.66
BW11	327	25.6	5.2	17	76.31	0.831	0.1822	0.42	0.023
BW12	396	18.75	8	8.35	81.44	0.700	0.0931	5.4	0.65
BW13	248	13.75	3.5	14.2	26.96	0.797	0.345	4.7	0.33
BW14	296	7.8	5.7	5.3	43.6	0.578	0.1084	3.3	0.94
BW15	209	12.2	6.74	16	41.3	0.644	0.7881	5.44	0.68
BW16	297	6.4	2.8	15	34.28	0.696	0.3058	0.54	0.04
BW17	115	6.34	10.68	5	2	0.373	0.8823	3.68	0.73
BW18	39.5	5.46	10.4	19	1	0.344	0.95	0.54	0.03
BW19	114	5.63	12.83	22	1	0.305	0.957	0.75	0.034

V.   DISCUSSION

5.1 Hydro-geochemical Evaluation Of The Results

.5.1.1 Groundwater Chemistry

Table 2 and Table 3, display the physiochemical composition of the groundwater samples and the descriptive statistical measures of the minimum, maximum mean and the standard deviation of the various parameter investigated and analyzed along with the World Health Organization Standards (WHO 2004). From the groundwater sample in the study area, the pH values ranges from (5.78-6.93) with a mean value of 6.21 which is less than the stipulated WHO pH acceptance range of 6.5-8.5 for portable water (WHO,2004). Decrease in pH according to the report

of Krishnaraj et al., (2011), is primarily due to oxidation of organic matter and anthropogenic activities. The slightly acidic nature of groundwater in the Niger Delta has been attributed partly to gas flaring (Nwankwola and Udom, 2011). The flaring of gas in the region releases carbon dioxide which reacts with the precipitation from the atmosphere to yield carbonic acid, this in turn infiltrates into the ground water system to reduce the pH of the water, thereby increasing acidity. Aside, mild acidity in the groundwater can also be attributed to organic acids resulting from the disintegration of Vegetation in swampy environments (Davidson,1995). This is however, natural acidification through Co_2 production and root respiration in the soil of such environment. Electrical conductivity (EC) of the groundwater samples ranges between 79.0 -2820 µs/cm, with an average value of 812µs/cm. EC is used to measure the salinity, which greatly affects the taste of the water and hence users acceptance of its quality for drinking according to Langenegger (1990). In the study area, only two samples, Agbia sprk, and Kpansia exceeded the maximum permissible limit of 1500µs/cm,WHO (2004).The concentration of TDS ranges from 39.5 to 1520 mg/L with an average value of 478.4mg/L. The TDS classification in (Table 5), revealed that more than 90% of the groundwater samples belong to fresh water type (TDS < 1,000mg/L) and the remaining 10% represent brackish water (TDS > 1,000mg/L). Total alkalinity ranges from 10 to 70mg/L with a meanvalue of 31mg/L. The mean concentration of the total alkalinity in all the samples were within the maximum permissible limit (Table 8), suggesting that the water is suitable for domestic use and drinking. Aside that, all the samples investigated fall within low sodium class (S1).This implies that there is no alkali hazard that is anticipated for the irrigation of crops with the water.

Total hardness ranged from 15 to 290mg/L with a mean value of 80.3mg/L. The classification based on hardness is presented in (Table 6). Sixteen (16) out of the nineteen(19) samples were analyzed, and considered as soft water while the remaining three (3) samples are classified as brackish water. Table 3 show the major cations and their mean concentrations. The mean concentration for the major cations Na+, K+ ,Ca2,Mg+2 and Fe are all low, except in the case of Fe. The mean concentration for the cations are 25,

12.5, 12.1,4.41, and 0.88mg/L, respectively For the anions HCO3, Cl-, SO4-2,NO3 are 75.63, 23, 3.5, and 0.423mg/L, respectively. The results obtained revealed that the concentration of dissolved major cations and anions in the groundwater vary spatially. The mass abundance was in the order of Na > K > $Ca+2$ >$Mg+2$ > Fe for cations and HCO3 > Cl- > SO42 > NO3 for anion respectively. The mean concentration of the major ions reveal that the groundwater in the study area is suitable for drinking except in few locations were the concentration of Fe is high (Fe, $0.5 \geq 12.6$). In general, the Niger delta has elevated Fe concentration, according to Amadi et al., (1987). Most of the time, the waters are clear on abstraction from the well but in a few minutes becomes gray or off-white and then brownish from precipitation to ferric hydroxides. We observe that some of the major factors that influences the solubility of iron concentration in ground water include: local geologic structure, hydrological conditions and complex physiochemical and biochemical factors, such as pH and redox potential (mV) etc. The correlation of the analyzed physiochemical parameter of the groundwater sample is presented in Table 4. Correlation coefficient is commonly apply to establish the existing relationship between two or more variables, how one variable can be used to predict another variable (Kurumbein et al., 1965). The Pearson correlation matrix (Table 4), shows that TDS-EC, TDS-Na, TDS-Ca, TDS-Cl, EC-TDS, EC-TH, EC-Na, EC-Ca, K-Ca, K-HCO3, Na-K, Na-HCO3 , Ca-HCO3, have a positive correlation, with paired R^2 in the range of 0.504-1.000 respectively (Table 4). On the other hand, TDS-TA, EC-K, EC-Mg, TA-Mg, show moderate positive correlation, with R^2 values in the range of 0.504-0.638 respectively, this suggest that the aquifer chemistry is controlled majorly by these parameters. There is no significant correlation exhibited among Fe, SO4, NO3, and pH display no significant correlation with any of the variables in the matrix. Table 4 does not show any significant correlation between Fe, SO4, NO3 and pH.

The US Salinity diagram (Richard, 1954),also known as the Wilcox Salinity plot was used to evaluate the groundwater samples (Fig:3). This diagram is frequently used to analyzed the Sodium absorption ratio (SAR) and Sodium alkalinity. The salinity in terms of electrical conductivity (EC), was measured in microhms/cm at 250C. The Nineteen (19) samples

plotted in the chat falls within the region of C1S1 to C4S1 (Fig 3) of which three (3) of the samples with location codes: (BW17),Dr Christian Premises,(BW18) Mr.Rewards compound Igbogene, and (BW19),Akenfa 11, indicate low salinity/sodium hazard. Nine (9) of the samples with location codes: (BW1) Agudama, (BW2) Akenfa III , (BW3) Akenfa II, (BW4) Agudama Ekpatiama, (BW11) Kpansia, (BW13) NDU Campus, (BW14) Amarata, (BW15) Ekeki WaterBoard and (BW16) CHS NDU, shows medium salinity/sodium hazard. Five (5) of the samples with location codes: (BW6) Azikoro, (BW7) Igbogene Town Hall NT, (BW8) Okaka,(BW9) Nedugo and (BW12) Ovom-Gwegwe indicate high salinity/sodium hazard, while the remaining two (2) samples: (BW5) Agbia Spark NT, and (BW10) Kpansia NT, indicate very high salinity hazard and low sodium hazard respectively. Thus, the groundwater in the study area can be used for irrigation in all types of soil with little danger of exchangeable sodium
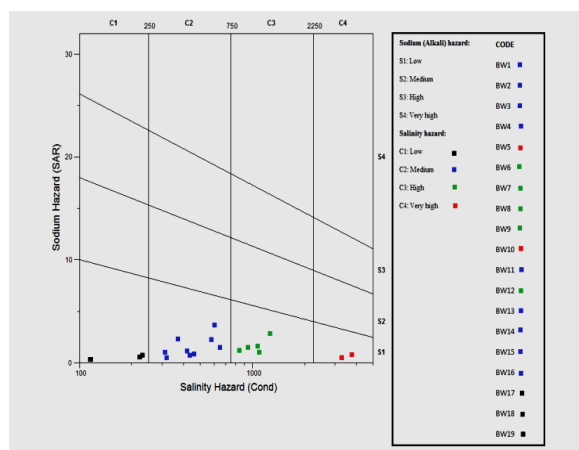
Fig 3 Wilcox salinity diagram

5.1.2 Geochemical processes and mechanism

Results from the chemical analysis were used to identify the geochemical processes and mechanism in the groundwater aquifer system. Gibbs plots of TDS versus ionic ratios Na/(Na+ Ca) and Cl/ (Cl + HCO3). Fig;4 (a) and Fig ; 4(b) below revealed that all plotted points in the log chat below fall on the intermediate region between the rock dominance end member and evaporation/precipitation

Fig . 4 (a) and Fig 4 (b). shows Gibbs plots of TDS vs Na/(Na + Ca), and TDS vs Cl/ Cl + HCO3

(a) TDS vs Na/(Na + Ca), (b) TDS vs Cl/ Cl + HCO3s
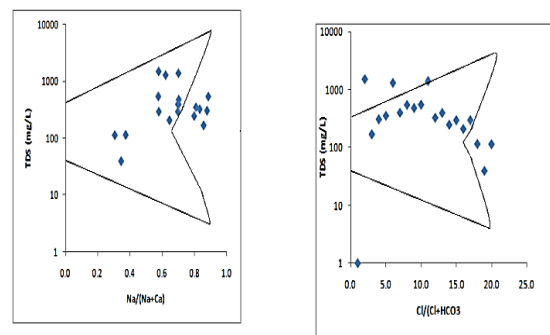
Fig 4 (c) Ca2+ Mg2 (meq/L) vs SO4 + HCO3 (meq/L)   Fig 4 (d) Plot of Na (meq/L) vs Cl(meq/L)
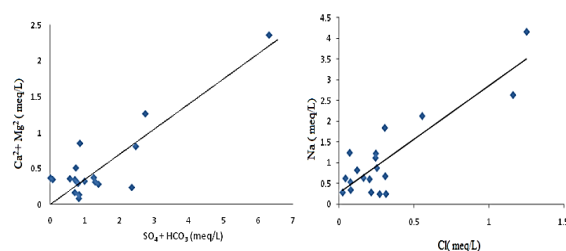
Dominance end member suggesting that rock weathering process was dominantly controlling the major ion composition of the groundwater in the study area (Gibbs 1970). Potential pyritic oxidation was confirmed with the calculated ratio of SO4/Cl. Where the ratio of SO4/Cl is ≥ 0.5 it reflects the oxidation of pyrite. The groundwater samples ratio of SO4/Cl ranges from 0.03 to 0.94 (Table 9), 60% of the groundwater samples in the study area indicated pyritic oxidation. The molar ratio of Na/Cl was also calculated for the groundwater samples. It ranges from 0.2 to 1.4, with a mean of 1.4. Samples having Na/Cl ratio greater than one suggest excess sodium, which is dominant and might have come from the weathering of silicate materials in the aquifer. If the source of sodium is probably through the weathering of silicate minerals, then the groundwater samples would have HCO3 as the most dominant abundant anion (Roger, 1989). This is because the reaction of feldspar minerals with carbonic acid in the presence of water

releases HCO3 (Elango et al., 2003). The dominant anion in the groundwater of the study area is HCO3 because silicate weathering was the primary process responsible for the release of Sodium cation (Na+), into the groundwater. conversely, samples with Na/Cl ratio around and less than one indicate the possibility of some other chemical processes, such as ion exchange (Elango et al.,2003). The plot of Ca+2 + Mg+2 vs SO4 + HCO3 is a major indicator to identify the process of ion-exchange according to the report of Cerling et al.,(1989), Fisher and Mulican (1997). If ion exchange is the process , the points tend to shift to the right side of the plot due to an excess of SO4 + HCO3,If reverse ion exchange is the process, points tend to shift to the left due to excess of Ca+2 + Mg 2+ over SO4 +HCO3

. Fig; 4 (c) and Fig4 (d),
shows the plot of Ca+2 + Mg 2+ vs SO4 + HCO3 in the study area of the groundwater samples. The plotted points clustered around and above the 1:1 line, indicating reverse ion-exchange (El-Sayed et al., 2012). The study area is characterized by shallow water table, underlain by wetland sediments (peat, lignite, and organic matter). These sediments contain inorganic sulphides including pyrite (FeS2) and other iron bearing minerals such as pyroxene, amphiboles, biotite, magnetite and olivine (Amadi et al., 1987). Transported oxygen enters into such layers either by convection or direct exposure to the air by lowering of the groundwater levels results in the oxidation of pyrite (FeS2). The oxidation of pyrite, dissolution of these iron-bearing minerals and disintegration of organic matter give rise to the release of acid, iron etc into the soil and groundwater system.
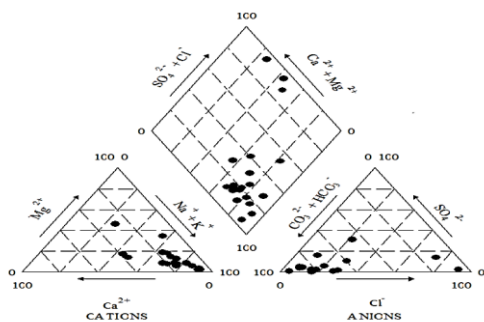

Fig:5. Piper Trillinear Diagram, showing the chemical character of the shallow groundwater in the study area.

To properly evaluate and interpret the groundwater chemistry in the study area, the Major ions were expressed in milliequivalents per liter (meq/l) and plotted on a Piper trilinear diagram Fig:5 .The trilinear plotting system was developed by Piper in (1953) to evaluate groundwater quality and types. The piper diagrams are combination of cations and anion triangles that lie on a common base line. The diamond shape between them is used to explicate and analyzed the water samples. Groundwater can generally be divided into four types according to their placement near the four corners of the diamond shape. Water samples plotted, that cluster at the top of the diamond are high in both (Ca+2 + Mg2+ and Cl- + So42+), which indicate an area of permanent hardness. Water samples plotted near the left corner arerich in (Ca2+ + Mg2+ and HCo3) and is the zone of temporary hardness. The water samples plotted at the lower point of the diamond mainly composed of alkali carbonates. (Na+ + K+and HCO32-).and lastly the water samples plotted near the right-hand area of the diamond may be considered saline.(Na+ + K+and Cl- + SO42+). The plot revealed a distinctive ionic features, where the two alkali metals (Na+ and K+) exceed the two alkaline earth metals(Ca2+ and Mg2+), while the weak acids (HCO3-, and CO32) exceed the strong acids anions Cl and SO42). The piper plot in Fig(5), was used to identify and classify the water based on the geochemical characters of the constituent elements/ ionic concentrations. The groundwater in the study area was classified into two major dominance facie,

They are:
1. Na-HCO3 water type.
2. Ca-Cl water type.

- . Na-HCO3 water type
Locations that have this water type are; Agudama Ekpetiama, Igbogene, Agudama,
Akenfa II , Akenfa III, Azikoro, Okaka, Ekeki and Amarata respectively.

- CaCl Water Type
From the analysis of the chemical plots of trilinear piper (1953) diagram. 5% of the samples
constitutes this water type in the study area. Only three locations have this water type, they
are; Amassoma, Agbia and Kpansia

5.1.3 Quality and Usability

The chemical nature of any ground water ascertain its quality and usability. The water quality is a function of certain physical, chemical, and biological parameters measured with the (WHO 2004). The shallow groundwater of the study area is largely unfit for the purpose of drinking because of the elevated concentration of dissolved Fe. It ranges from 0.01-12.1mg/L with an average mean value of 0.88mg/L which exceeds the 0.3mg/L recommendation of (WHO, 2004) for drinking water. When excessive amount of Fe is present, it causes metallic tasting, stains laundry, etc. In addition, the health implications of it, (Fe) in the body can triggered neurodegenerative disorders, cardiovascular diseases and cancer. All other physiochemical parameters tested fall below the WHO maximum permissible limit. The criteria for irrigation water are dependent on water conductivity, sodium-absorbtion- ratio (SAR),type of plants, amount of irrigation water used, soil and climate. The estimation of salinity hazard can be achieved by measuring the electrical conductivity of the water.

The two principal effects of sodium are a reduction in soil permeability and hardening of soil. Both effects are mostly caused by the replacement of Ca and Mg by Na ions on the sediments (soil clays and colloids). The Wilcox salinity diagram was used to plot 19 groundwater samples to access their usability for irrigation purpose. The Nineteen (19) samples plotted on the chat falls within the region of C1S1 to C4S1 (Fig:3). Three (3) of the samples: Dr. Christian premises (BW17), Mr. Rewards compound Igbogene (BW18), and Akenfa II (BW19), indicate low salinity/sodium hazard. Nine (9) of the samples : (BW1) Agudama, (BW2) Akenfa III , (BW3) Akenfa II, (BW4) Agudama Ekpatiama, (BW11) Kpansia, (BW13) NDU Campus, (BW14) Amarata, (BW15) Ekeki Water-Board and (BW16) CHS NDU. indicate medium salinity/sodium hazard. Five (5) samples (BW6) Azikoro, (BW7) Igbogene Town Hall NT, (BW8) Okaka,(BW9) Nedugo and (BW12) Ovom-Gwegwe indicate high salinity/sodium hazard, while the remaining two (2) samples (BW5) Agbia Spark NT. and (BW10) Kpansia NT indicate very high salinity hazard/low sodium hazard. Thus the water can be used for irrigational purpose in all types of soil with little danger of exchangeable sodium.

CONCLUSION

Groundwater samples obtained from the nearby boreholes show elevated concentrations of dissolved iron but other physico-chemical parameters are within WHO recommended limits with aquifers in Boreholes 3, 5 and 15 designated as low risk iron concentration aquifers having brownish-red sediments. Hydro-geochemical characteristics of the groundwater revealed that the water is fresh and mildly acidic in nature with pH values ranging from (5.78 - 6.93). Total hardness is between 15 to 290 mg/L with a mean value of 80.3 mg/L , this value is low compared to WHO maximum permissible limit of 500 mg/L. TDS in almost 90% of the samples is below the WHO recommended standard, ranging between 39.5 - 1520 mg/L. The concentration of major cations and anions in the groundwater samples such as Na^+ ,K^+ ,Ca^{2+} Mg^{2+}, and HCO_3 , NO_3, SO_4^{2} , Cl, were below WHO prescribed limits for drinking water. Most samples show medium to high salinity and low sodium. Prevalent water types in the study area are; $NaHCO_3$, and Ca-Cl respectively. The results of the multivariate statistical analysis and the conventional graphical methods indicated that the chemical composition of the groundwater of the study area is influenced and 54 controlled by rock-water interaction, Oxidation of inorganic sulphide including pyrite (FeS_2), weathering of silicate group of minerals enhanced by the processes of reverse ion-exchange. Major ions, namely; sodium, potassium, calcium, and magnesium are controlled by the weathering of silicate group of minerals. Nitrate and chloride have no significant lithologic source in the study area. Mass abundance of principal ions are in the order: Na >K>Ca>Mg>Fe and HCO_3 >Cl>SO4 >NO3 ,the alkali metals (Na^+ and K^+) exceeds the alkali earth metals($Ca2+Mg2+$), while the weak acids (HCO_3^- and CO_3^{2-}) exceeds the strong acids anions (Cland SO_4^{2}).

RECOMMENDATIONS

An hydrogeochemical investigation of shallow groundwater occurrence in Yenagoa and its environs has been studied and the results presented. The result provides critical insight about the hydrogeochemistry of the terrain studied. We therefore make the following recommendations:

(i).We recommend more or extensive Hydro geochemical investigation to be carried out so as to determine locations with low dissolved iron concentration.

(ii). Government should provide research grants and partner with the tertiary institutions in the state to carry out periodic assessment of groundwater resources to enable the state have geophysical data for water exploration and management system.

(iii). Waste controlled and management system is needed in the state, in order to avoid further contamination of the underground water resources particularly the aquifer.

(iv) Boreholes with elevated iron levels should be equipped with iron removal systems (e.g filtration, aeration, or oxidation methods) before the groundwater is used for drinking for domestic purposes.

(v) Borehole heads and casings should be properly maintained and sealed to prevent surface contamination, especially since weathering and oxidation process are active.

(vi) Since the groundwater is mildly acidic, pH adjustment (e.g., using neautralizing filters with limestone) could be recommended to prevent corrosion of pipes and improve taste.

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