Global Advanced Research Journal of Engineering, Technology and Innovation (ISSN: 2315-5124) Vol. 3(1) pp. 001-006, January, 2014
Available online http://garj.org/garjeti/index.htm

Full Length Research Paper

Ionic Ratios and Geochemical Characterization of Groundwater System in Parts of Port Harcourt, Nigeria

T. C. Dikeogu[1], J. I. Onyewudiala[2], A. C. C.Ezeabasili[3], O.N.K. Swift[4]

[1,]Department of Geosciences, Federal University of Technology, P.M.B. 1526,Owerri, Nigeria
[2]Department of Mechanical Engineering Federal University of Technology Owerri
[4]Anambra State University Uli
*Corresponding author. E-mail address: dikeogut@yahoo.comonyewudialajulius@yahoo.com,
accezeabasili@yahoo.com
Tel: +2348060114036, +2348063314201

Accepted 16 December 2013

Geochemical processes of aquifer systems in Port Harcourt were investigated using hydrochemicalfacies and ionic ratios determined using hydrogeochemical analysis of groundwater samples collected from ten (10) representative boreholes. Emphasis were placed on Electrical Conductivity, P^H, and major ion concentrations such as Ca, Mg, Na, K, Cl, HCO_3 and SO_4. Results of the analysis show that the concentrations of these cations and anions in the groundwater system exhibit spatial and temporal variations. Abundance of these ions is in the following order: Ca> Mg > Na > K >Cl> HCO_3 > SO_4> NO_3. The dominant facies of the area are Ca, Mg, Cl, HCO_3 and Ca, Mg, Cl, SO_4. Carbonate and silicate weathering as well as ion exchange processes are mechanisms controlling groundwater chemistry in the area. Minimal marine influence and low-salt inland waters were inferred on the basis of ionic ratios (Mg/Ca and Cl/HCO_3) and CationExchange values. Two (2) principal water types; Calcium-Magnesium-Chloride-Bicabonate and Calcium-Magnesium-Chloride-Sulphate were delineated.

Keywords:Groundwater, Hydrogeochemistry, Cations, Anions, Ionic ratios, Facies

INTRODUCTION

Groundwater in Port Harcourt has come under threats from indiscriminate drilling of boreholes, increasing demand and abstraction rate, geology and geochemical conditions, climate change, oil exploration and production activities as well as agricultural land use. The ever increasing groundwater abstraction rate has imposed enormous pressure on the groundwater resources of the area. Most of the industries in the area dispose their effluents indiscriminately, on land and into surface waters. Through percolation, and groundwater-surface water interactions, these effluents could find their way into the groundwater domain and subsequently alter the groundwater chemistry. Dikeogu (2005) observed that the quality of water is affected by the chemical reaction between water and its geologic environment. Thus groundwater chemistry is highly dependent on the geochemical characteristics of the aquiferous layers.

Martinez and Bocanegra (2002) noted that chemical compositions of groundwater are controlled by hydrogeochemical processes such as precipitation, dissolution, ion-exchange, and the residence time along the flow path. Etu-Effeotor(1981), Udom and others (1999) observed that the groundwater quality in the area is rapidly deteriorating. Urbanization and population growth has made groundwater the major source of water for domestic and industrial need. Thus, it is very

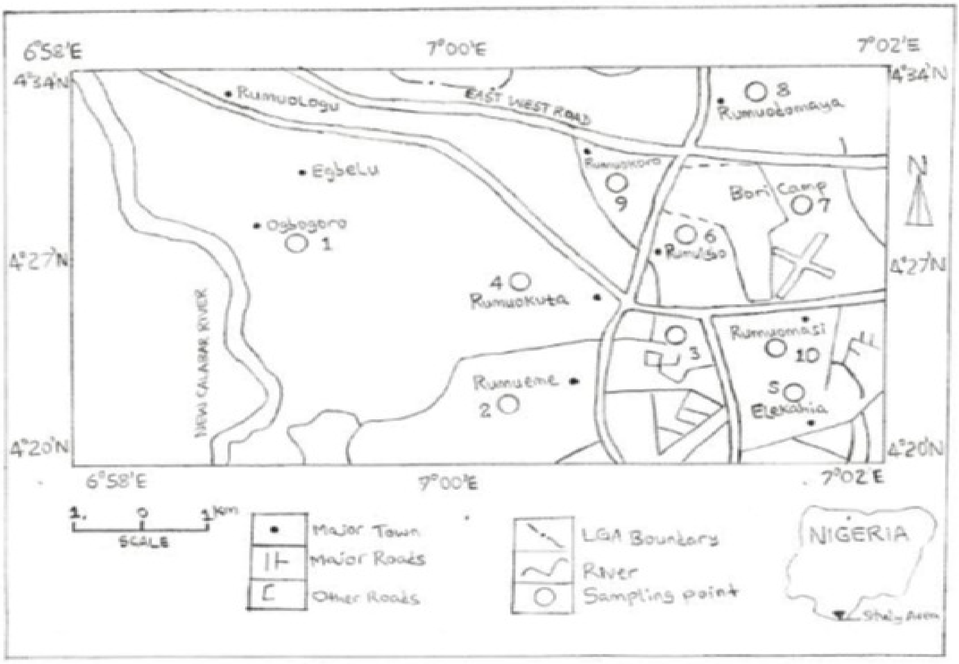

Figure 1. Location Map of the study area (Prepared by the Author)

Table1. Chemical composition of groundwater in the area

Borehole Number	LOCATION	Temperature (^{0}C)	P^H	EC µs/cm	TSS (Mg/l	TDS (Mg/l)	Cl Mg/l)	Fe (Mg/l)	Ca^{2+} (Mg/l)	Mg^{2+} (Mg/l)	Na^{2+} (Mg/l)	Mn (Mg/l)
BH1	Ogbogoro	24.9	5.15	52.00	-	22.00	16.00	0.002	4.625	2.960	1.740	0.003
BH2	Rumueme	27.8	6.18	25.42	1.00	40.50	15.50	0.070	7.998	2.890	1.880	0.001
BH3	Rumuola	25.6	5.00	48.00	-	20.00	12.00	0.030	5.570	0.350	0.822	0.07
BH4	Rumuokuta	27.4	6.32	50.00	-	85.00	25.20	0.002	7.200	0.190	1.511	-
BH5	Elekahia	26.7	6.45	15.00	-	25.00	10.05	0.001	4.320	1.005	2.295	0.001
BH6	Bori Camp	28.2	4.20	52.00	1.04	38.10	20.00	0.019	0.362	0.752	1.401	0.438
BH7	Rumuigbo	24.8	4.62	67.90	-	65.05	14.21	0.014	0.360	0.826	1.768	-
BH8	Rumuodomaya	28.8	5.87	80.32	0.92	75.30	19.00	0.360	0.400	0.640	1.502	-
BH9	Rumuokoro	26.0	4.71	68.00	0.90	41.00	18.90	0.200	0.370	0.560	1.360	0.430
B10	Rumuomasi	26.1	4.3	71.00	1.02	34.60	11.00	0.295	0.325	0.425	1.300	0.211
WHO 2004		NS	6.5-8.5	500	NS	500	250	0.3	7.5	50	200	0.1

important to understand the hydrogeochemical processes that occur beneath the land surface.

The Study Area

The study area (Port Harcourt) is located within the Niger Delta Basin of Nigeria. The area lies between latitudes 4°20′and 4°34′N and longitudes6°58′and 7°02′E (see figure 1). The area is characterised by alternate wet and dry seasons. The rainy season occurs between mid-April and early November and peaks in June and July. The dry season starts from November and ends in March. The harmattan period occurs in December and early January and is brought by hazy, dry, and dusty winds called the North East trade winds or Tropical Continental Air Mass emanating from the Arabia- Eurasia high pressure belt. The vegetation in the area is rain-forest vegetation.

Geology/Hydrogeology

The area is located within the Niger Delta Basin. Sediments of Agbada, and Benin formations composed of sand, gravel, shale, and occasional clay layers constitute the geology of the area.

Table1. Continued

Borehole Number	$K+$ (Mg/l)	**Eh (mv)**	**Coliforms (cfu/mu)**	**$S0_4^{2-}$ (Mg/l)**	**$P0_4^{3-}$ (Mg/l)**	**HCO_3 (Mg/l)**	**NO_3 (Mg/l)**	**Hardness (Mg/l)**	**Well Depth (m)**	**Salinity (Mg/l)**
BH1	0.050	126.00	0.00	19.00	0.012	8.090		4.05	160.00	0.00
BH2	0.666	128.30	0.00	3.82	0.000	41.340		10.11	38.50	-
BH3	0.091	-	0.00	0.02	0.000	10.00		16.00	80.00	0.00
BH4	0.811	131.00	-	0.09	0.160	22.700		9.00	80.00	-
BH5	0.512	-	-	0.07	0.572	28.550		9.00	80.00	-
BH6	0.700	152.20	0.00	48.00	0.644	11.121		15.00	80.00	0.00
BH7	0.550	133.80	0.00	12.00	0.612	16.220		16.00		0.00
BH8	0340	-	-	13.62	0.560	18.000		23.50	180.00	-
BH9	0.200	184.11	1.05	11.30	0.440	15.058		22.00	80.00	0.00
BH10	0.111	158.40	1.00	10.22	0.242	15.002		23.00	80.00	0.00
WHO	200	NS	NS	250	10	NS	50	500	80.00	NS

Table 2. Ionic ratios and cation exchange values

Borehole Number	**Location**	**Mg/Ca**	**Cl/HCO_3**	**CEV**
BH1 [[	Ogbogoro [	0.64 [	1.98 [[	0.90
BH2	Rumueme	0.36	0.37	0.08
BH3	Rumuola	0.06	1.20	0.92
BH4	Rumuokuta	0.03	1.11	0.90
BH5	Elekahia	0.23	0.35	0.72
BH6	Rumuigbo	2.07	1.80	0.90
BH7	Bori Camp	2.29	0.87	0.84
BH8	Rumuodomaya	1.60	1.05	0.90
BH9	Rumuokoro	1.51	1.26	0.91
BH10	Rumuomasi	1.31	0.73	0.87

Table 3 shows the major ion concentrations (meq/l) with % present in the groundwater and the corresponding water types Major ion concentration (meq/l) with % present in the groundwater samples

BH N0	**LOCATION**	**Na+ K^+ meq/l)**	**%**	**Ca^{2+} (meq/l)**	**%**	**Mg^{2+} (meq/l)**	**%**	**HCO_3^- (meq/l)**	**%**	**Cl+ $N0_3^-$ (meq/l)**	**%**	**$S0_4^{2-}$ (meq/l)**	**%**	**Water type**
BH1	Ogbogoro	0.0957	7	0.8970	73	0.2121	17	0.2468	15	1.0738	79	0.1702	10	$Cacl_2$
BH2	Rumueme	0.0202	9	0.3307	29	0.4275	41	0.155	19	0.0379	44	0.0010	41	$Mgcl_2$
BH3	Rumuola	0.0285	7	0.2475	76	0.0470	14	0.1623	27	0.4197	73	0.0001	1	$Cacl_2$
BH4	Rumuokuta	0.0340	19	0.1601	49	0.0218	19	0.1343	14	0.1040	46	0.1301	41	$Cacl_2$
BH5	Elekahia	0.0438	24	0.9970	39	0.5505	49	0.2193	24	0.3307	29	0.0111	18	$Macl_2$
BH6	Rumuigbo	0.0415	11	0.2474	77	0.0302	9	0.1558	34	0.2252	66	0.0001	0	$Cacl_2$
BH7	Bori Camp	0.0877	19	0.3515	76	0.0148	3	0.3538	29	0.8233	69	0.0012	1	$Cacl_2$
BH8	Rumuodomaya	0.1612	34	0.2178	46	0.0825	17	0.4869	59	0.1987	23	0.1251	14	$Ca(HCO_3)_2$
BH9	Rumuokoro	0.0410	15	0.2065	76	0.0194	6	0.1756	29	0.2252	39	0.1857	33	$Cacl_2$
BH10	Rumuomasi	0.0610	13	0.2941	69	0.0679	15	0.1679	19	0.4596	54	0.2063	24	$Cacl_2$

The clay units of the Benin formation have given rise to a multi-aquifer system in the area (Etu-Effeotor, 1981). Etu-Effeotor (1981) observed two (2) major aquifers in Rivers State from lithologic logs. The upper one is more prolific, with depth of about 80metres whereas the underlying one is less prolific.

MATERIALS AND METHODS

Groundwater samples were collected from ten (10) boreholes, and are believed to be representatives of all other boreholes in the area. Even though water samples collected from a pumping well may not provide an untrue

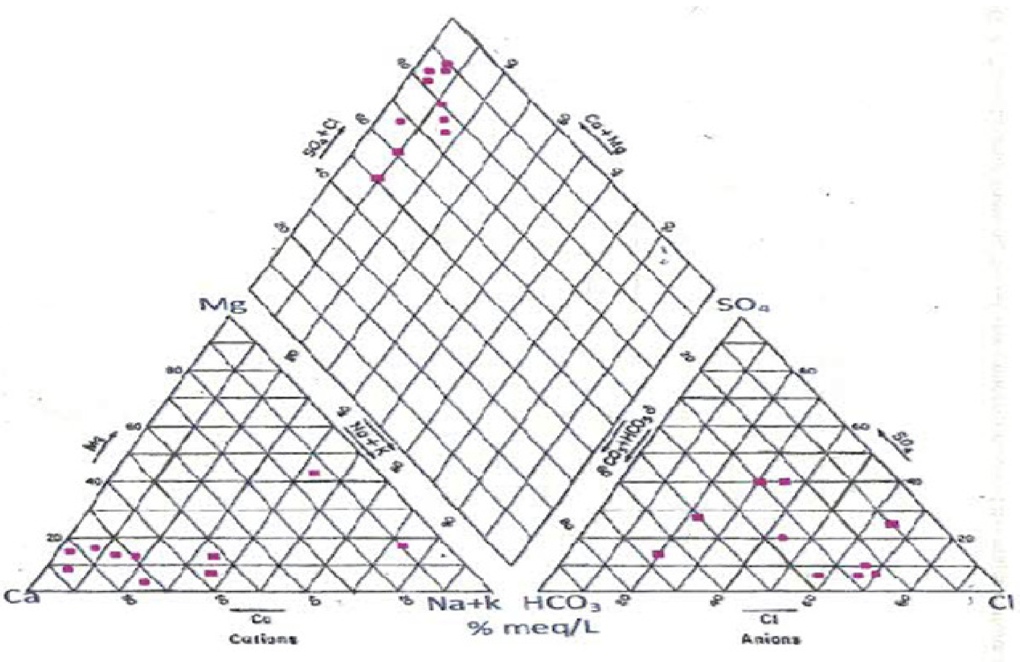

Figure 2. Piper diagram showing the relative concentrations of the major cations and anions

hydrogeochemical property of water in the groundwater domain, we recognize the fact that it is not the most ideal sampling method for groundwater. However, in the absence of a more ideal technique, samples were collected from the well head, and at points close to it.

The samples were collected with plastic containers that were, prior to sampling, sterilized and rinsed with the borehole water, so as to ensure that the chemical characters represent the actual condition in the groundwater system. The samples were labelled and taken to the laboratory in ice box within six (6) hours to avoid chemical character variation from field values. However, P^H, Temperature, and Electrical Conductivity were measured in-situ due to the instability associated with these values. The laboratory methods used are of international standards and include those of American Public Health Association and American Standards for Testing and Materials. Cations and anions were analysed using Atomic Absorption Spectrophotometer, and Calorimetric methods with UV-Visible Spectrophotometer respectively. Sampling and laboratory analysis were done in October and November, 2012.

DATA ANALYSIS AND DISCUSSION

Hydrochemical Analysis

Analyses were done with more emphasis on total ionic constituents. The chemical composition of the groundwater in the area is presented in table 1.

The hydrogen-ion concentration (P^H) of the groundwater in the area ranges from 4.20 to 6.45. Udom and others (1999) observed that this is the situation in most parts of the Niger Delta. The P^H values indicate that groundwater in the area is slightly acidic. Acidity in groundwater in the Niger Delta has been attributed to the presence of organic matter in the soil, and partly to gas flaring in the area. Gas flaring releases carbon dioxide which reacts with the atmospheric precipitation to form carbonic acid, which percolates into the groundwater system, reduce the P^H of the water thereby increasing acidity. The P^Hvalue falls below WHO (2004) standard for potable water.

The values obtained for hardness and TDS indicate that the groundwater is not highly mineralized. Thus, the groundwater in the area can generally be classified as soft water. For locations where P^Hvalue falls below 6.5, the method of base- exchange with dolomite could be used to reduce acidity. Most of the locations show low nitrate (NO_3) concentrations. This phenomenon may be attributed to redox processes which consumes nitrate.

Major Ion Chemistry And Chemical Processes

Chemical processes and hydrogeochemistry of the groundwater exhibit spatial and temporal variations. Lakshmanam and others (2003) observed that the concentrations of ions in groundwater depend on the hydrogeochemical processes that take place in the aquifer system. Thus, total dissolved solids (TDS) are partly composed of major ions present in groundwater. Considering that the chemical processes of groundwater are initiated when groundwater moves towards equilibrium in major ion concentrations, the determination of concentration of major ions present in groundwater becomes imperative, and is used in the identification of chemical process. The ratios of the cations and anions are presented in table 2.

Calcium (Ca) and bicarbonate (HCO_3^-) are the dominant cation and anion respectively. The abundance of these ions are in the following order Ca>Mg >Na >K = HCO_3>Cl>SO_4>NO_3. Concentration of dissolved salts could be influenced by atmospheric sources, and Chloride is the most reliable parameter for evaluating atmospheric input to water as it shows very little fractionation (Appelo and Postma, 1993). Sodium (Na) and Chloride (Cl) values ranged respectively from 0.82 mg/l to 2.29 mg/l and 10.05mg/l to 25.20mg/l. These values fall below WHO (2004) standards (see table 2). Sodium and Chloride contributions are likely to come from rainfall, as well as groundwater-surface water interactions. In both cases, the values will represent to a great extent, the ratios observed in sea water. However, reduction in Na concentration and high level of Cl may be attributed to cation exchange and halite dissolution respectively.

Ionic Relationships and Cation Exchange

The ionic relationships; Mg/Ca, Cl/HCO_3 and the CationExchangeValue (CEV = [Cl - (Na+K)]/ Cl) were determined so as to assess the salinity level and understand the origin of the groundwater in the area. Table 2 shows the values for the ionic relationships and cation exchange.

The CEV values for seawater ranges from +1.2 to +1.3 (see custodia, 1983). Low inland waters have values close to zero, with either positive or negative sign. The CEV values obtained ranges from 0.72 to 0.92 and this range of values indicates inland origin.

The Mg/Ca values ranges from 0.03 to 2.29. According to Sarma and Krishnaiah (1976), waters under marine influence would have values of about 5. Though, cation exchange could reduce the values of Mg/Ca ratio to 4, however, there is still a significant difference between 4 and 2.29. Thus, the groundwater in the area could be slightly of inland origin, based on this index.

The Cl/HCO_3 values range from 0.35 - 1.98 and this is in line with the range of values for inland water as given by Custodio (1987). Based on the hydrogeochemicalfacies and indices (Mg/Ca, Cl/$HCO_3$and CEV) analysed, the groundwater in the area is of inland origin.

Chemical Character And Water Types

Hydrochemical Water Types

The Piper diagram (figure 2) shows the relative concentrations of the major cations and anions.

Two principal water types were delineated; Calcium-Magnesium-Chloride-Bicarbonate and Calcium-Magnesium-Chloride-Sulphate. Bicarbonate and chlorides of Calcium and Magnesium dominate the groundwater system. Calcium Chloride predominates the cationfacies whereas Bicarbonate and Chloride predominate the anion facies. Considering the dominant cations and anions, the groundwater system can be classified as Calcium Chloride ($CaCl_2$), Magnesium Chloride ($MgCl_2$) and Calcium Carbonate ($Ca(HCO_3)_2$.

CONCLUSION

The P^H values indicate that groundwater in the area is acidic. On the basis of TDS and hardness values obtained, the groundwater in the area is not highly mineralized. The groundwater in the area exhibits secondary alkalinity and salinity, as well as carbonate and non-carbonate hardness, and is dominated by the following major ionic components; Ca, Mg, HCO_3, Cl and SO_4.

The hydrochemical indices indicate that the groundwater is of inland origin. The cation exchange value is generally below 1.0 and indicates low-salt inland water.

REFERENCES

AppeloCA, Postma R (1999).Chemical Analysis of Groundwater in: Geochemistry, Groundwater and Pollution. A. A. Balkema/ Rotterdam/ Bookfield.

Custodio E (1983). Hydrogeoquimica.InCustodio E. and Llamas, M.R. (Ed).HydrologiaSubterranean.Section 10.Omega, Barcelona.

Custodio E (1987). Groundwater in Coastal Areas. In: Studies and Reports in Hydrology (UNESCO).

Dikeogu TC (2005). The Geology of Ezillo and Its Environs.UnpublishedB.Sc Project work, Anambra State University, Uli, P 89.

Etu- Effeotor JO (1981). Preliminary Investigation Subsurface Waters in Parts of the Niger Delta. J. Min. Geol., 18 (1): 103- 107.

Sarma WJ, Krishnaiah N (1976).Quality of Groundwater in the Coastal Aquifer near Visakhapatriam, India. Groundwater, 14 (15): 290-295.

Lakshmanan E, Kannan R, Kumar MS (2003).Major Ion Chemistry Kancheepuran District, Tamil Nadu, India. Environ. Geosci. 10 (4) 157-166.

Martinez DE, Bocanegra EM (2002).Hydrogeochemistry and Cation Exchange Processes in the Coastal Aquifers of Mar Del Plata, Argentina Hydrogeol J., 12: 81- 87.

Piper AM(1944). A Graphical Interpretation of Water Analysis: Trans-Am. Geophysical Union, 25: 914-928.

Udom GJ, Etu-Effeotor JO, EsuEO (1999).Hydrochemical Evaluation of Groundwater in Parts of Port Harcourt and Tai- Eleme Local Government Area, Rivers State.

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