Research Article

Piper Trilinear and Gibbs Description of Groundwater Chemistry in Port Harcourt, Nigeria

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Abstract
Several studies have shown that there are high salinity values in the groundwater quality in certain areas within Port Harcourt city. However, a detailed investigation on the cause is not yet documented hence, this research investigated the factors governing the hydro-geochemistry of the said area. This was achieved by analysing concentrations of 7 ions (both cations and anions) and total dissolved solids (TDS) in water samples obtained from 26 drilled boreholes and 4 hand dug wells, evenly distributed within the study area. The examined ions are Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, HCO_3^- and SO_4^{2-}. Laboratory results were plotted on Piper trilinear and Gibbs diagrams through Aquachem 5.1 software package and it was revealed that 63.33% of the total samples fell in Na-Cl hydrochemical facies while the remaining 36.67% occurred in Ca-Cl facies. It was also revealed that the controlling factors for formation of the analysed ions were precipitation and rock weathering on 76.67% and 23.33% respectively. Hence, it was concluded that Na-Cl facies is the dominance hydrochemical facies in the study area while the main factor governing the formation of ions is precipitation. However, it was recommended that the rate of pumping out water from wells in certain parts of the study area should be reduced in other to avoid seawater intrusion.

Keywords: Facies, Gibbs, Intrusion, Ions, Origin

1 Introduction

Groundwater abstraction is a major source of water for Port Harcourt residents. Notwithstanding, the saline nature of the water in some parts of the city usually discourage people from drilling boreholes. Salinity is the concentration of dissolved salts in water [1]. Based on the mode of formation, it could be primary, secondary and tertiary. Primary salinity is initiated by dissolution of minerals from bedrocks or accumulation of salts from precipitation built up over thousands of years. Secondary salinity is as a result of rise in water level which brings salt accumulated through 'primary salinity' process to the surface. However, tertiary salinity occurs when irrigation water applied on fields or horticulture is recycled, were salt remains after evaporation and accumulates over time [2].

Salt, being a mineral and main cause of salinity in groundwater are of different types that could dissolved in groundwater as the water flow from one point to another. Hence, it is important to investigate the types of salts present in the groundwater samples of the study area as well as the factors governing their ion formations. This will help in understanding the
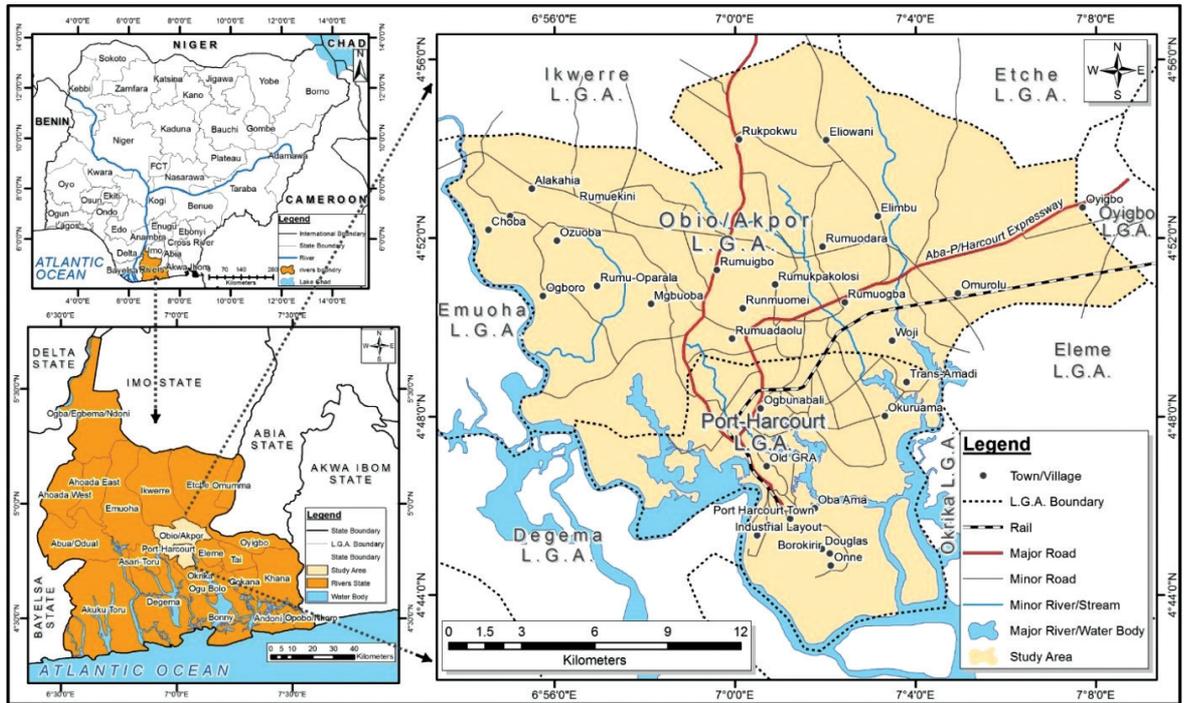
Figure 1: Map of Port Harcourt metropolis (Abio/Akpor and Port Harcourt LGAs).

origin of the abstracted water in the aquifers within the study area thus, suggesting a remedy to the saline nature of the water.

A hydrochemical facies is a hydrogeological term which utilised the chemical processes occurring within the lithology of an aquifer and flow pattern to describe the spatial variations in quality and origin of the water in an aquifer. In other words, knowing the dominance hydrochemical facies of the groundwater will reveal the origin of the water. The Piper trilinear diagram has been successfully used by numerous scientists to identify the hydrochemical facies existing in groundwater samples [3]–[7]. Similarly, numerous literatures have reported that the Gibbs diagram is a reliable tool in understanding the factors controlling the formation of ions in groundwater [8]–[12]. In other words, applying the Piper trilinear and Gibbs diagrams in analysing the groundwater quality of Port Harcourt will disclose the origin of salts in the water as well as the chemistry of the ions formation. These will help in knowing the main source of salinity in the groundwater thereby recommending a solution.

2 Materials and Methods

2.1 *Description of study area*

Port Harcourt is located in Southern Nigeria within Latitude 4º 42' 00" to 4º 57' 03" North and Longitude 6º 53' 11" to 7º 8' 49" East, occupying an area of approximately 369 km^2. It is the capital of Rivers state and it comprises two Local Government Areas (LGAs) of the state known as Obio/Akpor and Port Harcourt as could be seen in Figure 1.

The main source of aquifer recharge in the study area is rainfall, with an average annual value of 2500 mm. Usually, the rainy season starts in the month of March, get to the peak during the month of September and ends in October. However, the few dry months occasionally record reasonable rainfall especially February and November. The top soil is usually sandy or sandy loam and it is always leached due to the heavy rainfall experienced in the area.

The study area, which is part of the Niger Delta region of Nigeria, is of the sedimentary basement with three stratigraphic subdivisions known as Benin,
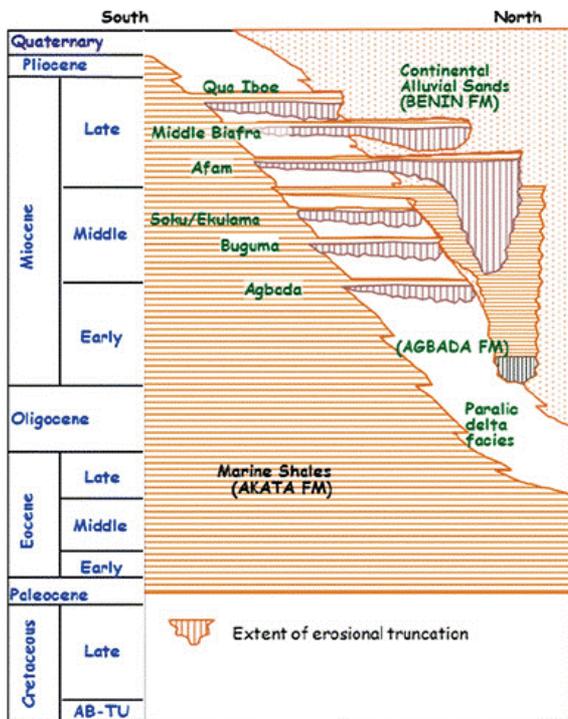
Figure 2: Stratigraphy of Niger Delta showing the different formations.

Figure 3: Hydrochemical facies in Piper trilinear diagram.

Agbada and Akata formations, in order of their increasing ages (Figure 2). However, the aquifers are found within the Benin formation which mostly consist of alluvial deposits. The aquifers are mostly sandy layers ranging from fine to coarse as well as sub-angular to sub-rounded grain particles. The groundwater quality for most analysed parameters were reported to be fairly good apart from iron and chloride contents [13], [14].

2.2 Data collection and analysis

Twenty six (26) drilled boreholes and four (4) hand dug wells, evenly distributed within the study area were selected for the purpose of sampling. However, the water sampling was done once during the month of December, 2019 and analysed for total dissolved solids (TDS), calcium ion (Ca^{2+}), magnesium ion (Mg^{2+}), sodium ion (Na^+), and potassium ion (K^+). Other ions examined includes chloride ion (Cl^-), bicarbonate ion (HCO_3^-) and sulphate ion (SO_4^{2-}). The justification for selecting the above listed ions was based on the assumption made by the inventor of the Piper trilinear diagram (Arthur M. Piper) which is stated as follows. '*Most natural waters contain cations and anions in chemical equilibrium with Ca^{2+}, Mg^{2+}, Na^+ and K^+ as the most abundant cations while Cl^-, HCO_3^- and SO_4^{2-} as the most common anions.*' On the other hand, TDS was analysed on the fact that it is required for preparing the Gibbs diagram.

The water samples were collected into well labelled clean polyethylene bottles after rinsing the bottles with the water being sampled. Thereafter, the samples were acidified with two drops of hydrochloric acid (HCl), and then transported in an ice packed cooler to the laboratory on same day. The geographical locations of all the sampled points were recorded using a portable GPS (Etrex 20x). Concentration of TDS in all the samples were determined in situ by means of a pocket-sized meter (TDS hold, ±2%) made by Griffin Company, USA [15]. However, other parameters (ions) were determined in the laboratory in accordance with standard methods [16].

Both Piper trilinear and Gibbs diagrams were drawn (plotted) by subjecting laboratory results in AquaChem 5.1 software package [17], [18]. Usually, the Piper trilinear diagram consist of two ternary plots positioned at the lower left and lower right with a diamond plot at the middle. The cations and anions were plotted on the lower left and right ternary plots respectively while the central diamond plot was used in identifying the hydrochemical facies based on the information given in Figure 3.

The Gibbs diagram was obtained by computing the ratios $(Na^+ + K^+)/(Na^+ + Ca^{2+} + K^+)$ and $Cl^-/(Cl^- + HCO_3^-)$ for cations and anions respectively. Thereafter, TDS concentrations were plotted on a logarithmic scale against the computed cations and anions ratios (separately) on a linear scale. The factors controlling the formation of ions in the water were known by identifying the regions were the plotted values fell in the Gibbs diagram.

3 Results and Discussion

The laboratory results of the various parameters examined in all the sampling locations alongside the geographical coordinate of wells are shown in Table 1. Piper trilinear diagram obtained from results shown in Table 1 is presented in Figure 4 while the Gibbs diagrams on TDS against cations and anions ratios are displayed in Figures 5 and 6 respectively.

Table 1: Laboratory results of water samples

Sample Code	Geographical Coordinate	TDS (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)	Cl⁻ (mg/L)	HCO₃⁻ (mg/L)	SO₄²⁻ (mg/L)
B1	N 04º 55' 42.9", E 007º 00' 39.8"	85.33	6.77	0.73	10.72	0.56	56.40	1.02	0.68
B2	N 04º 54' 05.8", E 006º 55' 37.7"	92.64	7.35	0.80	11.63	0.61	61.22	1.10	0.74
B3	N 04º 53' 21.5", E 006º 58' 52.7"	115.14	9.13	0.99	14.45	0.76	76.07	1.37	0.91
B4	N 04º 53' 33.4", E 005º 59' 56.6"	105.20	8.35	0.90	13.21	0.70	69. 54	1.25	0.83
B5	N 04º 53' 40.1", E 007º 02' 28.5"	111.33	8.83	0.96	13.97	0.74	73.55	1.32	0.88
B6	N 04º 52' 00.6", E 006º 55' 31.4"	230.69	18.29	1.98	28.95	1.52	152.40	2.74	1.83
B7	N 04º 52' 04.5", E 006º 56' 53.3"	217.72	17.26	1.87	27.33	1.44	143.90	2.59	1.73
B8	N 04º 52' 26.0", E 005º 58' 54.0"	132.35	10.49	1.14	16.61	0.87	87.44	1.57	1.05
B9	N 04º 51' 58.8", E 007º 00' 48.0"	137.91	10.94	1.19	17.32	0.91	91.15	1.64	1.09
B10	N 04º 52' 21.8", E 007º 02' 40.1"	129.55	10.27	1.11	16.27	0.86	85.62	1.54	1.03
B11	N 04º 52' 05.2", E 007º 04' 24.8"	148.47	11.77	1.28	18.64	0.98	98.09	1.77	1.18
B12	N 04º 52' 08.7", E 007º 06' 32.6"	140.29	11.12	1.21	17.61	0.93	92.66	1.67	1.11
B13	N 04º 50' 07.8", E 006º 57' 16.6"	272.41	21.63	2.34	34.21	1.81	180.30	3.24	2.16
B14	N 04º 50' 08.5", E 006º 58' 36.2"	244.55	19.39	2.10	30.70	1.62	161.60	2.91	1.94
B15	N 04º 50' 25.4", E 007º 00' 16.5"	219.36	17.39	1.88	27.54	1.45	144.90	2.61	1.74
B16	N 04º 53' 17.2", E 007º 02' 30.3"	266.50	21.13	2.29	33.46	1.76	176.10	3.17	2.11
B17	N 04º 50' 07.3", E 007º 04' 16.0"	293.94	23.31	2.53	36.91	1.94	194.20	3.50	2.33
B18	N 04º 48' 40.4", E 006º 57' 20.4"	425.35	33.73	3.65	53.43	2.81	281.70	5.06	3.37
B19	N 04º 48' 22.9", E 006º 59' 02.4"	471.90	37.43	4.06	59.26	3.12	311.90	5.61	3.74
B20	N 04º 47' 28.3", E 007º 00' 03.6"	637.44	50.53	5.47	80.21	4.21	421.00	7.58	5.05
B21	N 04º 48' 10.5", E 007º 02' 52.3"	598.76	47.49	5.14	75.18	3.96	395.70	7.12	4.75
B22	N 04º 48' 39.5", E 007º 04' 11.3"	735.63	58.35	6.32	92.38	4.86	486.10	8.75	5.84
B23	N 04º 47' 00.9", E 006º 58' 34.5"	996.20	79.01	8.56	125.10	6.58	658.50	11.85	7.90
B24	N 04º 45' 52.6", E 007º 01' 09.6"	967.98	76.69	8.31	121.40	6.39	639.30	11.50	7.67
B25	N 04º 46' 50.9", E 007º 02' 59.3"	975.25	77.34	8.38	122.50	6.45	644.50	11.60	7.73
B26	N 04º 45' 01.6", E 007º 02' 23.4"	1078.70	85.49	9.26	135.40	7.12	712.90	12.82	8.55
C1	N 04º 56' 06.0", E 007º 01' 25.4"	81.62	6.47	0.70	10.25	0.54	53.94	0.97	0.65
C2	N 04º 53' 11.9", E 007º 05' 46.6"	123.42	9.79	1.07	15.49	0.82	81.55	1.47	0.98
C3	N 04º 44' 07.7", E 007º 01' 42.1"	1006.30	79.75	8.64	126.20	6.65	665.70	11.95	7.98
C4	N 04º 48' 47.7", E 006º 56' 18.1"	557.99	44.25	4.79	70.07	3.69	368.80	6.64	4.43
Mean		386.66	30.66	3.32	48.55	2.56	261.97	4.60	3.07
Standard Deviation		332.29	26.34	2.85	41.71	2.19	220.64	3.95	2.63
Coefficient of Variation		85.94	85.91	85.84	85.91	85.55	84.22	85.86	86.67
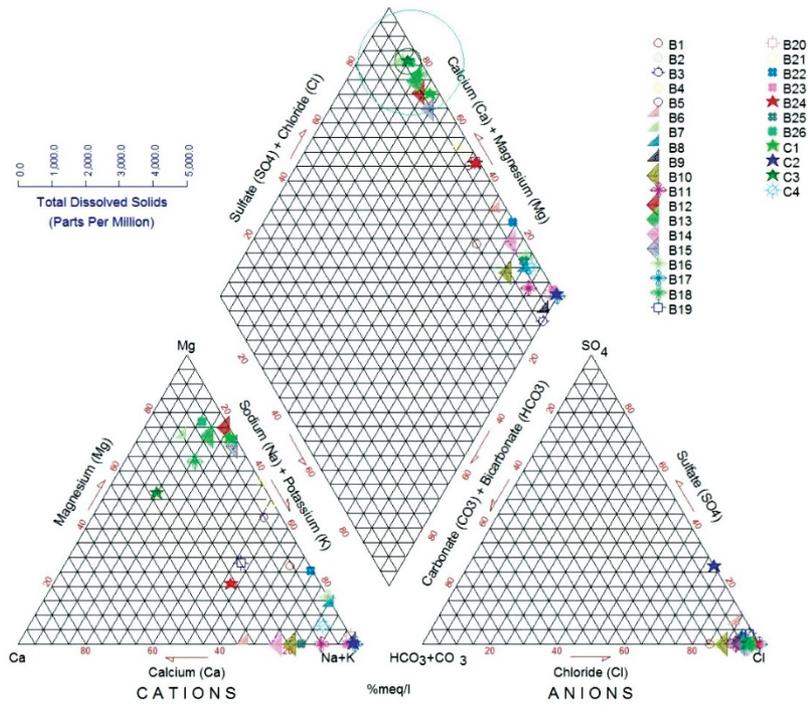
Figure 4: Piper trilinear diagram of water samples.
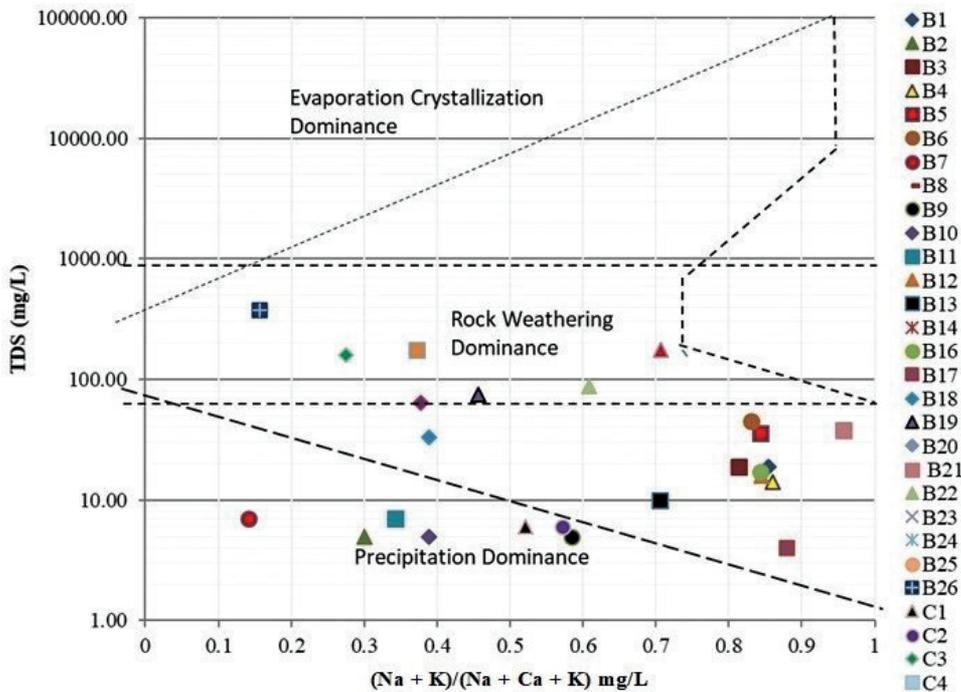
Figure 5: Gibbs diagram on TDS and major cations.
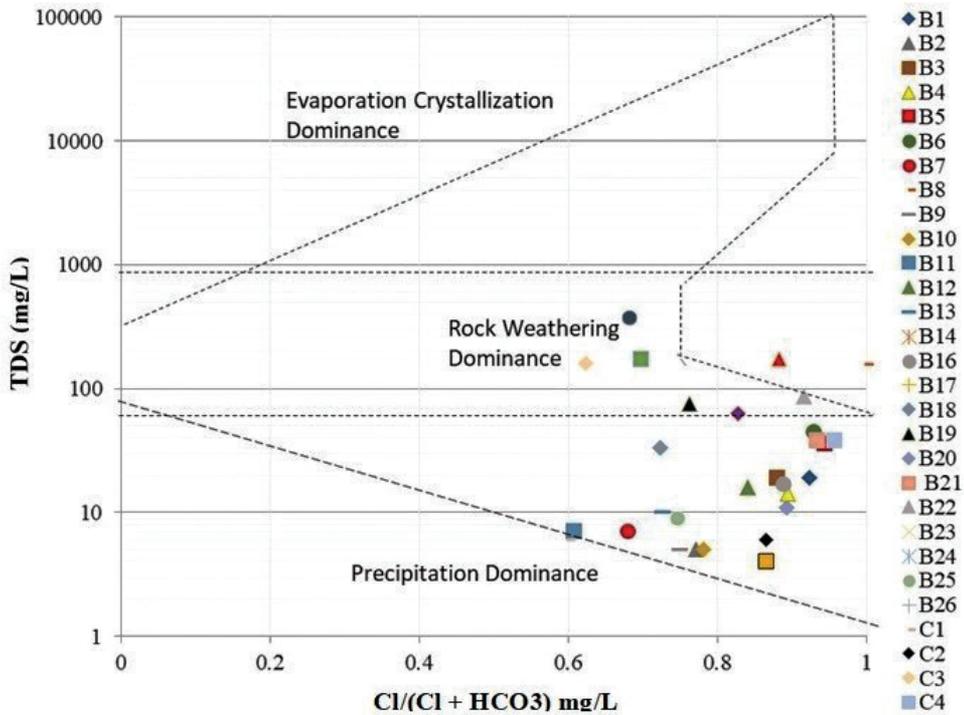
Figure 6: Gibbs diagram on TDS and major anions.

By comparing the central diamond plots in Figures 3 and 4, it is glaring that the groundwater of the study area fell into Ca-Cl and Na-Cl hydrochemical facies. In other words, the ions having significant concentrations among the analysed parameters are Ca^{2+}, Na^+ and Cl^- and could be attributed to both geogenic and anthropogenic processes. Similarly, Figures 5 and 6 revealed that the factors controlling the formation of the analysed ions are precipitation and rock weathering. The proportion of total water samples that fell in Na-Cl fecies is 63.33% however, most of these samples were obtained in southern part of the study area (Port Harcourt LGA) while the remaining 36.67%, which fell in Ca-Cl fecies mostly contain samples from northern part of the study area (Obio/Akpor LGA). Likewise, 76.67% of the total samples fell under precipitation as controlling factor for ion formation with majority from Port Harcourt LGA whereas rock weathering as controlling factor had 23.33% of total samples and mostly contributed by samples from Obio/Akpor LGA.

The water bearing formations (aquifers) in the study area are usually varieties of sand (SiO_2) hence, the occurrence of significant concentrations of sodium and chloride ions could be linked to salt water intrusion from the sea. This explains why water samples within Port Harcourt LGA mostly fell in the Na-Cl fecies since it is very close to numerous seas (Figure 1). In addition, the existence of precipitation dominance for most of the samples as could be seen in both Figures 5 and 6 suggest that the formation of ions in the groundwater is majorly influenced by ion precipitation from seawater. Port Harcourt sand particles are known to easily bind with each other naturally thus, signifying that it contains calcite ($CaCO_3$). Hence, the weathering of these silicate rocks/minerals (SiO_2) which already contain calcite ($CaCO_3$) might have released calcium and carbonate ions as cation and anion respectively from $CaCO_3$. This could be the reason why some of the samples fell in rock weathering dominance in both Figures 5 and 6. Sewage and oil field drainages as well as other industrial effluents are capable of adding significant amount of chloride to groundwater reservoir. These could be anthropogenic sources of chloride in the samples since Port Harcourt is heavily industrialised.

The high concentrations of TDS compared to other parameters (ions) as displayed in Table 1 is due to the fact that TDS is usually the amount of solids that cannot be evaporated when water is heated thus, comprising ions, certain inorganic and organic matters as well as other particles. In other words, the TDS concentrations were higher because the total concentration of all the analysed ions is just a fraction of TDS. Concentrations of Mg^{2+}, K^+, SO_4^{2-} and HCO_3^- were relatively low compared to Ca^{2+}, Na^+ and Cl^- as could be seen in Table 1. The low concentrations might be because the precipitation rate of these ions in seawater is very low when compared with Cl^-, Na^+ and Ca^{2+} [19]. Municipal effluents that were not properly discharged could as well be a source of Mg^{2+} and K^+ in the groundwater since Mg and K are naturally found in foodstuffs (especially green vegetables) and are also used as dietary supplements, while failed septic tanks could contribute SO_4^{2-}. Nevertheless, the concentrations of the analysed parameters were within permissible limits set by WHO apart from chloride ion and TDS in certain areas including Borokiri, Abuloma and Amadi-Ama towns in southern part of the study area (Port Harcourt LGA). Besides, chloride is the dominance ion among all the analysed ions for the entire study area. Notwithstanding, the cations preponderance is of the order: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ while that of anions is of the order: $Cl^- > SO_4^{2-} > HCO_3^-$.

4 Conclusions

Based on the results obtained and the analysis carried out, the research has shown that the groundwater quality of Port Harcourt belongs to Na-Cl and Ca-Cl hydrochemical facies while the factors governing the formation of ions are precipitation and rock weathering. The dominance hydrochemical facies and controlling factor for ion formations in the entire study area are Na-Cl facies and precipitation since their percentages are 63.33% and 76.67% respectively compared to Ca-Cl facies (36.67%) and rock weathering (23.33%). Notwithstanding, aquifers in southern part of the study area (Port Harcourt LGA) are more influenced by the Na-Cl facies and precipitation factor than those in the norther part (Obio/Akpor LGA). The existence of the dominance hydrochemical facies (Na-Cl) is accredited to seawater intrusion while the dominance factor controlling ion formations (precipitation) is attributed to precipitation of ions from seawater. Hence, the rate of pumping out water from wells in the study area especially within Borokiri, Abuloma and Amadi-Ama towns in Port Harcourt LGA should be reduced so that the radius of influence (R) of the wells will not expand towards the sea to permit salt water intrusion.

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