Hydrochemical Evaluation of Groundwater in Parts of Afikpo, Southeastern Nigeria

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Abstract:- This work assesses the hydrochemical properties of groundwater in parts of Afikpo and its suitability for human uses. Groundwater samples were collected from boreholes for hydrochemical analysis in dry and rainy season. Twelve (12) doublet samples collected in each season were analyzed for various physicochemical parameters and the results compared with World Health Organization (WHO) standard for drinking water. The results indicate that majority of the water samples were within the WHO standard for drinking water. About 11% of the samples were contaminated with Calcium, Magnesium, Lead, Arsenic and Mercury which could be as a result of anthropogenic sources such as poor waste management, poor sewage disposal and application of fertilizer and pesticide. The computed water quality index shows that about 50% and 67% of dry and rainy season samples respectively were of excellent quality, 42% and 33% of dry and rainy season samples respectively were of good quality, while 8% of dry season samples were of poor quality which could be attributed to improper waste management around the area. The concentrations of major cations and anions follow the trend $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ and $SO_4^{2-} > Cl^{-} > HCO_3^{-} > CO_3^{-}$ respectively for both seasons.

Keywords:- *Concentrations, Groundwater, Physicochemical parameters, Samples, Water quality index.*

I. INTRODUCTION

Groundwater is one of the most widely used natural resources in the world. It is known to occur within the earth's sediments and rocks. The occurrence and distribution of this natural resource is restricted to some rock units (geological formations) commonly referred to as aquifers [1]. Groundwater constitutes the most widely used source of water supply in Ebonyi State, Afikpo inclusive. Earlier, groundwater was considered safe, more appropriate and often meets the desired criteria for quality when compared with surface water but nowadays due to improper waste management; pollution load also increases in groundwater [2].

Groundwater is important in all aspects of life [3] – [4]. Despite the importance of groundwater as a source of water supply in Afikpo area, not much has been done to ascertain the chemical composition and various factors that are capable of affecting groundwater quality in various parts of the area. The constant pollution of surface water in this area by quarry operators who discharge waste waters into stream and river channels have increased possible cases of water quality deterioration. This has been worsened by the usual shortage of surface water sources in the dry season. The migration of dissolve constituents in the Carbonate and Ferroginized Sandstone which is the main aquifer in the area is also of great concern to hydrogeologists and hydrochemists. It is against this background that Hydrochemical Evaluation of Groundwater in parts of Afikpo, Southeastern Nigeria is being carried out. In this study, an effort will be made to calculate the groundwater quality index for the aptness of groundwater source for human uses. This study will be apt as it will provide a data bank on the hydrochemical characteristics of groundwater sources of the area, which could be useful in reducing the risk of water borne diseases in the area. This data will be used by agricultural agencies, water and environmental management agencies for proper developmental planning.

II. DESCRIPTION OF THE STUDY AREA

A. Location

This study covers parts of Afikpo including Ngodo, Amuro, Mgbom, Ndibe, Amangbala, Ukpa, New Site, Amaechera and Amaizu, covering an area bounded by Latitudes 6° 50'N and 5° 55'N and Longitudes 7^0 53'E and $8^0$0'E (Fig. 1). It covers a total area of about 120km^2. The area is accessible through the Abakaliki – Afikpo Road, Okigwe (Amasiri) – Afikpo Road, as well as Cross River – Afikpo Road. The dominant drainage pattern in Afikpo area is controlled by Ndibe River and Ozizza River. The study area falls within the tropical rainforest vegetative zones of Eastern Nigeria. The vegetation is dominantly made up of grasses, shrubs, and trees that are favourably supported by soil type in the area. The vegetation is controlled by many factors including the drainage, topography, geology and rainfall [5]. Two main climatic seasons exist in the study area, namely the dry and the rainy seasons. Rainy season (wet season) commonly begins in March and ends in October, while the dry season often begins in November and ends in February. The area has an annual rainfall range of 1500-2000mm, with a mean of 1800mm [6].

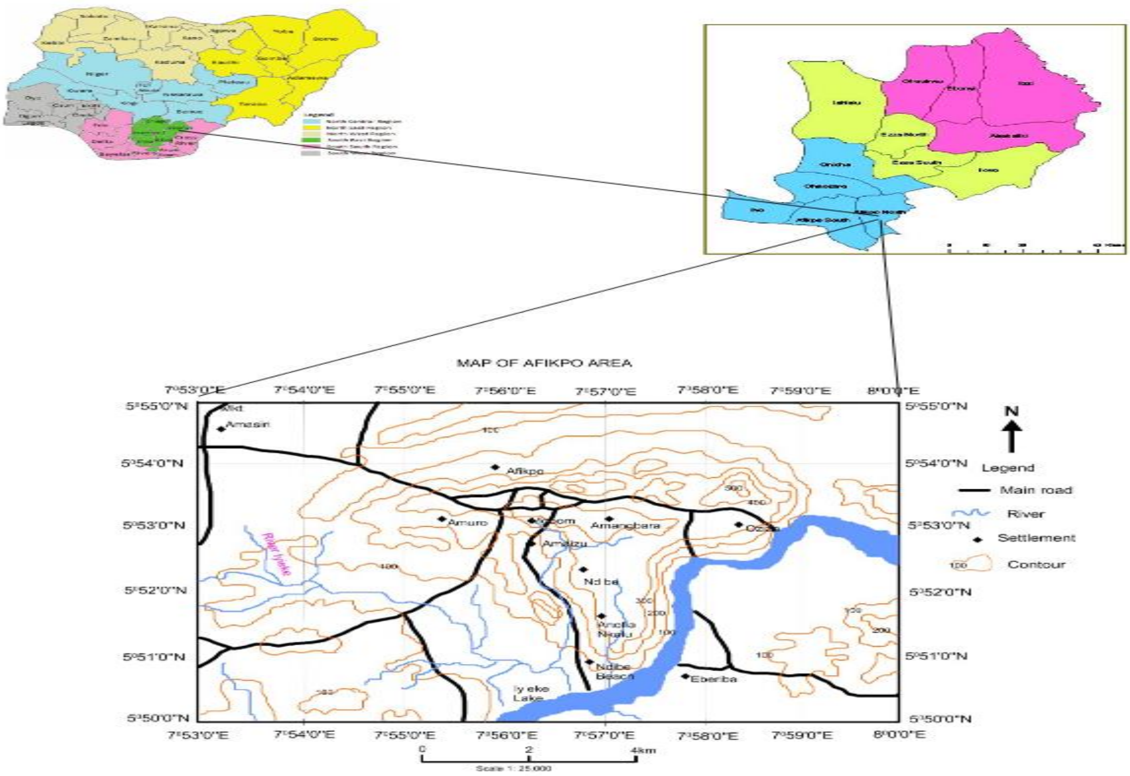

Fig. 1: Location and Accessibility map of the study area

B. Geology

Regionally, the area lies within the Southern Benue Trough, Southeastern Nigeria [7]. Benue Trough originated as a failed arm at the time of the opening of the South Atlantic Ocean during the separation of the African plate and the South American plate [8]. The lower Benue Trough comprises the Abakaliki Anticlinorium, Afikpo Synclinorium to the East and Anambra basin to the West. The Abakaliki Anticlinorium formed the axis of the Santonian uplift and represent stable structural feature, which controlled the development of the Anambra Basin and Afikpo Sub-Basin [9]. The evolution of the Southern Benue Trough was attributed to the differential phases of tectonic activities that occurred in the Cretacious time [10]-[11]. Locally, the study area consists of four components lithostratigraphic units; Ezeaku Group, which comprises of marine shales and limestones overlain by succession of dominant sandstones alternating with shales; Afikpo Sandstone, which consists mainly of fine to very coarse ferruginized sandstone and shale; Nkporo Formation which overlies the Afikpo Sandstone and consists of thick succession of fossiliferous dark-grey to black shales with intercalations of sandstone and ironstone and Mamu Formation that is made up of coal, shale and sandstone [13]. Afikpo area belongs to the lower and middle hydrogeological groups of Southeastern Nigeria and its aquifers are underlain by Ezeaku and Nkporo Formations [14].

III. MATERIALS AND METHODS

A. Sample Collection and Analysis

Groundwater samples were collected from boreholes for hydrochemical analysis in two different seasons (Dry and rainy season). Twelve (12) doublet samples were collected in each season using one (1) liter plastic water bottle which was rinsed with same water to sample, in order to avoid contamination from the container. One set for cation and heavy metal tests and the other set for anion tests. Samples for cation and heavy metal tests were stabilized with 2 drops of dilute HCl at the point of collection. This was necessary prior to transport to the laboratory in order to suppress hydrolysis, sorption and other processes that could influence concentration, all aimed at enhancing the accuracy of the result. The water samples were stored in an ice- packed cooler kit and sent to Springboard Analytical Laboratory, Awka, Anambra State for further analysis within twenty-four (24) hours of collection. Distilled water was used in the preparation of solutions and rinsing of all equipment after use. pH, conductivity and temperature were determined using pH Meter (Hanna model HI991300), electrical conductivity meter (Model DDS-307) and mercury -in- glass thermometers respectively. Total Dissolved Solid (TDS) was determined in the laboratory using TDS 139 tester. Hardness was determined in the laboratory by method of titration. Calcium and Magnesium ions were tested for using Varian Fast Sequential (FS) 240 Atomic Absorption Spectrophotometer (AAS). Flame photometer was used to analyze sodium and potassium ions. Anions comprising Sulphate, Bicarbonate, Carbonate and Chloride were tested by method of titration. Trace constituents including Arsenic,

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lead, mercury, cadmium, chromium were analysed using Varian AA240 Atomic Absorption Spectrophotometer.

B. Water Quality Index

The weighted arithmetic index method used by [15] in a similar study, in line with [16] was applied for the calculation of the WQI of the water samples. Further quality rating or sub-index (Q_n) was calculated using the following formula;

$$Q_n = \frac{Vn\text{-}Vo}{Sn\text{-}Vn} \times 100 \text{-------------- - } (1)$$

Where: Q_n = quality rating for the n^{th} water quality parameter V_n = estimated value of the nth parameter at a given sampling point, S_n = standard permissible value of the nth parameter Vo = ideal value of nth parameter in pure water (generally, V_o = 0 for most parameters except pH). Thus,

$$QpH = \frac{VpH\text{-}7}{8.5\text{-}7} \times 100 \text{----------------- } (2)$$

The unit weight was calculated by a value inversely proportional to the recommended standard value Sn of the corresponding parameter.

$$W_n = K/S_n \text{ - - - - - - - - - - - } (3)$$

Where: W_n = unit weight for the nth parameter S_n = standard value for the nth parameter K = constant for proportionality. The overall WQI was calculated by aggregating the quality rating with the unit weight linearly. Thus,

$$WQI = \frac{\sum QnWn}{\sum Wn} \text{ ------------------------- } (4)$$

Where: WQI = water quality index, ∑ = summation, Q_n = quality rating for the nth water quality parameter, W_n = unit weight for the nth parameter.

IV. RESULTS AND DISCUSSION

Results of dry and rainy seasons have been presented in table 1 and 2 respectively. The obtained values for the physicochemical parameters were compared with World Health Organization acceptable limits so as to ascertain if the concentrations were within the recommended limits.

Table 1: Concentration of various physicochemical parameters in dry season

Parameters	LC1	LC2	LC3	LC4	LC5	LC6	LC7	LC8	LC9	LC10	LC11	LC12	WHO, 2008
Temperature °C	28.40	27.20	28.00	28.60	27.40	28.20	26.80	27.00	27.20	26.80	28.00	27.00	
pH	7.04	7.54	7.70	7.82	7.60	7.40	7.02	7.50	7.80	7.90	6.90	7.92	6.5-8.5
EC µS/cm	100	60	50.25	40	80	70	60	50.50	100	90	40.25	60.25	500
Hardness mg/l	10.00	14.00	14.00	8.00	18.00	22.00	26.00	40.00	68.00	24.00	66.00	16.00	200
TDS mg/l	23	38	30	70	80	60	120	100	80	20	280	200	500
Calcium mg/l	0.922	1.562	1.461	0.852	4.342	8.431	12.53	8.956	120.6	3.864	92.24	14.24	75
Magnesium mg/l	5.693	4.783	4.289	4.178	3.479	6.871	4.361	3.875	64.42	3.672	23.376	8.749	50
Sodium mg/l	5.278	4.156	4.028	5.289	6.125	8.436	5.276	4.962	18.231	12.378	22.232	5.276	200
Potassium mg/l	2.899	3.267	3.082	3.863	3.231	5.347	6.212	3.872	9.259	8.371	12.561	2.341	50
Bicarbonate mg/l	22.50	15.00	12.50	12.50	16.00	12.50	12.00	40.50	120.0	22.50	100.0	16.00	250
Chloride mg/l	35	28	34	29	45	36	29	34	67	32	82	48	200
Sulphate mg/l	98.43	104.28	89.47	92.76	102.28	96.48	89.64	89.60	118.20	88.62	116.54	98.43	250
Carbonate mg/l	11.25	11.25	6.26	6.25	8.43	10.32	6.56	7.69	18.31	14.78	14.23	8.76	200
Lead mg/l	0.043	0.026	0.038	0.021	0.01	0.01	0.00	0.00	0.02	0.00	0.02	0.00	0.01
Arsenic mg/l	0.038	0.012	0.013	0.020	0.00	0.00	0.010	0.00	0.013	0.00	0.012	0.00	0.01
Cadmium mg/l	0.020	0.063	0.026	0.030	0.040	0.020	0.023	0.046	0.046	0.032	0.044	0.028	0.05
Chromium mg/l	0.037	0.032	0.018	0.007	0.007	0.019	0.024	0.036	0.042	0.032	0.027	0.016	0.05
Mercury mg/l	0.005	0.004	0.006	0.006	0.005	0.005	0.004	0.004	0.008	0.003	0.008	0.004	0.006

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Table 2: Concentration of various physicochemical parameters in rainy season

Parameters	LC1	LC2	LC3	LC4	LC5	LC6	LC7	LC8	LC9	LC10	LC11	LC12	WHO, 2008
Temperature °C	26.20	27.00	27.00	26.40	26.00	26.80	26.60	26.00	27.00	26.20	27.00	26.40	
pH	7.00	7.60	7.02	7.50	7.40	7.00	7.30	7.02	7.20	7.60	6.50	7.20	6.5-8.5
EC µS/cm	80	40	30	40	60.50	40.25	50	40.20	70	60	20	40.25	500
Hardness mg/l	12.00	14.00	12.00	18.00	16.00	24.00	26.00	28.00	52.00	16.00	48.00	10.00	200
TDS mg/l	20	30	30	60	80	60	140	120	60	40	180	160	500
Calcium mg/l	0.824	2.482	1.986	3.432	3.324	4.473	6.346	3.956	78.21	2.294	62.34	8.446	75
Magnesium mg/l	5.432	3.957	4.953	4.586	5.763	3.241	6.253	2.641	48.891	6.624	18.261	6.372	50
Sodium mg/l	5.276	3.126	3.456	6.289	5.456	6.435	4.569	4.901	10.211	8.925	11.261	4.761	200
Potassium mg/l	3.211	2.267	2.891	4.763	2.963	3.201	4.341	4.981	6.251	4.207	8.716	2.246	50
Bicarbonate mg/l	18.00	12.00	15.00	12.00	12.00	12.50	10.00	20.50	60.50	20.50	40.00	12.00	250
Chloride mg/l	30	20	28	32	36	28	27	30	45	22	52	42	200
Sulphate mg/l	88.23	94.28	86.42	94.70	98.26	76.46	78.64	83.60	98.87	84.62	96.92	72.46	250
Carbonate mg/l	11.20	9.26	6.24	6.22	7.34	11.23	4.66	5.62	12.33	9.72	14.30	6.76	200
Lead mg/l	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01
Arsenic mg/l	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.02	0.00	0.01	0.00	0.01
Cadmium mg/l	0.010	0.040	0.020	0.010	0.020	0.00	0.00	0.020	0.021	0.030	0.042	0.020	0.05
Chromium mg/l	0.030	0.029	0.010	0.009	0.010	0.016	0.020	0.031	0.038	0.031	0.021	0.014	0.05
Mercury mg/l	0.004	0.004	0.005	0.006	0.004	0.003	0.005	0.005	0.006	0.002	0.005	0.004	0.006

A. Hydrochemical Evaluation

The temperature of the water samples ranges from 26.80ºC to 28.60ºC, with mean value of 27.55ºC in the dry season while that of rainy season ranges from 26.00ºC to 27.00ºC with mean value of 26.55ºC. The relatively low temperature shows that the water sources were not affected by thermal pollution. pH values vary between 6.90 to 7.92 with mean value of 7.51 in the dry season and 6.50 to **7.**60 with mean value of 7.19 in the rainy season. This indicates that the water samples are slightly alkaline. Electrical conductivity values vary between 40µS/cm to 100µS/cm with mean value of 66.77µS/cm in the dry season and 20µS/cm to 80µS/cm with mean value of 47.60µS/cm in the rainy season. Total hardness values vary between 8mg/l to 68mg/l with mean value of 27.17mg/l in the dry season and 10 mg/l to 52 mg/l with mean value of 23.00mg/l in the rainy season, while Total Dissolved Solid (TDS) values vary between 20 – 280 mg/L with mean value 91.75mg/l in the dry season and 20 – 180 mg/L with mean value of 81.67mg/l in the rainy season. The physical parameters were all within World Health Organization (WHO, 2008) acceptable limit in both seasons.

Calcium concentration values for dry season water samples range from 0.852mg/l – 120.6mg/l, with mean value of 22.5mg/l, while those of rainy season water samples range from 0.824mg/l – 78.21mg/l with mean value of 14.843mg/l. The high concentration of calcium observed in the locations 9 and 11 could be attributed to the carbonaceous content of the dark gray shales present in the area. The concentration of magnesium in dry season water samples range between 3.479mg/l – 64.42mg/l with mean value of 11.478mg/l, while rainy season samples ranged from 2.641mg/l – 48.891mg/l with mean value of 9.74mg/l. WHO (2008) standards indicate that the permissible limit for magnesium is 50mg/l. The result shows that about 98% of the water samples in this study were all within the acceptable limit in both seasons. Sample location 9 in the dry season has a concentration of 64.42mg/l which is above the WHO permissible limit. The high concentration of magnesium in this location could be attributed to the presence of municipal waste around the area. The concentration of sodium and potassium ranges between 4.028mg/l – 22.232mg/l, with mean value 8.472mg/l and 2.341mg/l – 12.561mg/l, with mean value of 5.359mg/l, respectively in dry season and 3.126mg/l **-** 11.261mg/l, with mean value of 6.222mg/l and 2.246mg/l **-** 8.716mg/l, with mean value 4.169mg/l, respectively in rainy season. Sodium and potassium concentrations were all within permissible limit in both seasons.

Among the anions, the concentration of Bicarbonate, Chloride, Sulphate and Carbonate ranges between 12.00mg/l – 120mg/l with mean value 33.50mg/l, 28mg/l – 82mg/l with mean value of 41.58mg/l, 88.62m/l **-** 118.20mg/l with mean value of 98.73mg/l and 6.25mg/l – 18.31mg/l with mean value of 10.34mg/l, respectively for dry season and 10.00mg/l **-** 60.50mg/l with mean value of 20.41mg/l, 20mg/l **-** 52mg/l with mean value of 32.666mg/l, 72.46mg/l – 98.87mg/l with mean value of 87.79mg/l and 4.66mg/l – 14.30mg/l with mean value of 8.74mg/l respectively for rainy season. The major sources of chloride ion in the groundwater of the study area can be attributed to agricultural inputs and sewages. The results of the concentration of anions in the study area fall within permissible limit prescribed by World Health Organization (WHO, 2008). The concentrations of major cations and anions for follow the trend $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ and $SO_4^{2-} > Cl^{-} > HCO_3^{-} > CO_3^{-}$ respectively.

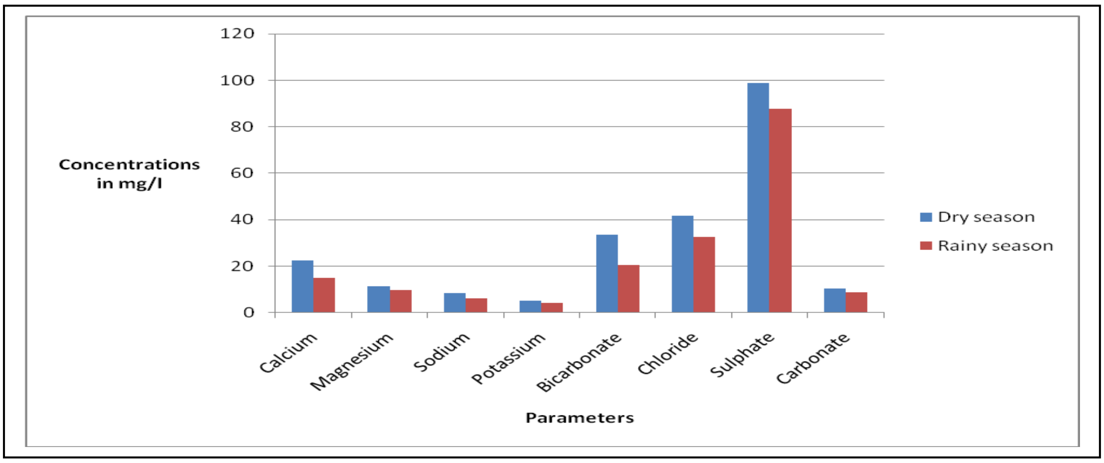

Fig. 2: Concentration of major ions in dry and rainy season

Lead concentration of dry season water samples range between 0.00mg/l - 0.043mg/l with mean value of 0.015mg/l, while rainy season sample ranges from 0.00mg/l - 0.01mg/l with mean value of 0.003mg/l. Locations 1, 2, 3, 4, 9 and 11 for dry season samples were above the WHO (2008) permissible limit of 0.01mg/l which could be attributed to waste product from paint industry and improper waste management around the area. Arsenic concentrations of dry season water samples ranges between 0.00mg/l - 0.038mg/l with mean value of 0.009mg/l, while rainy season sample ranges from 0.00mg/l – 0.02mg/l with mean value of 0.005mg/l. Locations 1, 2, 3, 4, 9 and 11 for dry season and locations 2 and 9 of rainy season samples were above the WHO (2008) guideline of 0.01mg/l for drinking water which could be attributed to anthropogenic activities such as application of fertilizer and pesticide in the area. The concentrations of Cadmium in dry season samples ranges between 0.02mg/l – 0.063mg/l with mean value of 0.034mg/l, while rainy season samples ranges from 0.00mg/l – 0.042mg/l with mean value of 0.019mg/. The result shows that about 8% of the samples have values above the WHO (2008) guideline of 0.05mg/l for drinking water which could be linked to incineration of wastes around the area. Chromium concentration in dry season samples range between 0.007mg/l – 0.042mg/l with mean value of 0.024mg/l, while rainy season samples range from 0.009mg/l – 0.038mg/l with mean value of 0.021mg/l. The water samples show low content for chromium in both seasons which is within the WHO (2008) permissible limit. Mercury concentration in dry season water samples ranges between 0.003mg/L – 0.008mg/L with mean value of 0.005mg/l while rainy season samples ranged from 0.002mg/L – 0.006mg/L with mean value of 0.004mg/l. About 12% of the samples have concentration of mercury above WHO (2008) permissible limit of 0.006mg/l. This can be linked to come from agricultural waste water.

B. *Water Quality Index (WQI)*

The values of water quality parameters were used to compute water quality index (WQI) using the standard for drinking water quality approved by [17]. The results of the Water Quality Index (WQI) of dry and rainy seasons are presented in table 3 and interpreted using Water Quality Index of [16] who classified water quality status as excellent (0 – 25), good (26 -50), poor (51 – 75), very poor (75 -100) and unfit for consumption (>100).

Table 3: Water Quality Index value for dry and rainy season samples

	Dry season		**Rainy season**	
Sample Locations	**Index Value**	**Water Quality Status**	**Index Value**	**Water Quality Status**
Location 1	5.272946	Excellent	3.53003	Excellent
Location 2	24.42909	Excellent	26.17484	Good
Location 3	30.30825	Good	4.022267	Excellent
Location 4	34.98822	Good	23.27089	Excellent
Location 5	27.08936	Good	19.41071	Excellent
Location 6	20.66267	Excellent	3.418057	Excellent
Location 7	5.93285	Excellent	16.07503	Excellent
Location 8	24.02033	Excellent	4.601499	Excellent
Location 9	60.33904	Poor	28.42911	Good
Location 10	39.60444	Good	27.24258	Good
Location 11	23.63447	Excellent	33.11576	Good
Location 12	41.35729	Good	12.00873	Excellent

Based on the computed water quality index, dry season samples LC1, LC 2, LC 6, LC7, LC 8 and LC11 (50% of the samples) were observed to be of excellent water quality, samples LC 3, LC 4, LC 5, LC 10, and LC 12 (42% of the samples) were found to be of good water quality while sample LC 9 (8% of the samples) were observed to be of poor quality. Also, the computed water quality index for rainy season shows that samples LC1, LC3, LC4, LC5, LC6, LC7, LC8, and LC12 (67% of the samples) were observed to be of excellent water quality while samples LC2, LC9, LC10, LC4, and LC11 (33% of the samples) were found to be of good water quality (Fig. 3a and 3b). The poor quality of sample Lc9 could be attributed to anthropogenic activities such as poor sewage disposal and application of fertilizer.

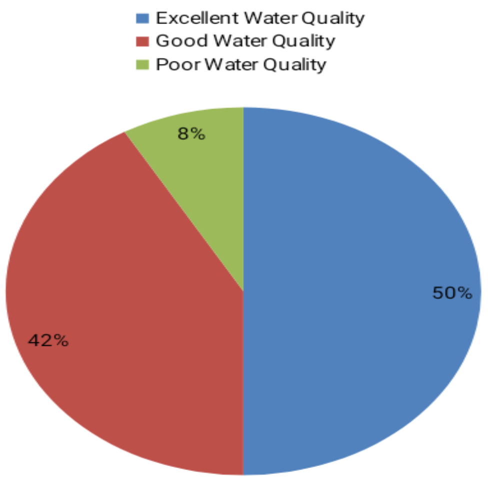

Fig. 3(a): WQI classification of dry season samples

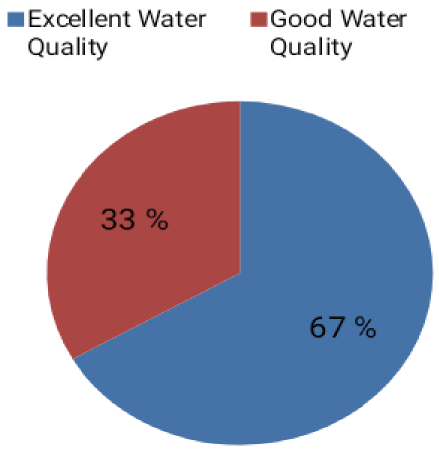

Fig. 3(b): WQI classification of rainy season samples

V. CONCLUSION

The study was carried out in Afikpo Area to assess the hydrochemical properties of the groundwater sources in the area. Hydrochemical analysis of the water samples were analyzed for various physicochemical parameters in both dry and rainy seasons. Results of hydrochemical analysis show that about 89% of the water samples were all within World Health Organization (WHO) permissible guidelines for drinking water. The high concentrations of Calcium, Magnesium, heavy metal such as lead, arsenic, mercury in some of the areas could be attributed to anthopogenic sources such as poor waste management, agricultural wastes water and application of fertilizers and pesticides. The computed water quality index for dry season shows that about 50% of the samples were of excellent quality, 42% of the samples were of good quality, while 8% of the samples were of poor quality. Results of water quality index for rainy season show that about 67% of the samples were of excellent quality, while about 33% of the samples were of good quality. The concentrations of major cations and anions follow the trend $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ and $SO_4^{2-} > Cl^{-} > HCO_3^{-} > CO_3^{-}$ respectively for both seasons.

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