Hydrogeochemical Characteristics and Quality of Groundwater fromOpoboTown in Rivers State Nigeria

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ABSTRACT

The hydrogeochemical characteristics and quality of groundwater from Opobo in Rivers State, were determined in this study. The levels of Physicochemical and Microbial Properties and Total Petroleum Hydrocarbonswere determined using standard methods recommended by the American Society for Testing and Materials,Gas Chromatography-Mass Spectroscopy for Polycyclic Aromatic Hydrocarbons and Atomic Absorption Spectrophotometer for Heavy Metals. Hydrogeochemical properties were determined by plotting Piper, Durov and Gibbs diagrams; Water Quality Indexwasdetermined using an adopted mathematical model. The results showed maximum mean levels of pH (8.0±0.1), Total Polycyclic Aromatic Hydrocarbons (1.106ppm), Total Heterotrophic Bacteria ($8.55 \times 10^2 \pm 9.12 \times 10^2$cfu/mL), Total Coliform Bacteria (2.00±2.83) and Faecal Coliform Bacteria (1.50±2.12) MPN/100mL.The pH levels of water in the areas were within set limits and the Total Petroleum Hydrocarbons levels were above acceptable limits. Plots of the Piper and Durov diagrams showed that the Hydrogeochemistry of the water in the area is characterized majorly by Ion Exchange, Reverse Ion Exchange and Simple Dissolution processes. Water Quality Indices showed that the water in the study area ranged from Excellent to Unsuitable for drinking. The results from this study showed that the water in the study area is poor for drinking purposes in some parts of the town and can pose health hazards to the population if consumed without proper treatment. Thus, adequate treatment of the groundwater water in the affected areas is recommended.

Keywords:Hydrogeochemical, Groundwater, Physicochemical, Water Quality Index, Opobo,

I. INTRODUCTION

Water is regarded as the second most essential component for human existence after air. Take away water human survival becomes a challenge. Water plays a critical role in human existence and its importance for individual health and well-being of a nation cannot be underestimated.

Globally, access to safe drinking water is a serious concern. A vast volume of the earth is composed mainly of water; nevertheless, fresh water resources consist of about 3% of the entire water obtainable and about 0.06% is readily accessible to mankind for survival. More than 80 countries in the world lacks assess to portable water and approximately 1.2 billion people consume water contaminated with pathogenic bacteria, protozoa and viruses. Every year, a significant number of (about 360 million) people suffer from water related illness which led to about 15 million deaths (Aluja, 2009;Tomar, 1999).

Interestingly, more than half of the water delivered for domestic and irrigation uses in the world is groundwater. The sad fact is that contamination of groundwater is a problem for about half of the world's population. A study conducted by the United Nation revealed that approximately 2.7 billion people will experience short fall of water supply by 2025 (Aluja, 2009).

In recent times, the global demand and assess for quality water has increased tremendously. This can be attributed to the rapid population growth, industrialization, urbanisation and climate change (Afolabi, 2017). The search for groundwater will continue to increase, and the consequent increase in demand, for safe drinking water, agricultural and industrial purposes in some part of the world due to the lack of rainy season or wet season (Afolabi,2017; Srinivan*et al,* 2014).

Groundwater is an important natural and primary source of freshwater for agricultural, domestic and industrial purposes in Nigeria. Approximately, 80 percent of rural water use and 50 percent of urban water supply is obtained from groundwater (Singh. *et al,* 2013). In recent times, groundwater extraction has gradually increased as a result of rapid growth in population, urbanization, industrialization and accompanying agricultural activities, hence, groundwater has turn out to be the main water resource for various uses (Satapathy and Syed, 2015). In the last three decades, groundwater resources have been under severe stress due to the ever-

increasing demand, leading to water deficit and deterioration of the quality of water in most parts of the world (Nandimandalam, 2012).

The geochemical study of groundwater plays a significant role, which help to identifying, assessing and evaluating the variation in the quality of water and its suitability for different uses. Knowledge on the chemical characteristics of groundwater is key, as groundwater quality depends on different factors including, quality of charge water, anthropogenic activities, climate variability, water-rock interaction, geological formation, degree of chemical weathering of the different rock types (Sophiya and Syed, 2013). The quality of groundwater resources is a source of concern, most especially in the coastal regions where groundwater is seen as the primary source for industrial, domestic and irrigation purposes. The quality of groundwater is mainly influenced by its over exploitation, mostly in the littoral areas in which large volume of freshwater extraction may result to invasion of sea water and subsequently increase the salinity of groundwater (Sophiya and Syed, 2013).

In addition to groundwater depletion, contamination and overexploitation of water resources has become a source concern and further complicates the low flow rate of groundwater in an aquifer and at the same time reducing the natural groundwater recharge (Hwang *et. al,* 2017).

All over the world, groundwater has become the primary source of water supply in both urban and rural areas for drinking, agricultural and industrial uses (Afolabi, 2017; Olayinka*et al.,*1999). Groundwater is replenished with precipitation and surface run-off. The dominant role of groundwater is clear and their uses and protections are, therefore, of paramount importance to human life and economic activity. In any hydrogeological setting, surface water and groundwater are the main sources of water supply.

These sources of water are prone to contamination and pollution by anthropogenic activities. Until recently, surface water has been the major source of water supply for domestic and industrial uses but, due to high population growth, the government has shown interest in the exploitation of groundwater over the years. Hence the need for water quality assessment for enhanced socio-economic growth and development (Ishaku, 2011).

Safe drinking water is a basic need for human development, and well-being and therefore an internationally accepted human right (Garg *et al.,* 2009). According to Oloke (1997), drinking water can act as a passive means of transporting nutrients into the body system. So therefore, the provision for good quality water for drinking, domestic and agricultural uses is very crucial for sound and good human and environmental health, economic and sustainable development (Al-Bassam and Al-Rumikhani, 2003).

Water quality depends on the physical, chemical and bacteriological composition of water. Variation in groundwater quality in an area is a function of physical and chemical parameters that are greatly influenced by geological formations and anthropogenic activities (Krishna *et al.,* 2011). According to Davis and Dewest (1966), drinking water standards are based on two main criteria namely; the presence of objectionable tastes, odour and colour and the presence of substances with adverse physiological effects.

However, mineral enrichment from underlying rocks can change the chemistry of groundwater, making it unsuitable for consumption (Ako*et al.,* 1990; 2011). In addition, water of poor physio-chemical quality may have adverse health effects causing avoidable economic and human losses. According to Hutchinson and Ridgeway, the water cycle is an obvious mode of transmission of enteric diseases.

Groundwater chemistry is altered as a result of the interaction between the subsurface formation and the percolating water. This brings about the need to understand the influence of the bedrocks on the groundwater system of the study area. Asides this geogenic influence, anthropogenic activity makes groundwater system prone to higher possibility of contamination. Therefore, a proper understanding of the groundwater in the study area is of importance as to maintain good quality water for drinking, domestic, industrial and agricultural purposes.

The people of Opobo Town primarily depend on groundwater mostly from domestic wells not until recently boreholes are been installedfor drinking and general uses. However, due to the anthropogenic activities within the community such as, raw sewage disposal, illegal oil bunkering, municipal discharge, indiscriminate dumpsites, human waste and unauthorized illegal exploitation of groundwater etc., there has been reported cases of communicable diseases, water borne diseases such as typhoid, cholera and skill diseases traceable to the quality of water in Opobo town. Thus, it is for this reason water is expected to be free from any form of health hazard hence it must be safe to drink, and suitable for domestic uses.

Therefore, in a way to protectthe healthand well-being of the people thereby reducing the rate of morbidity and mortality, it becomes pertinent to evaluate and monitor the quality of groundwaterin Opobotown.

II. MATERIALS AND METHODS
Description of the Study Area

The study area, Opobo town is located in River state, Nigeria. It is predominantly part of the Niger Delta between latitude 4°30′50″N (4.5138800^0) and long 7°32′16.6″E (7.5379400^0). It is positioned in the equatorial rain forest vegetation belt southeast Nigeria. Opobo Town forms part of the total area of 130 $km^2$of

the local government area with an average elevation of 4m above sea level. The study area is bounded on the South by the Atlantic Ocean, on the North by Khana, East by IkotAbasi and West by Andoni(Fig.1).

Sample Collection

Samples from domestic well and boreholes for physiochemical analysis were collected at different strategic locations of the study area. These wells and boreholes were selected, taking into consideration the anthropogenic activities carried out within the study area.
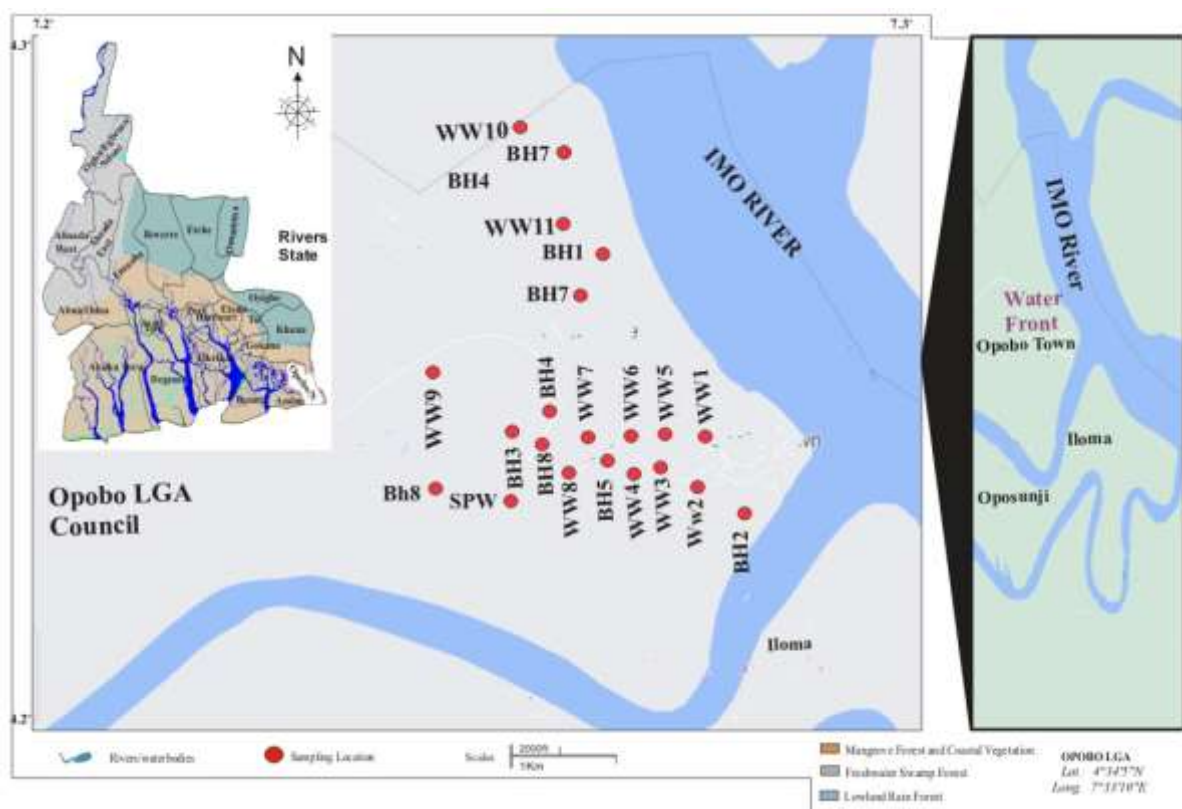

Figure 1:   Map of Study Area showing Sampling Points

Sample Pre-Treatment

Samples were collected in polyethylene bottles of one to two litre capacities. Prior to the collection of samples, the bottles were washed thoroughly and rinsed with water, dil. HNO_3, distilled water and a small quantity of the water to be sampled. All collected samples were properly and carefully labelled according to the name of the place or location.   Water samples collected were collected in sterile vials and transported to the laboratory and then filtered using the Whatman filter paper, then acidified using concentrated HNO_3 to maintain the pH at 2.Samples for microbial contents and heavy metals analysis were transported in an ice-box to the laboratory and stored in a refrigerator at $4°C$. Field (insitu) measurements of pH, electrical conductivity, turbidity and temperature weremade using Extecmultimeter.

Analysis of Physicochemical Properties

The research adopted the method proposed by American Public Health Association (APHA) (1995).

A pH meter (Model: Mettle Delta-340, England) was used to check the pH of the water samples. Calibration and standardization of the pH meter was done in the laboratory using a buffer solution and standard solution before using it to determine the pH of water samples.

Turbidimetric method was used to analyze the sulphate content of the water samples. Sulphate ion was precipitated in an acid medium with barium chloride to form barium sulphate crystals of uniform sizes. A spectrophotometer was used to measure the light absorbance of the barium sulphate at 450 nm.

A titrimetric method was used to determine the alkalinity. 3 drops of bromocresol green indicator was added to 10 mL of the water sample and was titrated against 0.01M solution of tetraoxosulphate (VI) acid. The titre value was used to calculate the alkalinity concentration in mg L^{-1} using the relationship:

$$\text{Total Alkalinity (mgL}^{-1}) = \frac{V \times N \times 1000}{\text{Vol of sample}} \qquad (1)$$

Where V is the Titre Value, N is the normality of tetraoxosulphate (VI) acid and 1000 is a constant.

The Argentometric method was used to determine the chloride content of the samples. Silver nitrate was reacted with chloride ion using potassium chromate as indicator. Quantitative precipitation of silver chloride was achieved before a red colour of silver chromate is formed.

The electrical conductivity of the water samples was determined using a JENWAY conductivity meter (Model, 4010) which had been calibrated in the laboratory using standard conductivity solutions. Electrical conductivity can be effectively converted to total dissolved solid by the following relationship:

TDS (mg L^{-1}) = EC (μS cm^{-1} at 25 ˚C) × 0.7 $\qquad$ (2)

Where, TDS is total dissolved salt or solid and EC is electrical conductivity.

EDTA titration method was used to determine total hardness. Calcium and Magnesium ions form complex with disodium salt of Ethylenediaminetetraacetic acid (EDTA). These complexes are more stable than their complex with indicators. Addition of EDTA to a solution of metal-indicator liberates the indicator which results in colour change. This principle is used for the detection of end point.Appropriate volume of samples was transferred into an Erlenmeyer flask and 1 ml of Ammonia buffer solution and 2 - 5 drops of Eriochrome black T indicator was added using a spatula.Samples were titrated with standard 0.01M EDTA solution till the colour changes to blue and burette reading was noted as R respectively.

$$\text{Total Hardness as CaCO3} = \frac{R \times M \times 100 \times 1000}{V} \qquad (3)$$

Where:
R $\qquad$ = Corresponding volumes in ml of EDTA added till end point.
M $\qquad$ = Molarity of EDTA solution.
V $\qquad$ = Volume in ml of sample taken

The cadmium reduction method was adopted for the measurement of nitrate content using a Lamotte smart-3-spectrophotometer.

Nitrate reagent powder was added to 25 mL of the sample previously poured into the sample cell and the concentration of nitrate was taken at a wavelength of 400 nm after 5 minutes; the nitrate concentration was determines as follows:

$$\text{Nitrate as NO}_3^{2-} = \frac{\text{Absorbance reading} \times 1000}{\text{Slope value} \times \text{Volume of sample(ml)}} \qquad (4)$$

Bacteriological AnalysisMicrobial Analysis

The pour plate method was adopted to perform Heterotrophic plate count (HPC) also known as standard plate count. Water to be tested is diluted serially and inoculated in lactose broth. Coliforms, if present in water, utilize the lactose present in the medium to produce acid and gas. The presence of acid is indicated by the color change of the medium and the presence of gas is detected as gas bubbles collected in the inverted Durham tube present in the medium. The number of total coliforms is determined by counting the number of tubes giving positive reaction and comparing the pattern of positive results with standard statistical tables (Microbesonline, 2021).After incubation, the gas production in Durham's tube was observed as well as the color change of the media.The number of positive results from each set was recorded and compared with the standard chart to give presumptive coliform count per 100 ml water sample (Aryal, 2018).

Determination of Heavy Metals

Samples collected from study area wereanalysed using Atomic Adsorption Spectrophotometer (AAS). To determine the number of heavy metals, the sample was aspirated into a flame where it became atomized. Abeam of light was directed through the flame into a monochromator and later into a detector that measured the intensity of the light energy absorbed. The quantity of light produced by a specific lamp, absorbed in the flame is directly proportional to the concentration of the element in the sample.

Determination of Polycyclic Hydrocarbons (PAHs)

Samples collected waskept in a micro vial of 100 micro litres, and preserved in the refrigerator until it was injected into gas Chromatography (GC-MS) equipment model 3800 Varian Gas Chromatograph equipped with a Varian Saturn 2200 mass spectrometry detector, coupled to a 30m x 0.25mm i.d. WCOTCP-S118CB column.

Water Quality Index (WQI)

The weighted numerical water quality index was used to assess the suitability for drinking purpose. In the method, water quality rating scale, relative weight and overall water quality index was calculated using the equation.

$$q_i = \frac{C_i}{S_i} X \ 100 \qquad (3.1)$$

where; q_i represents the quality rating scale, C_i indicates the concentration of the i parameter and standard value of i -parameter respectively

Therefore, the relative weight was computed as

$$w_i = \frac{1}{S_i} \qquad (3.2)$$

Such that the standard value of the ith parameter in inversely proportional to the relative weight

The overall water quality index (WQI) was determined using the equation below;

$$WQI = \frac{\sum_{i=1}^{n} q_i w_i}{\sum_{i=1}^{n} w_i} \qquad (3.3)$$

where; q_i = quality rating of ith water quality parameter, w_i = unit weight of ith water quality parameter =1

In this study, the National Sanitation Foundation water quality approach (NSF-WQI) of United State was adopted. The National Sanitation Foundation water quality NSF-WQI includes the following nine parameters of quality; total of dissolved solid (TDS), turbidity, pH, Nitrate, Phosphates, Coliforms, Dissolved Oxygen, BOD and temperature.

WQI- NSF is a positive integer ranging between 0-100; where, w_i indicates the weighing factor for each parameter, Q_i is the sun-index of the quality parameter which can be obtained from the conversion curve. Curves that convert parameters determine by values ranging between 0-100 (Ichwena et al, 2016).

III. RESULTS AND DISCUSSION

Results

The mean levels of physicochemical properties in groundwater samples from the study are shown in Tables 1 and 2.

Mean pH levels ranged from 6.8±0.9 - 8.0±0.1;Temperature levels were between 27±0.0 and 28±1.5 ˚C; Turbidity levels ranged from 0.80±0.00 - 10.65±13.93 NTU; Conductivity levels ranged from 116.1±18.2 - 4960.0±396.0μS/cm; Salinity levels ranged between 0.055±0.007 and 2.550±0.212 ‰; Total Dissolved Solids (TDS) levels were between 81.5±13.4 and 3475.0±275.8 mg/L; Total Hardness levels ranged from 12.1±3.8 - 181.0±28.2 mg/L; Alkalinity levels were between 47.0±24.0 and 207.0±171.1 mg/L; Chloride levels ranged from 13.1±3.8 and 377.9±338.8 mg/L; Sulphate levels were between 1.0±0.0 and 88.6±114.1 mg/L; Nitrate levels ranged from 0.050±0.000 to 2.593±0.893 mg/L; Phosphate levels were between 0.037±0.012 and 0.403±0.389 mg/L; Calcium levels ranged from 1.02±0.26 to 66.33±9.95 mg/L; Magnesium levels ranged between 2.38±0.42 and 21.65±25.96 mg/L; Sodium levels were from 8.64±2.49 to 362.39±494.42 mg/L; Potassium levels ranged from 5.02±0.00 to 68.84±0.00 mg/L; Bicarbonate levels were between 47.0±24.0 and 207.0±171.1 mg/L; Carbonate levels ranged from 1.66±1.90 to 51.13±27.98 mg/L and Total Hydrocarbon (THC) levels ranged from 11.32±13.85 - 50.29±40.42 ppm.

Variations in the levels of the physicochemical properties analyzed in the groundwater samples across the stations in the study area are shown in Figs. 2 – 3.

Table 1: Mean Levels of Physicochemical Parameters

STATION	pH	Temp °C	Turbidity NTU	Conductivity µS/cm	Salinity ‰	TDS mg/l	T Hard. mg/l	Alkalinity mg/l	Chloride mg/l	Sulphate mg/l	Nitrate mg/l
Well 1	7.0±0.5	27±1.0	1.55±0.78	571.5±539.5	0.275±0.262	399.0±376.2	88.4±13.4	63.0±52.3	35.8±33.2	15.3±17.1	1.372±1.899
Well 2	7.5±0.2	27±1.3	1.35±0.07	730.5±283.5	0.350±0.141	509.5±195.9	98.2±17.3	113.0±77.8	55.6±1.7	14.8±9.9	1.844±0.736
Well 3	7.5±0.4	27±1.3	0.80±0.00	991.5±227.0	0.490±0.113	694.5±159.1	132.6±52.7	163.0±69.3	59.3±17.5	14.8±10.6	2.593±0.893
Well 4	7.6±0.4	27±1.3	1.05±0.07	845.5±245.4	0.415±0.120	592.0±172.5	121.9±46.2	164.0±84.9	53.1±19.2	29.1±31.1	1.359±0.469
Well 5	7.7±0.4	28±1.3	5.15±5.73	665.0±275.8	0.325±0.134	465.5±193.0	90.5±31.9	137.0±55.2	50.6±1.7	7.0±3.7	0.050±0.000
Well 6	7.5±0.9	28±1.3	2.95±2.62	768.0±258.8	0.370±0.127	537.5±180.3	94.4±55.0	135.0±66.5	59.3±0.0	9.8±5.5	0.050±0.000
Well 7	8.0±0.1	28±1.2	1.15±0.21	900.0±499.2	0.325±0.092	628.5±347.2	98.9±1.3	146.0±48.1	46.9±10.5	40.5±47.6	1.723±1.011
Well 8	7.5±0.5	28±1.4	1.00±0.28	864.0±277.2	0.420±0.141	605.0±193.7	181.0±28.2	146.0±53.7	39.5±27.9	88.6±114.1	2.315±0.470
Well 9	7.8±0.5	28±1.3	1.95±1.77	921.0±239.0	0.540±0.000	644.5±167.6	153.4±45.8	195.0±97.6	38.3±26.2	54.1±68.3	0.966±0.025
Well 10	7.8±0.2	28±1.3	1.20±0.57	853.0±618.0	0.410±0.311	597.5±433.5	75.2±34.9	110.0±19.8	42.0±3.5	34.2±37.4	0.798±0.192
Well 11	7.5±0.7	28±1.5	7.90±10.18	883.5±258.1	0.510±0.014	618.0±179.6	116.8±20.6	134.0±31.1	51.9±45.4	33.0±34.4	2.068±0.760
BH 1	7.3±0.6	28±0.8	10.65±13.93	4960.0±396.0	2.550±0.212	3475.0±275.8	102.5±121.6	181.0±94.8	377.9±338.8	87.1±0.9	1.661±0.030
BH 2	8.0±0.0	27±0.0	1.10±0.00	413.0±0.0	0.190±0.000	282.0±0.0	108.9±0.0	70.0±0.0	29.6±0.0	19.0±0.0	2.009±0.000
BH 3	7.4±0.5	28±0.7	0.90±0.14	424.5±96.9	0.180±0.028	296.0±69.3	96.7±5.4	98.0±59.4	43.2±33.2	6.8±1.9	1.463±0.300
BH 4	7.4±0.4	28±0.8	2.15±1.48	346.8±389.2	0.170±0.198	243.0±271.5	71.9±81.5	99.0±114.6	43.5±53.8	1.0±0.0	0.690±0.801
BH 5	7.3±0.6	28±0.7	1.55±0.64	615.0±127.3	0.375±0.177	431.5±88.4	134.8±13.2	90.0±19.8	60.5±5.2	7.7±3.6	1.826±0.991
BH 6	7.5±1.3	28±0.8	1.30±0.57	731.0±164.0	0.355±0.092	508.5±119.5	114.7±2.2	207.0±171.1	79.0±17.5	8.4±7.3	1.863±1.047
BH 7	7.8±0.5	28±0.9	1.00±0.14	505.0±101.8	0.235±0.049	353.5±71.4	105.5±17.4	132.0±33.9	42.0±14.0	16.5±4.3	2.144±0.069
BH 8	7.1±0.6	28±0.9	0.90±0.14	124.6±20.4	0.055±0.007	87.5±14.8	33.3±31.9	47.0±24.0	31.1±25.8	3.7±3.4	0.050±0.000
Spring	6.8±0.9	28±0.6	5.30±5.66	116.1±18.2	0.055±0.007	81.5±13.4	12.1±3.8	49.0±21.2	13.1±3.8	3.0±1.7	0.155±0.138

Table 2: Mean Levels of Physicochemical Parameters

| STATION	Phosphate mg/l	Calcium mg/l	Magnesium mg/l	Sodium mg/l	Potassium mg/l	HCO_3^- mg/l	CO_3^{2-} mg/l	THC ppm	Total PAHs ppm
Well 1	0.054±0.005	30.80±4.33	2.82±0.62	27.17±5.37	19.72±0.00	63.0±52.3	1.72±0.04	50.29±40.42	1.106
Well 2	0.048±0.003	34.70±5.15	2.83±1.09	19.78±9.09	19.90±0.00	113.0±77.8	8.70±2.54	49.91±40.96	0.880
Well 3	0.096±0.037	48.94±19.58	2.55±0.94	45.45±17.76	19.72±0.00	163.0±69.3	14.20±5.21	11.32±13.85	0.857
Well 4	0.037±0.012	41.79±16.71	4.28±1.08	26.63±13.42	16.32±0.00	164.0±84.9	18.79±6.78	11.94±12.83	1.105
Well 5	0.049±0.004	32.36±12.11	2.38±0.42	12.30±2.47	10.06±0.00	137.0±55.2	18.28±6.29	12.04±12.97	0.993
Well 6	0.131±0.104	31.44±20.51	3.89±0.92	35.85±12.55	25.76±0.00	135.0±66.5	18.35±20.87	15.34±8.21	0.849
Well 7	0.084±0.033	32.37±1.84	4.41±1.43	45.99±27.39	40.60±0.00	146.0±48.1	51.13±27.98	13.67±10.56	0.846
Well 8	0.049±0.000	66.33±9.95	3.77±0.81	19.88±9.91	19.00±0.00	146.0±53.7	13.35±8.63	20.01±1.61	1.155
Well 9	0.178±0.116	35.86±16.21	15.54±1.30	28.66±14.28	35.32±0.00	195.0±97.6	35.78±21.25	12.99±11.48	1.014
Well 10	0.298±0.025	24.35±17.90	3.51±2.37	75.92±90.98	30.96±0.00	110.0±19.8	22.51±4.33	11.63±13.33	0.979
Well 11	0.234±0.116	38.17±7.28	5.24±0.59	44.33±19.57	41.60±0.00	134.0±31.1	16.69±16.69	11.94±12.83	0.960
BH 1	0.197±0.227	5.38±5.93	21.65±25.96	362.39±494.42	5.02±0.00	181.0±94.8	12.02±8.29	14.34±9.62	1.063
BH 2	0.066±0.000	32.88±0.00	6.53±0.00	26.88±0.00	17.70±0.00	70.0±0.0	22.42±0.00	23.31±3.25	0.903
BH 3	0.068±0.039	32.46±2.02	3.82±2.54	25.45±2.96	6.16±0.00	98.0±59.4	7.35±4.20	27.99±9.72	0.622
BH 4	0.376±0.468	22.71±29.65	3.71±1.81	22.30±25.80	6.84±0.00	99.0±114.6	4.78±3.27	17.82±4.70	0.384
BH 5	0.403±0.389	38.80±4.09	9.23±0.74	54.47±3.30	21.62±0.00	90.0±19.8	8.14±7.85	38.97±25.30	0.372
BH 6	0.265±0.060	31.16±1.48	8.98±1.44	79.88±1.47	34.34±0.00	207.0±171.1	37.44±47.16	44.97±11.45	0.432
BH 7	0.082±0.015	31.12±3.66	6.76±2.02	29.55±2.90	26.54±0.00	132.0±33.9	29.46±24.32	27.67±9.33	0.567
BH 8	0.050±0.023	6.27±7.55	4.30±3.18	11.67±6.18	68.84±0.00	47.0±24.0	2.33±1.87	16.67±6.33	0.486
Spring	0.060±0.014	1.02±0.26	2.31±0.76	8.64±2.49	11.40±0.00	49.0±21.2	1.66±1.90	13.27±11.23	0.939
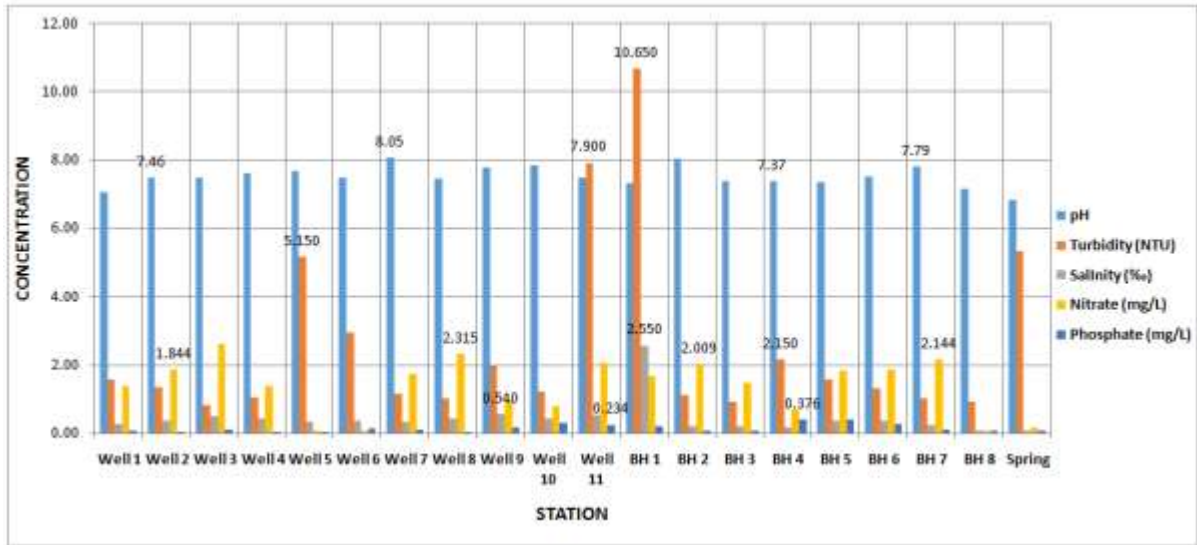
Fig. 2: Variations in Levels of some Physicochemical Properties
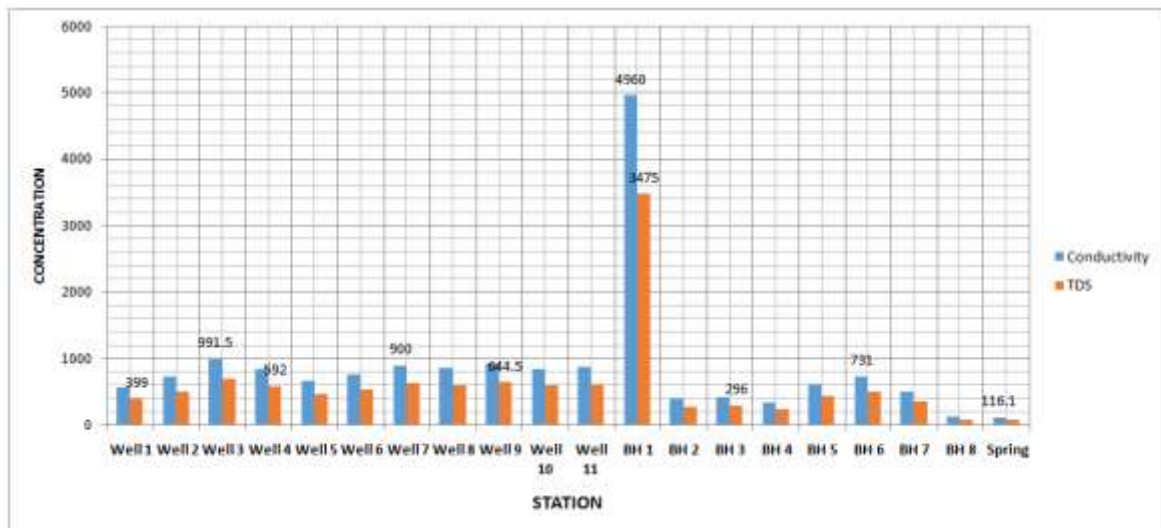

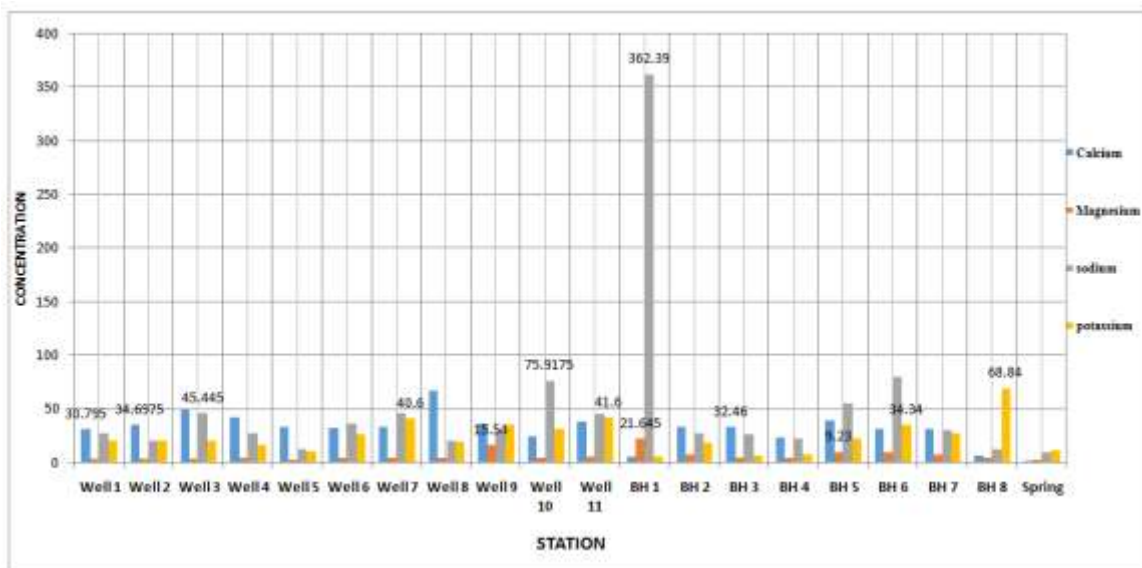**Fig. 3: Variations in Levels of some Physicochemical Properties**

Fig. 4: Variations in Levels of some Physicochemical Properties

Microbial Content Analysis

Results of microbial analysis of the groundwater samples are shown in Table 4.3.

Mean FaecalColiform Bacteria (FCB) count was between 0.00±0.00 and 1.50±2.12 MPN/100mL; Total Coliform Bacteria (TCB) count ranged from 0.00±0.00 to 2.00±2.83cfu/mL while Total Heterotrophic Bacteria (THB) count ranged between $1.10\times10^1\pm0.00$ and $8.55\times10^2\pm9.12\times10^2$cfu/mL.

Table 3: Mean Levels of Microbial Content and Total Hydrocarbon Parameters

STATION	FCB MPN/100ml	TCB cfu/ml	THB cfu/ml
Well 1	0.00±0.00	1.00±1.41	$3.05\times10^2\pm2.12\times10^1$
Well 2	1.50±2.12	2.00±2.83	$1.16\times10^2\pm9.12\times10^1$
Well 3	0.00±0.00	0.00±0.00	$8.40\times10^2\pm5.09\times10^2$
Well 4	0.00±0.00	0.00±0.00	$1.24\times10^2\pm1.36\times10^2$
Well 5	0.00±0.00	1.50±2.12	$5.05\times10^2\pm4.88\times10^2$
Well 6	0.00±0.00	$1.00\times10\pm0$	$7.60\times10^1\pm0.00$
Well 7	0.00±0.00	0.00±0.00	$3.90\times10^2\pm2.83\times10^1$
Well 8	0.00±0.00	0.00±0.00	$1.66\times10^3\pm1.33\times10^3$
Well 9	0.00±0.00	0.00±0.00	$3.54\times10^3\pm3.76\times10^3$
Well 10	0.00±0.00	0.00±0.00	$3.60\times10^3\pm3.68\times10^3$
Well 11	0.00±0.00	0.00±0.00	$7.50\times10^2\pm2.12\times10^2$
BH 1	0.00±0.00	0.00±0.00	$8.50\times10^9\pm1.20\times10^{10}$
BH 2	0.00±0.00	0.00±0.00	$1.10\times10^1\pm0.00$
BH 3	0.00±0.00	1.00±1.41	$4.80\times10^2\pm4.95\times10^2$
BH 4	0.00±0.00	0.00±0.00	$8.55\times10^2\pm9.12\times10^2$
BH 5	0.00±0.00	0.00±0.00	$1.33\times10^3\pm1.51\times10^3$
BH 6	0.00±0.00	0.00±0.00	$1.42\times10^3\pm1.53\times10^3$
BH 7	0.00±0.00	1.50±2.12	$4.50\times10^2\pm1.41\times10^2$
BH 8	0.00±0.00	0.00±0.00	$4.10\times10^2\pm2.12\times10^2$
Spring	0.00±0.00	0.00±0.00	$3.88\times10^3\pm3.54\times10^1$

Water Quality Index
The Water Quality Index values obtained for groundwater samples in the study area are shown in Fig. 5. The index values ranged between 36 and 643.

Hydrogeochemistry
Groundwater quality is also dependent on nature of bedrock, topography, geology, soils, climate, atmospheric precipitation and quality of the recharged water in addition to anthropogenic pollution sources in terms of agricultural and industrial activities. Gaining a clear understanding of the main factors governing groundwater chemistry is important for managing groundwater resources. The hydrogeochemical properties of groundwater in the study area were investigated by plotting the Piper, Durov and Gibbs diagrams.

Piper Trilinear Diagram
Piper Trilinear Diagram, developed by Piper (1944), evaluates the evolution of the river water and relationship between rock types and water composition. Plotting of samples on the Piper Trilinear Diagram reveals the composition of the water in the different sampling stations, indicating the water type.The milliequivalents of the various anions and cations are used and are plotted in two different triangular graphs as shown in Figure 4.5. The points of these anions and cations on the x, y and z axes of the triangular graphs are extrapolated to determine the dominant ion types. The extrapolated points on the triangular graphs are further projected onto the diamond graph to determine the water type.
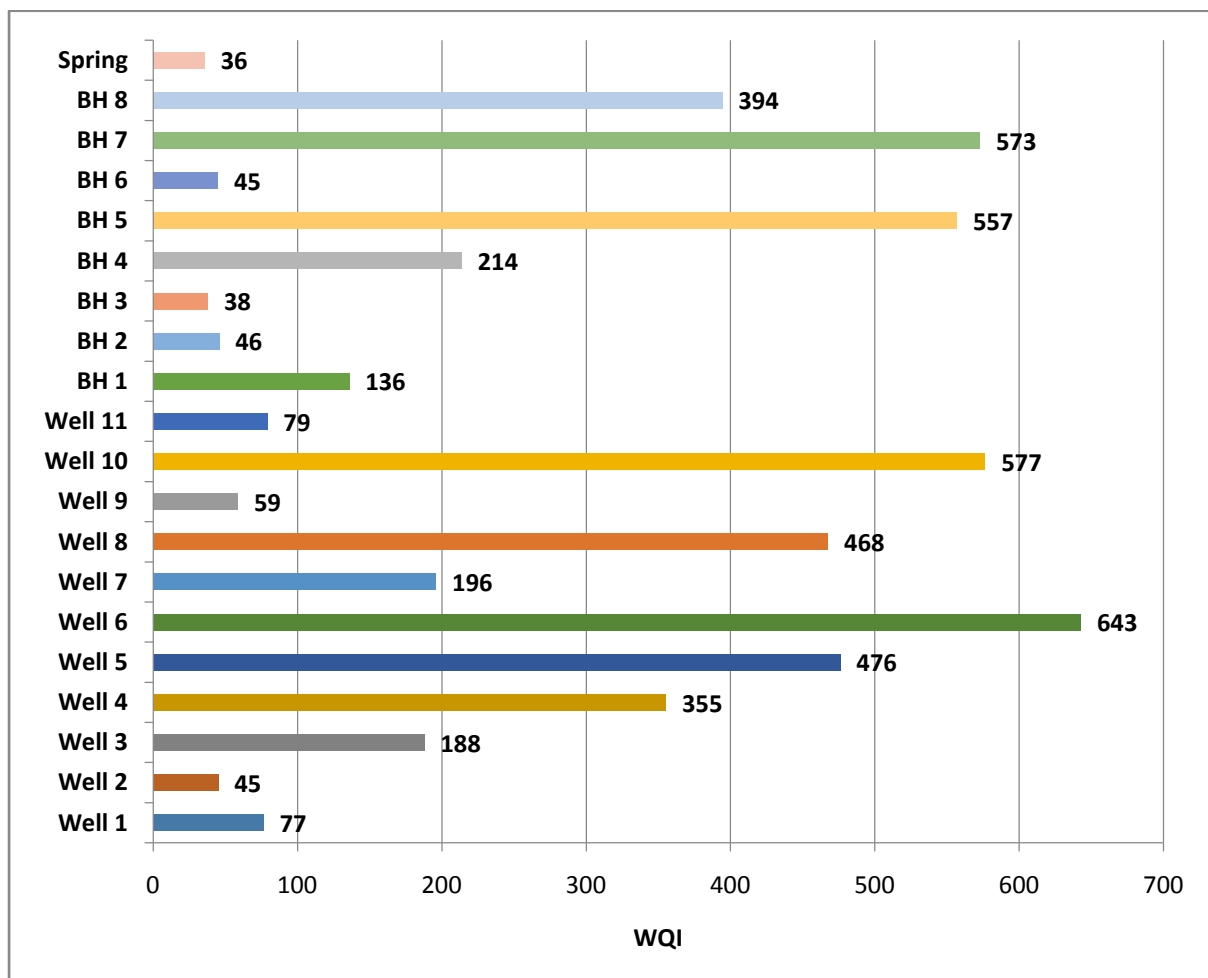

Fig. 5: Water Quality Index

WQI Rating:
0 – 50   = **Excellent,** 50 – 100 = **Good,** 100 – 200 = **Poor,** 200 – 300 = **VeryPoor**
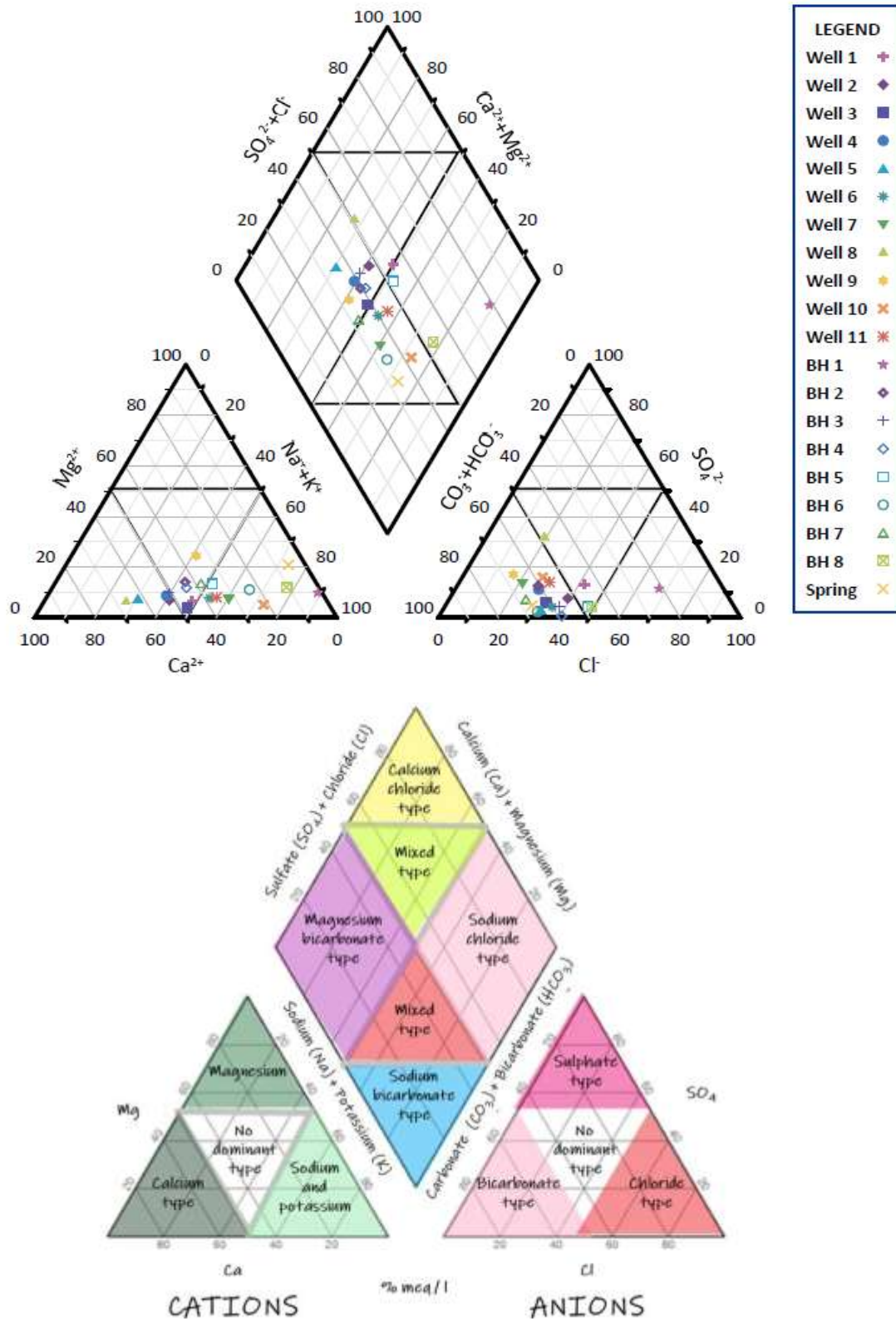>300 = **UnsuitableforDrinking**

Fig. 6: Piper Trilinear Diagram

Durov diagram
A Durov diagram (Fig. 7) is a useful graphical tool that is widely used to identify the chemical relationship and evolution of groundwater samples (Chen *et al*, 2019), and helps in the interpretation of the evolutionary trends and the hydrogeochemical processes occurring in the groundwater system. Like the piper diagram, milliequivalents of cations and anions are plotted on the triangular graphs and the extrapolated points are projected onto the square plot to determine the hydrogeochemical process.
Water in the study areas was plotted on the Durov's diagram and classified according to Lloyd and Heathcoat (1985) as shown in Table 4.

Gibbs Diagram
The Gibbs diagram is widely used to establish the relationship of water composition and aquifer lithological characteristics (Gibbs, 1970). According to the relationship between TDS vs $[Na^+/ (Na^+ + Ca^{2+})]$ and TDS vs $[Cl^-/ (Cl^- + HCO_3^-)]$, groundwater formation mechanisms are classified in three distinct fields such as Precipitation Dominance, Evaporation Dominance and Rock–Water Interaction Dominance areas, as shown in the Gibbs diagram (Fig. 4.7).
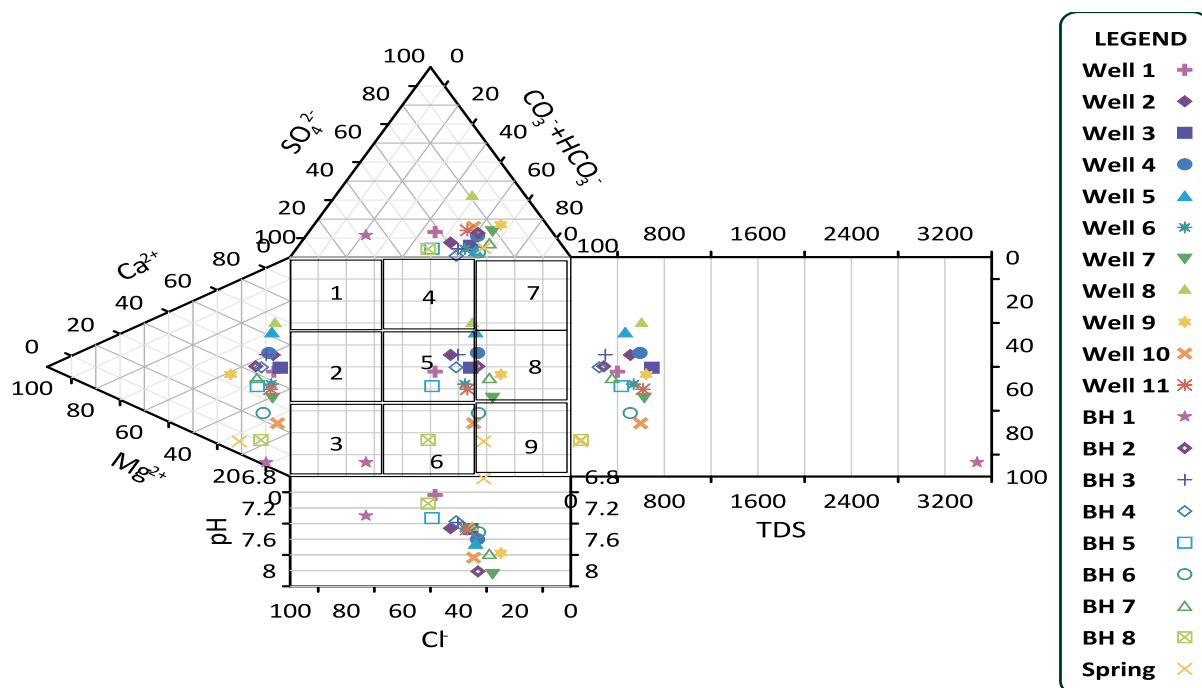

Fig. 7: DurovDiagram

Table 4: Classification of Water Based on Durov Diagram (Lloyd and Heathcoat, 1985)

Square No.	Description of Water Type
1	HCO_3^- and Ca^{2+} are dominant; this frequently indicates recharging waters in limestone, sandstone, and many other aquifers
2	This water type is dominated by Ca^{2+} and HCO_3^- ions. Association with dolomite is presumed if Mg^{2+} is significant. However, those samples in which Na^+ is significant, an important ion exchange is presumed
3	HCO_3^- and Na^+ are dominant; this normally indicates ion exchanged water, although the generation of CO_2 at depth can produce HCO_3^- where Na^+ is dominant under certain circumstances
4	SO_4^{2-} dominates, (or anion discriminant) and Ca^{2+} dominant; Ca^{2+} and SO_4^{2-} dominance frequently indicates recharge water in lava and gypsiferous deposits, otherwise mixed water or water exhibiting simple dissolution may be indicated.

| 5	No dominant anion or cation, indicates water exhibiting simple dissolution or mixing.
6	SO_4^{2-} dominant (or anion discriminate) and Na^+ dominant; this is a water type that is not frequently encountered and indicates probable mixing or uncommon dissolution influences.
7	Cl^- and Na^+ dominant; this is frequently encountered unless cement pollution is present, otherwise the water may result from reverse ion exchange of Na-Cl waters.
8	Cl^- dominant anion and Na^+ dominant cation; this indicates that the ground waters may be related to reverse ion exchange of Na-Cl waters.
9	Cl^- and Na^+ dominant frequently indicate end-point down gradient waters through dissolution
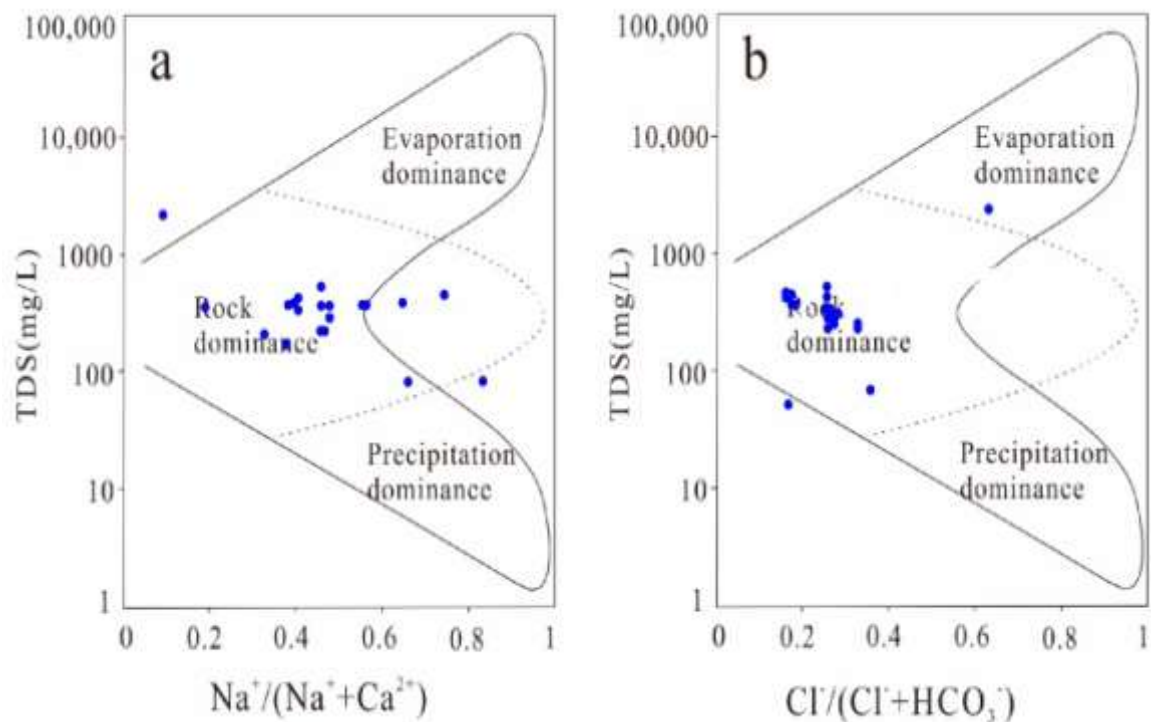
Fig. 8: Gibbs Diagram

Discussion
Physicochemical Properties

Levels of physicochemical properties analyzed in the groundwater samples were compared with acceptable limits set by WHO (1996), USEPA (2004) and NSDWQ (2015).

The mean pH levels of the groundwater samples were all within the WHO and USEPA acceptable limits of 6.5 – 8.5. The recorded pH levels in this study are not in agreement with those obtained for similar studies in Rumuola by Victor and Fortune (2020); who recorded lower pH levels, outside the permissible limits. The permissible pH levels may be attributed to the absence of decomposition of waste materials from dumpsites around the communities with the emission of landfill gases (Adoki, 2012). Also it could be due to the minimal level of anthropogenic activities that lead to pollution in the area (Udom and Acra, 2006).

The temperature levels obtained from the groundwater samples were within the NSDWQ acceptable limits. Temperature influences the reduction in solubility of gases in water, amplification of taste and colour and also

controls the rate of chemical reactions (Olajire and Imeppeoria, 2001). Generally, cool water is more potable than warm water; high water temperature enhances the growth of microorganisms and may increase problems related to taste, odour, colour and corrosion (WHO, 2011).

Turbidity levels in the groundwater samples were below the WHO acceptable limit of 5.0 NTU; except for samples at stations Well 5 (5.15 NTU), Well11 (7.90 NTU), Spring (5.30 NTU) and BH1 (10.65 NTU) which indicate the presence of particles in the Turbidity is an important parameter in drinking water analysis and it's also related to the population of disease-causing microorganisms present in water which could come from soil runoff (WHO, 2011).

All groundwater samples analyzed in the study area had electrical conductivity levels below the NSDWQ acceptable limit of 1000 μS/cm, except for borehole station 1 (BH1) which had EC levels of 4960 μS/cm. This was also in agreement with electrical conductivity levels recorded at Eliozu Community by Adesuyi*et al.* (2015). Meride and Ayenew (2016) reported similar conductivity values in a study carried out at Wondo Genet Campus, Ethopia. Electrical conductivity measures the degree of ions in water, which greatly affects taste and thus has a significant impact on the user's acceptance of the water.

The acceptable limit for TDS in drinking water is 500 mg/L as set by USEPA and NSDWQ. Analysis revealed that the stations, BH1 (3475.0 mg/L), BH6 (508.5 mg/L), Well2 (509.5 mg/L), Well3 (694.5 mg/L), Well4 (592 mg/L), Well6 (537.5 mg/L), Well7 (628.5 mg/L), Well8 (605 mg/L), Well9 (644.5 mg/L), Well10 (597.5 mg/L) and Well11 (618 mg/L) had TDS levels above the acceptable limit. TDS affect the taste of drinking water if present at levels above the standard limits. According to Otobo (1995), "the concentration and relative abundance of ions in waters is highly variable and depends mainly on the nature of the bedrock, precipitation and evaporation and crystallization processes".

Station BH1 recorded the highest salinity level of 2.550 ‰; and there are no set limits for salinity by WHO, USEPA or NSDWQ. The levels of electrical conductivity, salinity as well as TDS mostly go together (Amangabara*et al.*, 2012). High levels of salinity in water and soil may cause corrosion of machinery and infrastructure such as fences, roads and bridges, poor health or death of native vegetation, leading to a decline in biodiversity through dominance of salt-resistant species, potentially altering ecosystem structures and reduction in crop yields by impairing the growth and health of salt intolerant crops (Water Quality Australia, 2018).

The acceptable limit for total hardness (TDS) in drinking water is 150 mg/L as set by NSDWQ. All groundwater samples had total hardness levels below the acceptable limit except for stations Well8 (181.0 mg/L) and Well9 (153.4 mg/L). Ayozie (2022) also obtained similar levels of TDS in groundwater in a study carried out at Rumuola, Rumuigba and Rumuokwuta Communities, Rivers State. Hard water does not pose a health hazard, but may constitute a nuisance concerning its use for other domestic activities such as washing and household cleaning. Hardness is an important parameter in reducing the harmful effect of poisonous elements in water (Bhatt *et al.*, 1999); also continued intake of soft water has been linked to cardiovascular diseases (Miroslav and Vladimir, 1999).

Alkalinity levels were below the acceptable limit of 120 mg/L set by WHO for drinking water in all the groundwater samples. Alkalinity levels recorded in this study are in agreement with those obtained by Ayozie (2022). Alkalinity is a measure of weak acid and their salts present in water or as the acid neutralizing capacity of water body.

All groundwater samples analyzed in the study area had chloride levels below the NSDWQ and USEPA acceptable limit of 250 mg/L, except for borehole station 1 (BH1) which had chloride levels of 377.9 mg/L. Ayozie (2022) recorded chloride levels below permissible limits in a similar study carried out at Rumuola, Rumuokwuta and Rumuigbo Communities in Rivers State. Chloride is mainly obtained from the dissolution of salts of hydrochloric acid such as table salt (NaCl) and Na_2CO_3, and added through industrial waste, sewage, sea water etc. It has key importance for metabolism activity in human body and other main physiological processes. High chloride concentration damages metallic pipes and structure, as well as harms growing plants (Meride and Ayenew, 2016).

Sulphate levels in the groundwater samples were all below the NSDWQ and WHO acceptable limits of 100 mg/L and 250 mg/L respectively. Station Well7 recorded the highest sulphate level of 88.6 mg/L. The low concentrations of sulphate recorded in the groundwater samples could be due to the absence of anthropogenic activities that influence its concentration in water bodies. Sulphates naturally occur in groundwater via sulphides dissolution by percolating water, passing through the interstratified materials, such as pyrite, producing sulphate ions (Olobaniyi and Owoyemi, 2006).

Nitrate levels recorded in the groundwater samples were below the standard limits of 10 mg/L set by USEPA and 50 mg/L set by NSDWQ and WHO. The highest level of 2.32 mg/L was recorded at station Well8. Ayozie (2020) also recorded low nitrate levels in a similar study carried out at Rumuola, Rumuigbo and Rumuokwuta Communities. The low concentrations of nitrate recorded in the groundwater samples could be due to the absence of anthropogenic activities that influence its concentration in water bodies. Prolonged

exposure to nitrite and nitrate at levels above the maximum acceptable concentration could cause such problems as diuresis, increased starch deposits and hemorrhaging of the spleen (Reimann*et al*., 2003).

Calcium levels in the groundwater samples fell below the acceptable limit of 50 mg/L by WHO for drinking water, except for that of station Well8 which recorded level of 66.33 mg/L. The acceptable limits for magnesium are 50 mg/l and 20 mg/L as set by WHO and NSDWQ respectively. All samples fell below these set limits except for station BH1 (21.65 mg/L) which had level above the NSDWQ limit. Ayozie (2020) reported low calcium and magnesium levels, below their respective permissible limits, in a similar study carried out in Rumuola, Rumuigbo and Rumuokwuta communities. Leoni *et al.,* (1985), in studies carried out in Abruzzo, Italy, reported an inverse relationship between the hardness (Calcium and Magnesium ions content) of drinking water and cardiovascular diseases. It has also been reported that calcium and magnesium in drinking water may help protect against gastric, colon, rectal cancer, and pancreatic cancer, and magnesium may help protect against esophageal and ovarian cancer (Pallav, 2013).

The recorded potassium levels in the groundwater samples were all below the acceptable limit of 200 mg/L set by NSDWQ. Station BH8 recorded the highest level of 68.84 mg/L.

The highest and lowest bicarbonate levels of 207 mg/L and 47 mg/L were recorded at stations BH8 and BH6 respectively, while the highest and lowest carbonate levels of 51.13 mg/L and 1.66 mg/L were recorded at stations Well7 and Spring respectively. Edet*et al* (2011) reported a HCO_3^- level of 71.50 mg/L within the Niger Delta area. There is no set limit for bicarbonate and carbonate by WHO and NSDWQ. According to Davis and Dewiest (1966), bicarbonate rarely exceeds 40 - 400 mg/L in groundwater. Bicarbonate helps to buffer lactic acid generated during exercise and also reduces the acidity of dietary components (Mason, 2001).

Microbial Properties
Groundwater at stations Well1 (1.00 cfu/mL), Well2 (2.00 cfu/mL), Well5 (1.50 cfu/mL), Well6 (1.00×10 cfu/mL), BH3 (1.00 cfu/mL) and BH7 (1.50 cfu/mL) had Total Coliform Bacteria present and above the safety limit of 0.00 cfu/mL by NSDWQ. Total Heterotrophic Bacteria present and above the NSDWQ safety limit in all the stations with station BH1 having the highest count of $8.50×10^9$. However, all the groundwater samples showed no presence of Faecal Coliform Bacteria which, thus no rick of faecal contamination, except for station Well2 which had FCB count of 1.50 MPN/100mL above the NSDWQ acceptable limit of 0.00 MPN/100mL.

Water Quality Index
The Water Quality Index values obtained for the groundwater samples in the study area showed that stations Well2 (45), BH2 (46), BH3 (38), BH6 (45) and Spring (36) had their water quality rated as excellent for drinking; Well1 (77), Well9 (59) and Well11 (79) had their water quality rated as GOOD for drinking; Well3 (188), Well7 (196) and BH1 (136) had their water quality rated as POOR for drinking; BH4 (214) had its water quality rated as VERY POOR for drinking; Well4 (355), Well5 (456), Well6 (643), Well8 (468), Well10 (577), BH5 (577), BH7 (573) and BH8 (394) had their water quality rated as unsuitable for drinking.

Hydrogeochemistry
The plots of the Piper, Durov and Gibbs diagrams revealed the hydrogeochemical characteristics of the groundwater samples.

Piper Trilinear Diagram
The triangular plots of the Piper diagram reveal the ion types of the groundwater samples. The Cations showed dominance of the Na^++K^+ type, having 45% of the groundwater samples - Well 6, Well 7, Well 10, Well 11, BH 1, ABH 5, BH 6, BH 8 and Spring; 30% of the groundwater samples were of the mixed ion type - Well 1, Well 3, Well 9, BH 2, BH 4 and BH 7; while 25% of were of the Ca^{2+} type - Well 2, Well 4, Well 5, Well 8 and BH 3.
The Anions showed a dominance of the HCO_3^- type, having 75% of the groundwater samples - Well 2, Well 3, Well 4, Well 5, Well 6, Well 7, Well 9, Well 10, Well 11, BH 1, BH 2, BH 3, BH 4, BH 6, BH 7 and Spring; 20% were of the mixed ion type – Well1, Well1, BH5 and BH8; while 5% was of the Cl^- type (BH1).
The diamond plot reveals the classification of the water types. 45% of the groundwater samples (Well 2, Well 3, Well 4, Well 5, Well 9, BH 2, BH 3, BH 4 and BH 7) were classified as the Magnesium Chloride type; 40% (Well 1, Well 6, Well 7, Well 8, Well 10, Well 11, BH 6 and Spring) were classified as the mixed ion type; while 15% (BH 1, BH 5 and BH 8) of the samples were classified as the Sodium Chloride type.

Durov Diagram
The classification by Lloyd and Heathcoat (1985) was used to interpret the Durov Diagram.
The diagram revealed that 5 % of the samples (BH1) was plotted in square 3, indicating an exhibition of ion exchange process; 5 % (Well8) fell in square 4, indicating they exhibit simple dissolution or mixing process; 45

% (Well1, Well2, Well3, Well5, Well6, Well11, BH3, BH4 and BH5) fell in square 5, indicating they exhibit simple dissolution or mixing; 10 % of the samples (Well10 and BH8) were plotted in square 6, indicating an exhibition probable mixing or uncommon dissolution process; 25 % (Well4, Well7, Well9, BH2, and BH7) fell in square 8, indicating they exhibit reverse ion exchange process; while 5 % of the samples (BH6) was plotted in square 9, indicating an exhibition of dissolution process.

According to Lloyd and Heathcoat (1985), the three major water-rock interactions are Ion Exchange, Reverse Ion Exchange and Simple Dissolution or Mixing. Depending on the components of the rock type, groundwater quality is affected by either of these processes. For example, ion exchange with clay materials in rock formations can be responsible for the concentration of ions in groundwater. Direct ion exchange and reverse ion exchange processes can be expressed as shown in equations 5.1 and 5.2 respectively.

$$2Na^+ + CaX_2 = 2NaX + Ca^{2+} \qquad\qquad (5.1)$$
$$Ca^{2+} + 2NaX = CaX_2 + 2Na^+ \qquad\qquad (5.2)$$
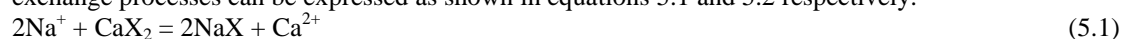
Where X indicates the soil exchanger

An excess of Ca^{2+} or Mg^{2+} in groundwater may be due to the exchange of Na^+ in the water by Ca^{2+} or Mg^{2+} in clay material, while an excess of Na^+ may be due to the exchange of Ca^{2+} or Mg^{2+} in the water by Na^+ in clay material.In simple dissolution, $CaCO_3$ in rocks, for example, can be readily dissolved by water giving rise to Ca^{2+} ions.

\Gibbs Diagram

The Gibbs diagram revealed that the groundwater chemistry in the study area is principally controlled by rock dominance. The 'rock-water interaction dominance' field indicates the interaction between rock chemistry and the chemistry of the percolation waters under the subsurface (Singh and Kumar, 2015).

IV. CONCLUSION

Results from the assessment of groundwater from twenty stations comprising eleven wells, eight boreholes and one spring, in the study area found pH levels to be within set limits. Levels of total hydrocarbons were found to be above permissible limits. Some stations had TDS levels above permissible limits. Most of the stations had Faecal Coliform Bacteria (FCB) countwithin standard limits. Total Polycyclic Aromatic Hydrocarbon (PAH) levels exceeded the permissible limit.Piper diagram revealed that Sodium-potassium ions and bicarbonate ions were found to be the dominant cations and anions respectively. As shown in the Durov diagram, simple dissolution/mixing, ion exchange and reverse-ion exchange and were the main hydrogeochemical processes governing the groundwater in the study area.The Water Quality Index classified the water in the area as ranging from Excellent to Unsuitable for drinking purposes.

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