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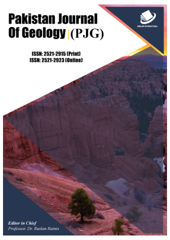

HYDROGEOCHEMICAL SIGNATURES AND QUALITY ASSESSMENT OF GROUNDWATER IN OKPOKO AND ENVIRONS, SOUTHEASTERN NIGERIA

Nwankwoala, H. O[1]*, Ememu, A. J[2]

[1]Department of Geology, University of Port Harcourt, Nigeria
[2]Department of Geology, Gregory University Uturu, Abia State, Nigeria
**Corresponding Author Email: nwankwoala_ho@yahoo.com*

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ABSTRACT

This study is aimed at assessing the hydro-geochemical signatures of groundwater in Okpoko and Environs in Anambra State, Southeastern Nigeria. Fifteen groundwater samples were collected and analyzed for physico-chemical, heavy metals and hydrocarbon content. Heavy metals in groundwater were analyzed using Atomic Absorption Spectrometer. The groundwater analyses revealed that average pH (6.05), Fe (0.68 mg/L) and Ni (0.028 mg/L) values exceeded WHO and NSDWQ guidelines. Total Petroleum Hydrocarbons (TPH) in groundwater were relatively very low and recorded only in BH1 (0.04 mg/L) and BH2 (0.002 mg/L) and below detectable limit for all other sampled boreholes. Piper diagram revealed two hydro-chemical facies: Mg-HCO_3 and Ca-HCO_3 rich water, while Stiff diagrams confirmed four distinct water types (Ca^{2+}, Mg^{2+}, HCO_3; Ca^{2+}, HCO_3; Ca^{2+}, Na^{+}+K^{+}, Cl^{-}, HCO_3; Ca^{2+}, Cl^{-} Class). Gibb's diagrams revealed that chemical weathering of rock and precipitation are the major influences on the groundwater quality. The various ionic ratios: Mg/Ca (0.56), HCO_3/Cl (3.31), (Na + K)/Cl (1.45), Na/K (1.61), Ca/Na (7.0), SO_4/Cl (0.67) and CEV (-0.45) suggests the groundwater sources are of inland origin. Groundwater flow direction shows that the area is drained by the Niger River on the western part of the study area.

KEYWORDS

Groundwater quality, water types, hydro-geochemistry, facies, heavy metals.

1. INTRODUCTION

Water is a major constituent all living things need to survive and it consists of approximately two-thirds of the human body weight [1]. Groundwater is very essential for life on earth as it is a good source of freshwater resource. As at 2012, over two billion people worldwide could not gain access to safe drinking water [2]. The consequences of drinking unsafe, contaminated water are enormous. According to World Health Organization, drinking contaminated water is one of the major causes of some illnesses such as diarrhea diseases; these diseases are one of the second leading cause of child mortality, which has led in the death of about 760,000 children aged <5 years yearly [2]. For this reason, WHO has identified the lack of access to clean drinking water as the most major factor that negatively influences the general health and well-being of populations in developing countries. Overall, providing safe drinking water can limit or eliminate preventable deaths and improve the quality of life for low-income households around the world [3].

Water quality, otherwise known as potability can be defined as the chemical, physical and biological properties of water as it concerns safe intake. It also involves the process of evaluating their physical, chemical and biological properties in relation to the natural quality and health effects [4,5]. Some researchers reported that water quality is enormously dependent on the indigenous geology, ecosystem, as well as human activities [6]. The potability of water may be dependent on the intended use of the water. For instance, much concern given to water required for direct human use compared to water used for industrial and other environmental purpose [7].

People around the world have used groundwater as a source of drinking water, and presently even more than 50 percent of the world's population depends on groundwater in order for them to survive [8]. Even in sub-Saharan Africa, groundwater has proven to be the most reliable source of drinking water [9]. Yet, groundwater is one of the biggest problems facing policy makers in order to sustain it. Natural filtration through soil and sediments makes the groundwater free from being contaminated by organic impurities. But as a result of some anthropogenic activities such as rapid urbanization, industrialization, exploitation of natural resources, pollution, heavy agricultural activities, the quality of soil and groundwater is greatly diminishing. Therefore, assessment of quality of soil and groundwater resources and the related hydro chemical study is necessary to undertake suitable management strategies to ensure that the water resources are fit for human needs.

2. BRIEF GEOLOGY AND HYDROGEOLOGY OF THE AREA

The area of study is located in Onitsha North Local Government Area of Anambra State and bounded geographically by longitudes 06° 06′ 00″ N to 06° 09′ 00″ N and latitudes 06° 45′ 00″ E to 06° 49′ 30″ E (Figure 1). Communities situated within the study area include Woliwo and Awada layout on the eastern part of the area. The town within which the site is located is thickly populated. Several fuel filling and service stations are cited at very close proximities. The major station in the area is located along Onitsha-Owerri Expressway at about 20m from the main road, about 30m from Power Holding Company of Nigeria (PHCN) High Tension cable, about 50m from residential buildings, about 200m from New motor parts dealers market, about 540m from St. Lwangas Hospital and Maternity, School of Health and Technology, about 300m from Sako Oil and Gas LTD fuel filling station at the left hand side of the road, and about 400m from Lake side Petroleum filling station on the right hand side of the road.Generally, the study area has very good road network and link roads. Two major rivers are responsible for draining the area which includes the Niger River and its major tributary, Ulasi River. However, there are local creeks and ponds all over the vicinity of the area [10].

The Anambra Basin which includes the study area is located at the southwestern extreme of the Benue Trough formed after the Santonian tectonic depression, dating back to 84 MYA [11]. It is a Cretaceous

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sedimentary domain partly bounded between the southern Benue Trough below and the Niger Delta Basin above. 1t originated following the subsidence of a platform in the southern Benue Trough, concurrent with the lateral translocation of the depocentres during the Santonian thermotectonic event that folded and was also elevated the Abakaliki region [12].

The basin is believed to have been formed as a direct impact of the stresses generated by the movement along the fracture zones. It is bounded to the west by the Precambrian basement complex rocks of the Western Nigeria and on the east by the Abakaliki Anticlinorium. At the Southern part, the boundary is at Onitsha, which is the northern-most limit of the Niger delta basin. The northern boundary of the Anambra basin is not well defined. The basin is connected with the NW-SE trending Bida Basin. Before the Santonian period, the south-western area of its rift valley was the tectonically stable Anambra platform. The Santonian compressional event was followed by magmatism, folding and faulting, which led to the formation of the Abakaliki Anticlinoruim. To the west and southward areas of the Anticlinorium was the depocentre, creating the Anambra and the Afikpo basins respectively [13]. Subsidence in these basins continued after the Santonian compression [14]. The 1sostatic response to the Early Cretaceous Crustal thinning and post drift thermal relaxation of the lithosphere was believed to be due to the accelerated subsidence that continued till the Eocene.

The Nkporo Group facies are dominantly aquicludes and aquitards. The Mamu Formation also made upg of mostly aquicludes and aquitards in its Lower parts, improving to fine sandstones at the top [13]. The Mamu Formation contributes nearly all the groundwater entering the Enugu coal mines. The source of recharge is by rainfall [15,16]. The main aquiferous formation of the Anambra Basin is the Ajali Formation. Its highly favorable texture allows for easy and rapid recharge in its extensive area in economic water yield in the upper units of the shales [13].

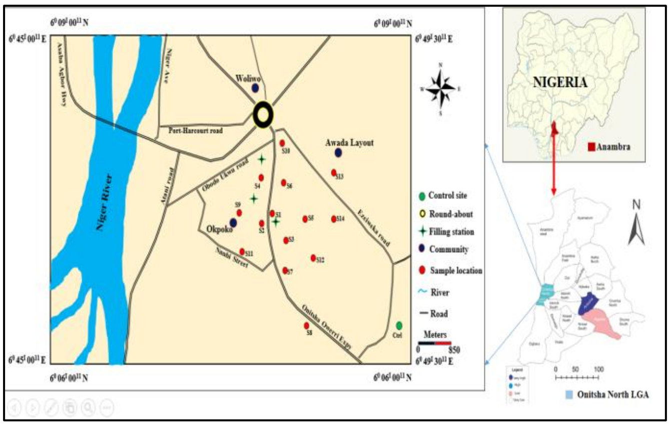

Figure 1: Map of the study area showing sampled locations

3. METHODS OF STUDY

3.1 Groundwater Sampling

Groundwater sampling in the study area was carried out during the raining season (March 2017). Fifteen (15) groundwater samples were collected from boreholes distributed randomly in Okpoko and Environs. The water samples were collected as close as possible to the well head to prevent loss of ions or contamination of the water. The water samples were collected in washed and pre-cleaned plastic bottles. Before sampling, the water was allowed to flow for about three minutes to prevent sampling of ions that have settled in the pipes. The sampling containers were washed with the water to be sampled several times before sampling began, and immediately corked to prevent introduction of oxygen. All the groundwater samples were carefully labelled and stored in ice before transportation to the laboratory for analysis. Parameters that were analyzed in-situ in the field include: pH, temperature and electrical conductivity using potable -held meters.

3.2 Groundwater Analysis

The physical, chemical, hydrocarbons and heavy metals were ascertained from each groundwater sample at Zetta Allied Digital Energy Laboratory, Elelenwo, Port-Harcourt, Nigeria. The pH of the samples was determined electronically using a Mettler Toledo Seven Easy pH Meter. Electrical Conductivity (EC) was determined using a conductivity meter. Temperature was determined using Mecury in glass thermometer. Turbidity was determined using a HACH2100AN Tubidimeter. Total Dissolved Solids (TDS) were determined gravimetrically. Alkalinity and Total hardness (TH) were determined by titrimetric method. Chloride was determined using titration method. Sulfates were determined using gravimetric method while nitrates were determined using Brucine method. Cations were analyzed using Flame photometer. Total Organic Carbon was determined by the Walkley-Black Titrimetric method. The Soxhlet Extraction Gravimetric method was used for determination of petroleum hydrocarbon such as Total Petroleum Hydrocarbons (TPH). Heavy metal concentrations were determined by acid digestion using nitric acid and further analyzed with Perkin Elmer A Analyst 200 Flame Atomic Absorption Spectrometer.

3.3 Results and Discussion of Groundwater Analysis

The results of physicochemical, heavy metals and hydrocarbon content in groundwater samples from the study area are presented in Table 1, while results of univariate statistical analysis are presented in Table 2 and compared with both World Health organization and Nigerian Standard for Drinking Water Quality [2,17].

Groundwater pH ranges from 5.3 to 7.1 with mean and standard deviation (SD) of 6.05±0.6 (Table 1). This indicates that groundwater in the area is predominantly acidic in composition. Only BH11 located 1km southwest of a major petrol filling and service station shows slightly basic composition. Hardness ranges from 5 to 108 mg/L with mean and SD of 48.22±35.52 mg/L. The high values of standard deviation and variance (1261.82 mg/L) shows a wide degree in the variability of groundwater hardness in the area. Hardness of water is highest at BH1 (filling station) and lowest at BH12. Turbidity ranges from 0.7 NTU at BH1 to 11 NTU at BH15 with mean and SD of 4.69±3.38 NTU. Temperature ranges from 24.11 at BH4 to 29.30^{0}C at BH1 with mean and SD of 27.01±1.58 ^{0}C. Electrical conductivity and TDS are relatively low and range from 3.20 to 139.32 mg/L and 8.65 to 180 mg/L with mean and SD of 47.32±45.20 mg/L and 78.49±58.71 mg/L respectively (Table 2). Total Petroleum Hydrocarbons (TPH) in groundwater were relatively very low and recorded only in BH1 (0.04 mg/L) and BH2 (0.002 mg/L) and below detectable limit for all other sampled boreholes (Table 1).

Table 1: Results of physicochemical and heavy metal concentrations in groundwater of the study area

Parameter	**Units**	**BH1**	**BH2**	**BH3**	**BH4**	**BH5**	**BH6**	**BH7**	**BH8**	**BH9**	**BH10**	**BH11**	**BH12**	**BH13**	**BH14**	**BH15**
pH		5.80	5.60	5.50	5.30	6.20	5.40	6.30	5.50	6.20	6.90	7.10	6.80	6.60	6.20	5.40
Hardness	mg/L	108.00	96.70	55.00	62.30	17.00	24.00	70.00	48.00	24.00	104.00	66.00	4.00	12.00	24.00	8.30
TDS	mg/L	140.00	118.00	35.32	180.00	77.21	81.43	104.57	11.23	18.32	10.44	145.22	134.21	100.32	8.65	12.43
Turbidity	NTU	0.70	4.00	10.00	3.20	0.90	3.40	2.00	0.89	7.60	3.20	8.00	5.60	2.30	7.50	11.00
EC	µS/cm	10.00	98.34	18.77	139.32	29.87	39.45	66.32	8.84	9.32	3.20	65.97	122.32	78.23	10.78	9.06
Temperature	^{0}C	29.30	26.20	25.40	24.11	28.00	28.40	26.54	28.50	24.32	27.40	25.60	28.00	28.30	27.30	27.80
Alkalinity	mg/L	12.30	10.00	11.20	8.40	12.00	18.00	23.00	9.40	18.00	13.00	14.20	10.00	11.30	12.43	16.00
TPH	mg/L	0.04	0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Cl^-	mg/L	13.30	20.00	18.98	10.00	17.00	13.54	36.00	34.94	45.00	23.44	23.10	67.32	12.47	18.00	16.55
SO_4^{2-}	mg/L	8.00	6.00	10.00	6.00	8.23	5.00	9.40	12.00	9.00	10.00	10.54	6.40	14.00	8.00	9.50
NO_3^-	mg/L	0.80	7.00	3.00	4.40	8.20	3.30	4.50	6.80	11.00	35.00	12.43	0.95	3.30	14.00	12.40
CO_3^{2-}	mg/L	32.00	30.00	23.00	45.00	19.00	24.00	43.00	12.00	40.00	18.00	30.00	23.20	18.00	19.00	23.00
HCO_3^-	mg/L	210.00	240.00	229.00	38.00	54.00	53.00	47.00	42.00	11.00	223.00	18.00	3.20	12.00	195.00	162.00
Ca^{2+}	mg/L	23.00	34.00	39.00	62.00	29.00	54.00	45.00	64.00	28.00	33.00	26.00	24.00	25.30	36.21	34.56
Mg^{2+}	mg/L	15.00	18.00	21.00	4.00	12.00	8.00	2.20	5.30	4.70	18.00	3.00	7.89	3.50	23.70	19.90

Na$^+$	mg/L	3.03	4.50	8.30	12.00	18.00	3.40	2.43	16.00	14.50	4.60	12.00	13.00	18.00	23.43	3.40
K$^+$	mg/L	8.20	8.70	6.80	24.00	18.40	16.00	17.60	15.00	14.80	7.80	18.00	18.44	7.30	6.80	8.30
Fe	mg/L	3.70	2.40	1.67	0.53	0.21	0.30	0.007	0.001	0.021	0.025	0.014	0.001	<0.001	<0.001	0.022
Pb	mg/L	0.0012	0.007	0.004	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.0011	<0.001	<0.001	<0.001	<0.001
Cd	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ni	mg/L	0.048	0.05	0.056	0.034	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	<0.001	<0.001	0.006
Cu	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Zn	mg/L	1.09	2.43	0.43	0.77	0.34	1.65	0.83	2.30	0.71	2.20	1.09	3.12	0.04	0.07	0.21
Mn	mg/L	0.31	0.21	0.034	0.05	0.04	0.06	0.02	0.001	0.07	<0.001	0.01	<0.001	0.07	<0.001	<0.001
Hg	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Table 2: Results of Univariate statistical analysis of groundwater quality compared with regulatory limits

Parameters	**Units**	**Min**	**Max**	**Mean**	**SD**	**Variance**	**WHO (2011)**	**NSDWQ (2007)**
Physical properties								
pH		5.3	7.1	6.05	0.6	0.36	6.5-8.5	6.5-8.5
Hardness	mg/L	4	108	48.22	35.52	1261.82	500	150
TDS	mg/L	8.65	180	78.49	58.71	3446.7	1200	500
Turbidity	NTU	0.7	11	4.69	3.38	11.46	5	5
EC	µs/cm	3.2	139.3	47.32	45.2	2042.92	1250	1000
Temp	^{0}C	24.11	29.3	27.01	1.58	2.5	Ambient	Ambient
Alk	mg/L	8.4	23	13.28	3.96	15.67	400	NA
TPH	mg/L	<0.001	0.04	0.02	0.03	0	NA	NA
Chemical properties								
Cl$^-$	mg/L	10	67.32	24.64	15.38	236.48	250	250
SO$_4^{2-}$	mg/L	5	14	8.8	2.41	5.83	500	100
NO$_3^-$	mg/L	0.8	35	8.47	8.49	72	50	50
CO$_3$	mg/L	12	45	26.61	9.86	97.16	NA	NA
HCO$_3$	mg/L	3.2	240	102.5	93.48	8739.14	NA	NA
Ca	mg/L	23	64	37.14	13.39	179.3	75	70
Mg	mg/L	2.2	23.7	11.08	7.53	56.64	50	30
Na	mg/L	2.43	23.43	10.44	6.73	45.29	200	200
K	mg/L	6.8	24	13.08	5.62	31.58	55	200
Heavy metals								
Fe	mg/L	<0.001	3.7	0.68	1.17	1.38	0.3	0.3
Zn	mg/L	0.04	3.12	1.152	0.967	0.936	5	3
Ni	mg/L	0.001	0.056	0.028	0.024	0.001	0.02	NA
Mn	mg/L	0.001	0.31	0.08	0.095	0.009	0.2	0.2
Pb	mg/L	0.001	0.007	0.003	0.003	-	0.01	0.01
Cu	mg/L	<0.001	<0.001	<0.001	0	-	1	1
Cd	mg/L	<0.001	<0.001	<0.001	0	-	0.003	0.003
Hg	mg/L	<0.001	<0.001	<0.001	0	-	NA	NA

Cations and anions were relatively very low in groundwater samples from the study area (Figure 2). For cations, calcium ranges from 23 in BH1 to 64 mg/L in BH8 with mean and SD of 37.14±13.39 mg/L while magnesium ranges from 2.20 to 23.70 mg/L with mean and SD of 11.08±7.53 mg/L (Table 2). Sodium and potassium ranged from 2.43 to 23.43 mg/L and 6.80 to 24.0 mg/L with mean and SD values of 10.44±6.73 and 13.08±5.62 mg/L respectively. For anions, bicarbonate and carbonate has the highest average concentrations, ranging from 3.20 to 240 mg/L and 12 to 45 mg/L with mean and SD of 102.48±93.48 and 26.61±9.86 mg/L respectively, whereas, nitrate had the lowest mean concentration, ranging from 0.80 to 35 mg/L with mean and SD of 8.47±8.49 mg/L. Chloride and sulphate has both mean and SD values of 24.64±15.38 mg/L and 8.80±2.41 mg/L respectively.

For heavy metals, zinc and iron recorded the highest concentration, ranging from 0.04 to 3.12 mg/L and <0.001 to 3.70 mg/L, with mean and SD of 1.15±0.97 and 0.68 to 1.17 mg/L respectively (Table 2). Nickel and manganese ranges from 0.001 to 0.056 mg/L and 0.001 to 0.31 mg/L with mean and SD values of 0.028±0.024 and 0.08 to 0.095 mg/L. Lead composition ranged from 0.001 to 0.007 and have mean and standard deviation values of 0.03±0.003 mg/L. Copper, Cadmium and mercury had compositions too low to be detected by the measuring equipment.

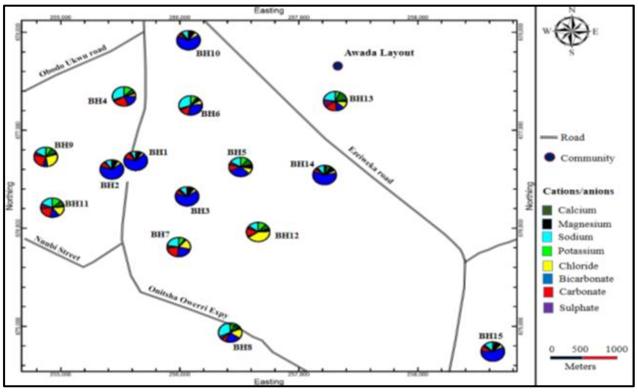

Figure 2: A map showing the anions and cations distribution within the study area

3.4 Groundwater Classification and Hydro-geochemical Signatures

3.4.1 Piper Diagram

A researcher introduced a Trilinear diagram for evaluating the geochemical evolution of water and relationships between rock type and water composition. Analysis of piper's trilinear plot for groundwater in the area shows that Mg, Ca and HCO_3 are the dominant cations and anions, hence, the groundwater samples are classified asMg-HCO_3 and Ca-HCO_3 hydro chemical facies (Figure 3).

3.4.2 *Stiff Diagram*

Stiff (1951) diagram classifies groundwater quality on the basis on similarity in shape. Water of similar quality has a distinctive shape. The diagram is plots cations on the left and anions to the right hand side. This classification method is a complement to Piper Trilinear diagram. Four different shapes were distinguished from the Stiff plots for the groundwater sources (Figure 4). Groundwater from BH1, BH2, BH3, BH10, BH14 and BH15 display identical shapes, with Ca^{2+} and Mg^{2+} being the dominant cations, while bicarbonate is being the dominant anion. Class II groundwater includes BH4, BH6, BH7 and BH8, which all display similar shapes, with Ca^{2+} being the dominant cation, while bicarbonate is the predominant anion. Class III water includes BH5, BH9, BH11 and BH13, and has Ca^{2+} and $Na^+ + K^+$ as the dominant cations and Cl^- and bicarbonate as the dominant anions. Only BH12 belongs to Class IV category, having Ca^{2+} as the dominant cation and Cl^- as the dominant anion. The distribution of the various hydro-chemical facies can be clearly visualized on map view (Figure 4).

3.4.3 *Durov Diagram*

The major ions of the groundwater samples were plotted on Durov's diagram because it helps in the interpretation of evolutionary trends and reveals the hydro-chemical processes occurring in any groundwater system. The Durov diagram revealed three geochemical processes that could affect the water genesis in the area. The plot was contoured and colored using Total Dissolved Solids concentration (Figure 5). Most of the groundwater samples (8 samples) plotted in Field 3, which is Na and HCO_3 dominant (Figure 5). These usually result from ionic exchange of Ca-HCO_3 rich waters. Two of the groundwater samples plots in Field 5, which is a field of no dominant anion or cation and indicates water exhibiting simple dissolution or mixing. The remaining 5 samples plotted in Field 6, which are SO_4 and Na dominant. This water type is not frequently encountered and indicates probable mixing or uncommon dissolution influences.

3.4.4 *Gibbs Diagram*

Gibbs plot (Figure 6) is used to interpret the effect of hydrogeochemical processes such as precipitation, rock–water interaction and evaporation on groundwater geochemistry. With a view to discerning the source of contamination of water in an area, Gibbs ratio (GR) plot is a useful tool to find the interaction between rock and water. The concentration of dissolved ions in groundwater samples are generally governed by lithology, nature of geochemical reactions and solubility of interaction rocks. The functional sources of dissolved ions can be broadly assessed by plotting the samples, according to the variation in the ratio of $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ as a function of TDS [18].

$$\text{GR-I (for anion)} = Cl^-/\ Cl^- + HCO_3^- \qquad (1)$$

$$\text{GR-II (for cation)} = Na^+ + K^+/\ Na^+ + K^+ + Ca^{2+} \qquad (2)$$

Where all ions are represented as meq/L.

Gibbs ratios for the all samples are plotted against TDS (ppm) in Figure 6 to know whether the groundwater chemistry is due to rock dominance, evaporation dominance or precipitation dominance. From the pot of the Gibbs Ratio plot it is visible that, most of the samples are rock dominated (shown in dash line area) and rest of the samples suggested to be precipitation dominated. This scenario suggests that the evaporation control field increases salinity by the increasing ions of Na and Cl in relation to increase in TDS and agricultural fertilizers.

3.5 Mechanism Controlling Groundwater Quality

The chemical data of groundwater samples were plotted in Gibbs's diagram (Figure 6a & b) which is widely employed to assess the functional sources of dissolved chemical constituents, such as precipitation-dominance, rock-dominance, and evaporation-dominance [18]. The distribution of groundwater samples suggests that the chemical weathering of rock-forming minerals along with precipitation from the surface is influencing the groundwater quality. Hence, rock-water interaction and rainfall are responsible for the ions in the groundwater sources.

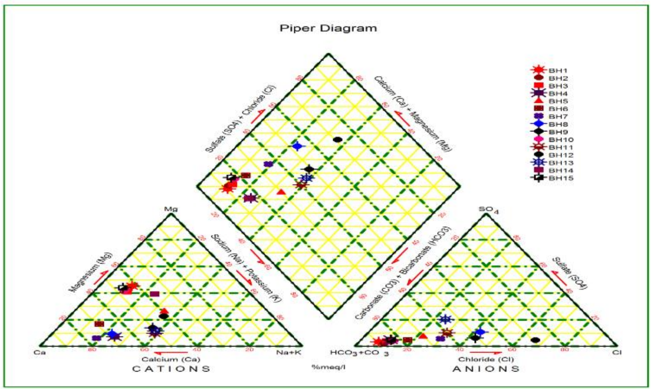

Figure 3: Piper Trilinear diagram of Cations and Anions of the study area

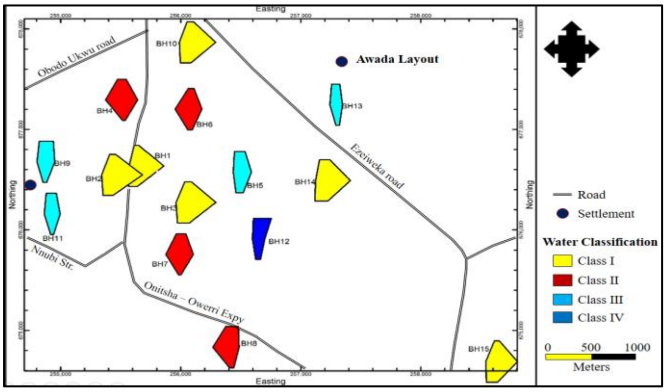

Figure 4: Map of the study area showing groundwater classification using stiff diagrams

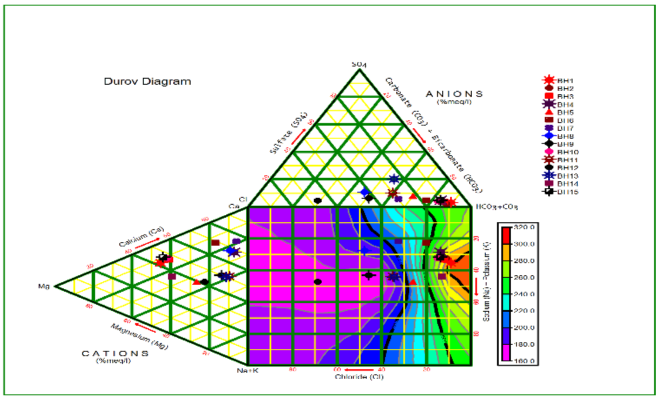

Figure 5: Durov plot depicting hydrochemical processes acting on groundwater sources in the area.

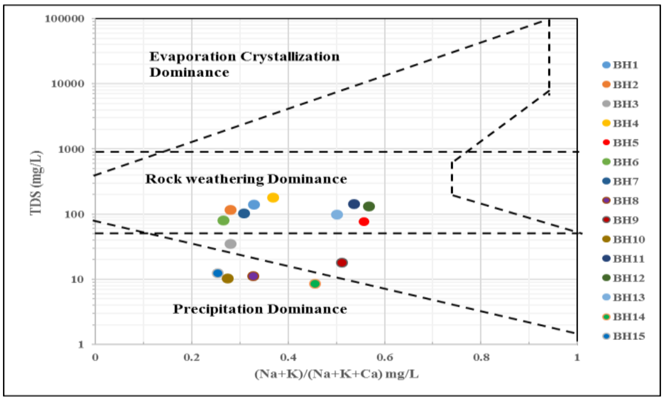

Figure 6(a): Gibbs diagram of $Na^+ + K^+/(Na^+ + K^+ + Ca^{2+})$ versus TDS depicting the mechanism controlling groundwater quality

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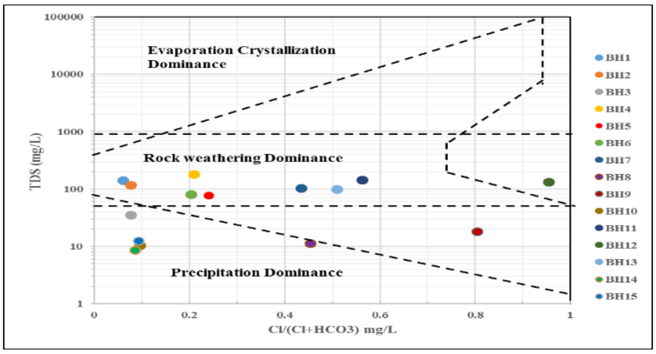

Figure 6(b): Gibbs diagram of $Cl^-/(Cl^-+HCO_3^-)$ versus TDS depicting the mechanism controlling groundwater quality

3.6 Ionic ratios

Ionic ratios are usually utilized to determine sea water intrusion in coastal areas. In this study, the following ionic relationships were determined to infer the salinity and origin of the ions in groundwater of the study area. These include: Mg/Ca, HCO_3/Cl, (Na + K)/Cl, Na/K, Ca/Na, SO_4/Cl and cationic exchange value (CEV) (Table 3). The ionic ratios were calculated (in meq/L) and results compared with sea water values and Early cretaceous brine. Calcium is dominant in freshwater whereas magnesium is dominant in sea water. Hence, Mg/Ca ratio acts as an indicator for delineating freshwater saltwater interface. The results of Mg/Ca ratio in this study ranges from 0.08 to 1.09, with mean and SD of 0.56±0.39 (Table 2). This result shows a strong deviation from those obtained from average sea water (3.30), whereas, the results are similar with those of Early Cretaceous brine (0.501) obtained from a study in Israel by a researcher [19]. The average chemical ratios of ions of the groundwater in the area deviates from the seawater ratio, however, there are some locations where the ionic ratio in groundwater closely approximates those of sea water. The critical ratio (Na+K)/Cl ranges from 0.55 to 4.04, with mean and SD of 1.45±1.03 (Table 3). Apart from BH1, BH2, BH9 and BH15 which ratios are similar to sea water and indicate possible freshwater seawater mixing, all other boreholes have ionic ratios which deviate from average sea water [21-23]. The CEV for seawater ranges from +1.2 to +1.3, where low salt inland waters give values close to zero, either positive or negative [20]. The CEV values for groundwater of the study area are generally below 0.5, ranging from -3.04 to 0.45, indicating that the groundwater provenance is inland. The variations of HCO_3/Cl, Na+K and Mg/Ca ratios with TDS shows similar trends and are subject to a similar interpretation, whereas the plot of (Na+K)/Cl versus TDS showed a different trend (Figures 5 - 6). Figure 7 shows the ionic ratio of HCO_3/Cl versus TDS while Figure 8 shows the ionic ratio of Na+K versus TDS. Figure 9 shows the ionic ratio of Mg/Ca versus TDS while Figure 10: Ionic ratio of (Na+K)/Cl versus TDS.

Table 3: Ionic Ratio compared to seawater values

Parameters	**Mg/Ca**	**Na/K**	**Ca/Na**	**(Na+K)/Cl**	**HCO_3/Cl**	**SO_4/Cl**	**CEV**
BH1	1.09	0.63	8.73	0.91	9.19	0.89	0.09
BH2	0.88	0.88	8.69	0.74	6.98	0.44	0.26
BH3	0.90	2.07	5.40	1.00	7.02	0.78	0.00
BH4	0.11	0.85	5.94	4.04	2.21	0.89	-3.04
BH5	0.69	1.66	1.85	2.62	1.85	0.72	-1.62
BH6	0.25	0.36	18.26	1.46	2.28	0.55	-0.46
BH7	0.08	0.23	21.30	0.55	0.76	0.39	0.45
BH8	0.14	1.81	4.60	1.10	0.70	0.51	-0.10
BH9	0.28	1.66	2.22	0.80	0.14	0.30	0.20
BH10	0.91	1.00	8.25	0.61	5.54	0.63	0.39
BH11	0.19	1.13	2.49	1.51	0.45	0.67	-0.51
BH12	0.55	1.20	2.12	0.55	0.03	0.14	0.45
BH13	0.23	4.18	1.62	2.76	0.56	1.66	-1.76
BH14	1.09	5.84	1.78	2.35	6.30	0.66	-1.35
BH15	0.96	0.69	11.69	0.77	5.70	0.85	0.23
Parameters	**Mg/Ca**	**Na/K**	**Ca/Na**	**(Na+K)/Cl**	**HCO_3/Cl**	**SO_4/Cl**	**CEV**
Min	0.08	0.23	1.62	0.55	0.03	0.14	-3.04
Max	1.09	5.84	21.30	4.04	9.19	1.66	0.45
Mean	0.56	1.61	7.00	1.45	3.31	0.67	-0.45
SD	0.39	1.51	6.09	1.03	3.11	0.35	1.03
Sea Water*	3.300	46.970	0.044	0.871	0.004	0.105	-
E.Cret.**	0.501	105.060	0.105	0.882	0.007	0.009	-

*Based on average values of data for seawater [21].
**Based on data for Early Cretaceous brines in Israel [19].

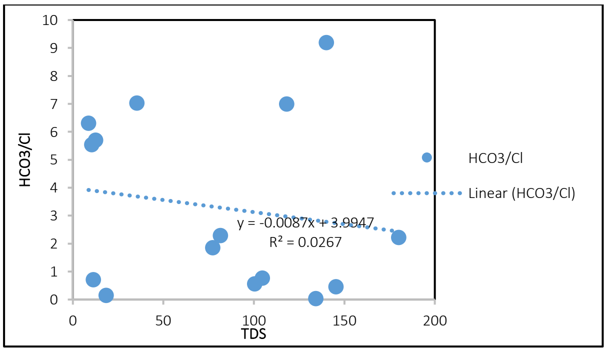

Figure 7: Ionic ratio of HCO_3/Cl versus TDS

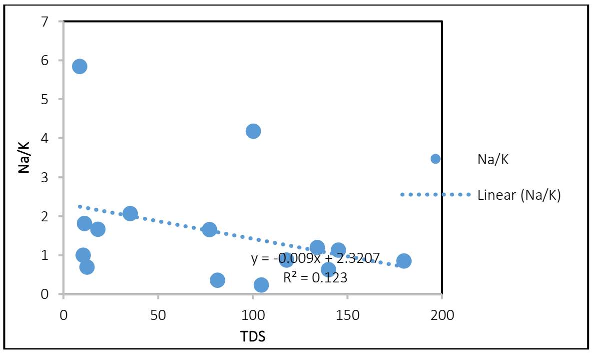

Figure 8: Ionic ratio of Na+K versus TDS

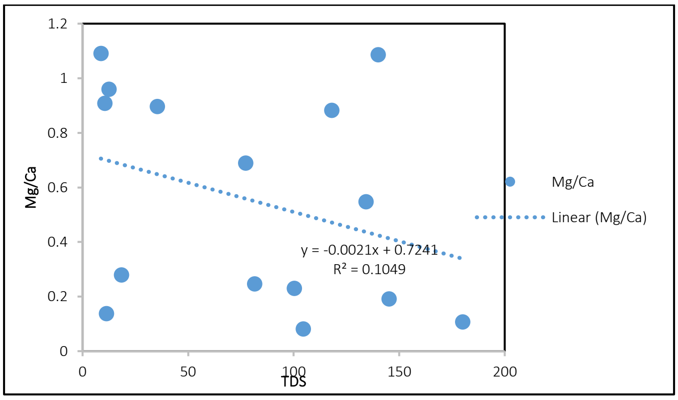

Figure 9: Ionic ratio of Mg/Ca versus TDS

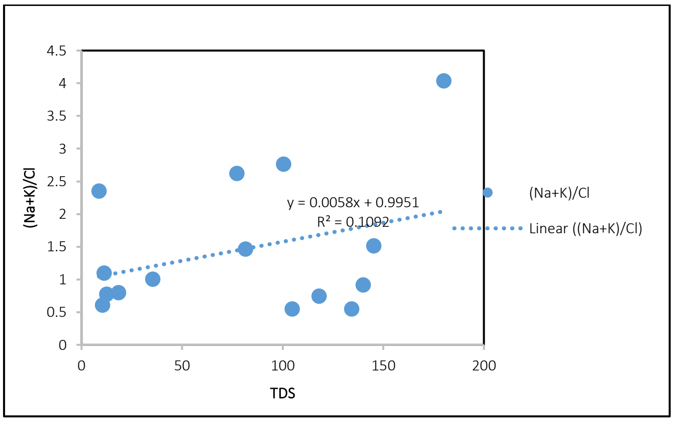

Figure 10: Ionic ratio of (Na+K)/Cl versus TDS

4. CONCLUSION

Classification of groundwater was achieved using Piper, Durov, Stiff and Gibb's diagrams. Piper diagram reveals two dominant water types; Mg-HCO_3 and Ca-HCO_3 hydro chemical facies. Stiff diagram reveals four distinct shapes representing different origins for the groundwater in the area. Class I groundwater includes BH1, BH2, BH3, BH10, BH14 and BH15 which are Ca^{2+}, $Mg^{2+}$and HCO_3 rich. Class II includes BH4, BH6, BH7 and BH8 which are $Ca^{2+}$and HCO_3 rich. Class III includes BH5, BH9, BH11 and BH13 which are Ca^{2+}, $Na^{+}+K^{+}$, Cl^{-} and HCO_3 rich. Class IV include BH12 which are $Ca^{2+}$and Cl^{-} rich. Durov diagram revealed three geochemical processes that could affect the water genesis which includes; (i) ionic exchange, (ii) simple dissolution or mixing, and (iii) probable mixing or uncommon dissolution influences. Gibbs diagrams shows that chemical weathering of rock and precipitation are the major influences on the groundwater quality. The various ionic ratios; Mg/Ca, HCO_3/Cl, (Na + K)/Cl, Na/K, Ca/Na, SO_4/Cl and CEV suggests the groundwater sources are of inland origin.

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