International Research Journal of Earth Sciences _____ISSN 2321 – 2527
Vol. **6(10),** 1-11, October **(2018)** *Int. Res. J. Earth Sci.*

Geochemical evaluation of groundwater origin using source rock deduction and hydrochemical facies at Umuoghara Mining Area, Lower Benue Trough, SE Nigeria

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Available online at: www.isca.in
Received 3rd July 2018, revised 20th October 2018, accepted 25th October 2018

Abstract

The research is aimed at geochemical evaluation of the origin of groundwater at Umuoghara area. The parameters listed below were analyzed following APHA, 2012 standard: pH, EC, TDS. Cations; (magnesium) Mg^{2+}, potassium (K^+), calcium (Ca^{2+}) while anions; bicarbonate (HCO_3^-), chloride (Cl^-) and sulphate (SO_4^{2-}). Twelve groundwater samples were collected within the study, with the aim to get baseline information regarding source of groundwater origin. This was done using source rock deduction proposed by Hounslaw, 1995 and hydrochemical facies (Gibbs, Piper, Durov, Schoeller plots and Slotan classification). From source rock deduction approach it was observed that weathering played a major role in groundwater chemistry. Gibbs plot showed that rock water interaction is has greater influence on groundwater chemistry, from Piper plot the dominant ions are; Ca^{2+}, Cl^- and SO_4^{2-}, dominant ions in Durov are; Ca^{2+}, Cl^- and SO_4^{2-}, from Schoeller diagram water trend of $Ca^{2+}>Mg^{2+}>Cl^->SO_4^{2-}>Na^++K^+>HCO_3^-$. From Piper, Durov and Schoeller. From detailed interpretation, it was observed that groundwater origin is of different source. Soltan classification, it was observed that groundwater source is of deep meteoric.

Keywords: Groundwater, interaction, ion exchange, weathering and Asu River group.

Introduction

Groundwater geochemistry is concern with the study of groundwater and relationship with its subsurface environment[1]. Generally information on groundwater quality of any given area can be traced to reaction with its environment. While composition of groundwater is also controlled by its reaction with the environment. Omo-Irabor O.O. et al.[2] are of the view that surface and groundwater quality is usually affected by soil, vegetation, geology, human activities and geomorphology. The study area is richly blessed with limestone, this has resulted in drastic increase in population and also attracted artesian miner who carry out illegal mining activities. Increase in population and illegal mining activities is believed to affect the geochemical constituents of water resources of the area, as most of the mining wastes are channeled into surface water and infiltrate into groundwater (Figure-1 and 2). The above listed factor increase or decrease the quality of water resources more so, physicochemical properties of water is considered as an important factor that may directly or indirectly affect water quality. Jong Y. Hwang[3] groundwater quality may give information about the environment through which groundwater circulate, residence and flow path. Insight on groundwater origin can be deducted from source rock deduction. Source rock deduction (SRD) is analytical check used in determining origin of groundwater that is not yet known[4]. Hounslaw W.[4] derived SRD from simplistic mass balance approach from water quality data. While in some situation source rock minerals may be deduced from the groundwater composition. It is an approach for explaining groundwater chemistry, as groundwater chemistry plays major role in determining its quality and origin. Generally, rock weathering usually alter the composition of anion and cation, as the amount of cations can be linked to rock mineralogy. Aside having knowledge of origin of groundwater from SRD. Hydrochemical facies can also be used to determine water type of a particular locality. Suitability of groundwater for domestic, agricultural and industrial use, can also be determine from hydrochemical facies or geochemistry[5-11]. Hence the integration of this two approach in determining hydrogeochemistry of groundwater of the study area.

Geology and Hydrogeology: Geographically the area is located between latitude $6^0 17^l$N-$6^0 22^l$N and longitude $8^0 06^l$ E-$8^0 11^l$E (Figure-1). It located close to Abakaliki the state capital in Ebonyi State. The area is accessible through Enugu- Abakaliki express way and network of other roads. Geological the area falls within the Southern Benue Trough (SBT). Murat R.C.[12] and Hoque M.[13] gave detailed information on SBT using three tectonic sedimentary cycles, namely: marine transgressions and regressions which started from the Albian to the Coniacian in age[14]. Marine transgression was the first that occurred in Benue Trough within the middle Albian period, with the deposition of

the Asu River Group (ARG)[12]. The ARG sediments are predominantly underlie by shales as stated by Reyment R.A.[16] (Figure-3), siltstone, sandstone and limestone facies as well as extrusive and intrusive. Benkhelil J.[15] stated that ARG has an average thickness of about 2000 m and uncomfortably overlies the Precambrian Basement. The Santonian tectonic phase give rise to series of fracturing and folding of these rocks, giving rise to chains of anticlines and syncline known as the Abakaliki Anticlinorium[16]. The dominant fracture trend that hosts the lead-zinc forming minerals is in NW- SE and NNW- SE[17]. In addition[18] demarcated the ARG sediment into Abakaliki and Ebonyi Formations. The Abakaliki formation is predominantly dark grey colored shale (weathered to brownish material in the greater part of the formation), blocky, and indurated in most locations, yet fissile in some locations. Movement of groundwater and storage within the study area is primarily influenced by thickness, lithology, and structure of rock formation. Shale is an aquiclude and does not permit reasonable passage of water, especially when fresh and unweathered. But when fractured in most case, it serves as water bearing formation. As water bearing formation within the study area exists in fractured shale and limestone[14]. The major sources of water are stream, hand-dug well, manual borehole and motorized borehole.

Figure-1: Abandon Mining Pit at Umuoghara were Inhabitant of the area source for water for domestic use.

Figure-2: Waste from Abandon mining pit flowing into surface Water bodies within Umuoghara.

Methodology

Laboratory analysis: For detailed groundwater study, twelve (12) groundwater samples were collected at various location, to analyze their physicochemical parameters (Figure-3 and Table-2). In other to achieve accurate results, sampling bottles where thoroughly washed with clean water, cleaning reagent and were rinsed with distilled de-ionized water prior to collection of groundwater sample from site. TDS, EC and pH and were determined at sampling points, water samples were sealed and kept in ice chests and later taken to the laboratory within an hour of the collection. TDS and EC and were determined using the HACH Conductivity and TDS meters respectively.

The pH was measured using a pH meter and the HACH. Potassium (K^+), magnesium (Mg^{2+}), and sodium (Na^+) ion concentrations were obtained with a Jenway clinical flame photometer. Calcium (Ca^{2+}), sulphate (SO_4^{2-}), bicarbonate (HCO_3^-) and chloride (Cl^-) ions were determined using appropriate titrimetric methods described by APHA[19] and the sulphate concentration was determined by turbidimetry. Water samples were analysed following APHA, 2012 standard. Equation 1 to 7 were used in evaluation of the origin groundwater of the study area.

Source rock deduction summary equation

$$\frac{Na^+ + K^+ - Cl^-}{Na^+ + K^+ - Cl^- + Ca^{2+}} \quad 4 \qquad (1)$$

$$\frac{Na^+}{Na^+ + Cl^-} \quad 4 \qquad (2)$$

$$\frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \quad 4 \qquad (3)$$

$$\frac{Ca^{2+}}{Ca^{2+} + SO_4^{2-}} \quad 4 \qquad (4)$$

$$\frac{Ca^{2+} + Mg^{2+}}{SO_4^{2-}} \quad 4 \qquad (5)$$

$$\frac{Cl^-}{Sum\ of\ Anions} \quad 4 \qquad (6)$$

$$\frac{HCO_3^-}{Sum\ of\ Anions} \quad 4 \qquad (7)$$

Gibb's Plot

For Cations

$$Na^+/(Na^+ + Ca^{2+})\ meq/L \quad 20 \qquad (8a)$$

For Anions

$$Cl^-/(Cl^- + HCO_3^-)\ \text{meq/L} \quad 20 \qquad (8b)$$

Soltan classification

$$r1 = (Na^+ - Cl^-)/SO_4^{2-}\ meq/L \quad 21 \qquad (9a)$$

$$r2 = [(K^+ + Na^+) - Cl^-)]/SO_4^{2-}\ meq/L \quad 21 \qquad (9b)$$

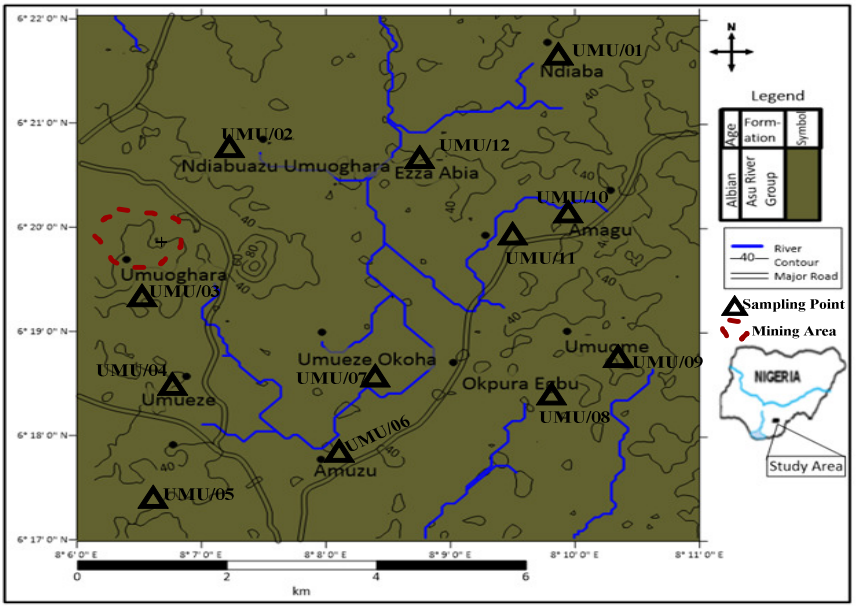

Figure-3: Geological Map and Water Sample Collection points (Source-Shell BP. 1957).

Table-1: Source-Rock Deduction Summary of Reasoning.

Parameters	Value	Conclusion
$\frac{Na^+ + K^+ - Cl^-}{Na^+ + K^+ - Cl^- + Ca^{2+}}$	>0.2 and <0.8 <0.2 or >0.8	PWP PWU
$\frac{Na^+}{Na^+ + Cl^-}$	>0.5 = 0 <0.5 TDS >500 <0.5 TDS <500> 50 <0.5 TDS < 50	Sodium source other than halite HS Reverse softening, sea water AE Rain water.
$\frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}}$	= 0.5 < 0.5 >0.5	DW LD DD, calcite precipitation or seawater.
$\frac{Ca^{2+}}{Ca^{2+} + SO_4^{2-}}$	= 0.5 < 0.5 PH < 5.5 <0.5 neutral >0.5	GD PO Calcium remove-ion exchange Calcium source other than gypsum
$\frac{Ca^{2+} + Mg^{2+}}{SO_4^{2-}}$	>0.8 and <1.2	D
TDS	>500 <500	CW or brine, seawater SW
$\frac{Cl^-}{Sum\ of\ Anions}$	>0.8 TDS >500 >0.8 TDS <100 <0.8	Sea water, or brine or evaporate RW RW
$\frac{HCO_3^-}{Sum\ of\ Anions}$	>0.8 <0.8 Sulphate High <0.8 Sulphate low	Silicate or carbonate weathering GW SWB
Conclusion	Aquifer mineralogy	
Conclusion	Reactions	

Where: DW=Dolomite weathering, LD=Limestone Dolomoite, DD=Dolomite Dissolution, GD=Gyspum Dissolution, PO=Pyrite Oxidation, D=Dedolomitiztion, CW=Carbonate weathering, GW=Gypsum weathering, RW=Rock weathering, PWP=Plagioclase weathering possible, PWU=Plagioclase weathering unlikely, SW=Silicate weathering, SWB=Sea water brine, HS=Halite solution, AE=Analysis error and RW=Rain water.

Table-2: Result of Physicochemical Parameters.

Sample Code	E.C (US/cm)	pH	TDS (mg/L)	SO_4^{2-} meq/L	NO_3^- meq/L	Cl^- meq/L	Na^{2+} meq/L	K^+ meq/L	Ca^{2+} meq/L	Mg^{2+} meq/L	HCO_3^- meq/L
UMU/01	1100	6.9	687.5	0.06	1.19	0.64	0.32	0.15	6.00	1.93	0.25
UMU/02	400	6.8	250	1.62	1.01	0.28	0.31	0.17	5.82	1.37	0.16
UMU/03	360	6.5	225	1.35	0.80	0.15	0.26	0.12	4.99	0.80	0.24
UMU/04	420	6.9	262. 5	0.05	0.62	0.24	0.25	0.14	2.35	1.85	0.06
UMU/05	395	6.3	246.9	0.00	0.03	0.19	0.36	0.21	3.91	1.97	0.00
UMU/06	340	6.4	212.5	0.93	0.05	0.39	0.38	0.16	4.39	0.57	0.03
UMU/07	470	7.0	293.8	2.06	0.00	0.24	0.28	0.21	3.49	1.30	0.22
UMU/08	390	6.8	243.8	1.16	0.00	0.27	0.24	0.04	5.98	0.44	0.30
UMU/09	20.17	5.2	12.22	1.49	0.00	12.52	0.37	0.19	2.49	0.00	0.15
UMU/10	17.44	7.2	0.44	1.89	0.00	6.65	0.35	0.04	1.06	0.00	0.00
UMU/11	11.67	5.2	0.42	0.93	0.00	2.08	0.34	0.19	0.51	0.54	0.07
UMU/12	56.8	6.5	0.34	0.47	0.19	0.48	0.05	0.04	1.65	0.00	0.18

Table-3: Results Obtained from application of SRD within the Study Area.

Sample Code	$\frac{Na^+ + K^+ - Cl^-}{Na^+ + K^+ - Cl^- + Ca^{2+}}$	$\frac{Na^+}{Na^+ + Cl^-}$	$\frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}}$	$\frac{Ca^{2+}}{Ca^{2+} + SO_4^{2-}}$	$\frac{Ca^{2+} + Mg^{2+}}{SO_4^{2-}}$	TDS	$\frac{Cl^-}{Sum\ of\ Anions}$	$\frac{HCO_3^-}{Sum\ of\ Anions}$
UMU/01	-0.029	0.33	0.24	0.99	32.16	687.5	0.0153	0.005
UMU/02	0.033	0.52	0.19	0.78	4.43	250	0.0067	0.003
UMU/03	0.044	0.63	0.13	0.78	4.28	225	0.0035	0.005
UMU/04	0.06	0.06	0.44	0.97	84.00	262. 5	0.003	0.001
UMU/05	0.088	0.65	0.33	1.00	0.00	246.9	0.004	0.00
UMU/06	0.033	0.49	0.11	0.81	5.33	212.5	0.0093	0.00
UMU/07	0.066	0.41	0.27	0.62	1.56	293.8	0.0057	0.005
UMU/08	0.0016	0.12	0.068	0.83	5.53	243.8	0.006	0.007
UMU/09	1.26	0.014	0.00	0.62	1.67	12.22	0.300	0.003
UMU/10	1.20	0.005	0.00	0.35	0.56	0.44	0.15	0.00
UMU/11	1.49	0.08	0.98	0.35	1.12	0.42	0.049	0.001
UMU/12	-0.309	0.076	0.00	0.77	3.51	0.34	0.0115	0.004

Discussion

From SRD, it was observed that groundwater geochemistry is majorly controlled by weathering as in Table-4. Most times, groundwater composition can be used to deduced source rock. Groundwater quality can be deduced from SRD[3]. Disintegration of magnesium ions and calcium ion in groundwater play a major role in understanding of source rock for the dolomite under average TDS conditions, however, the magnesium ion to calcium ratio approaches one, it is very likely that calcium could be expunge from the solution and this process is referred to as dedolomitization[4-3]. Hounslaw W.[4] as shown in Figure-5 and Table-1.

From Figure-6. It was observed that six sampling points fall above the equiline while the remaining six fall below the equiline this implies that CW and SW are the main physical action for making the source for calcium ion in the groundwater[22].

Figure-7 shows that, most of the samples have a Na/Cl ratio around or above 1, this implies that ion exchange process is more dominant in the study area. Figure-8 shows the ion exchange reactions, where Na^+ is plotted against Ca^{2+} in which Ca^{2+} levels are ranges from 0.51 to 6.00 (meq/L), while Na^+ levels are ranges from 0.05 to 0.38 (meq/L). From Figure-9 it was observed evolution of groundwater is primarily controlled by silicate weathering. Whenever bicarbonate and sulfate are dominating than calcium and magnesium, it implies that SW was dominating and, therefore, was responsible for the increase in the concentration of HCO_3^- in groundwater.

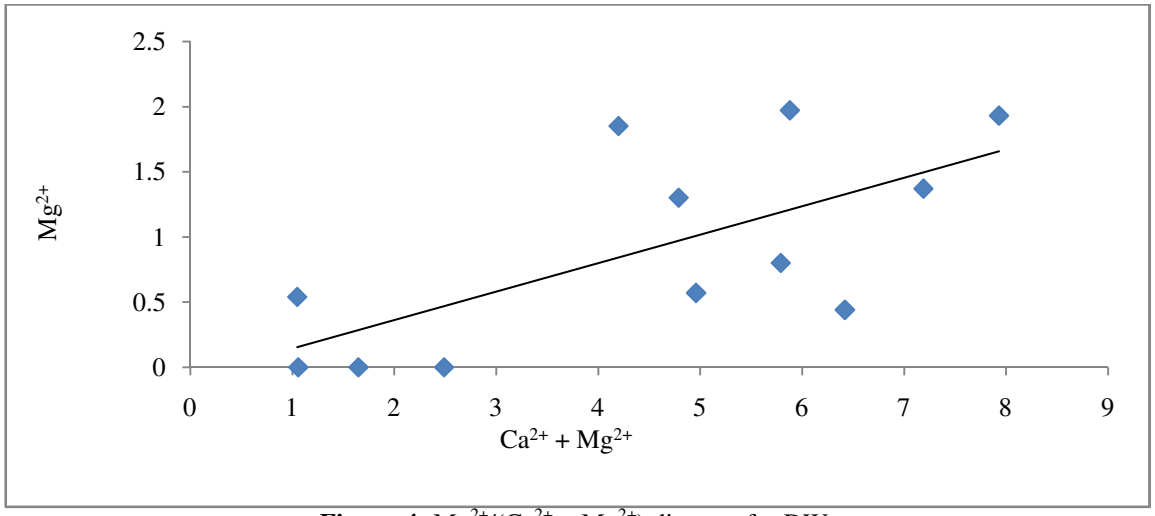

Figure-4: $Mg^{2+}/(Ca^{2+} + Mg^{2+})$ diagram for DW.

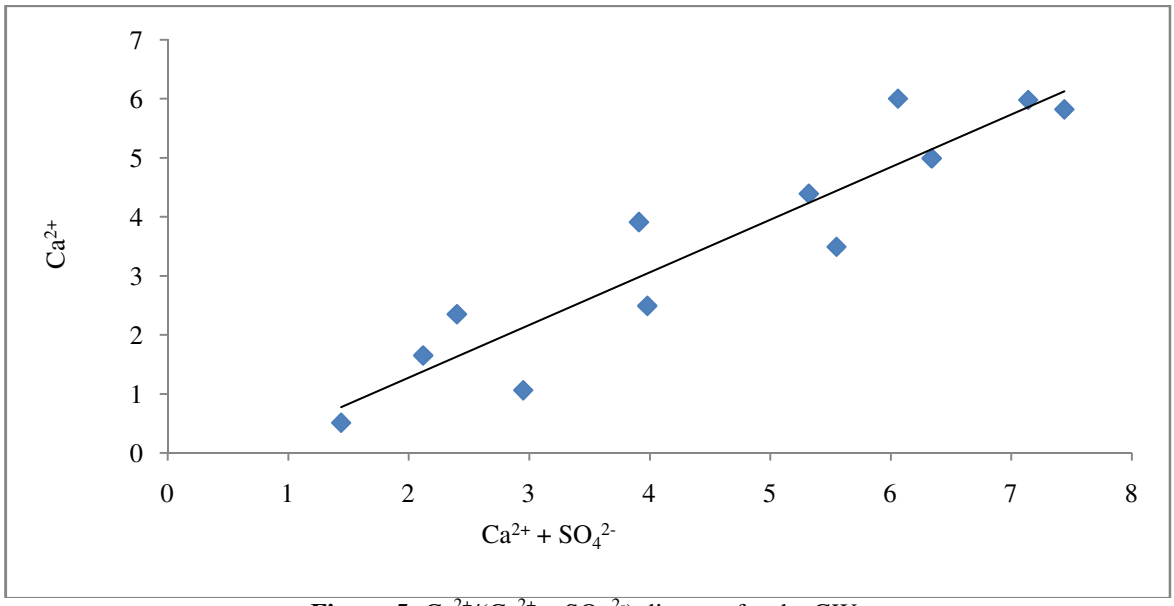

Figure-5: $Ca^{2+}/(Ca^{2+} + SO_4^{2-})$ diagram for the GW.

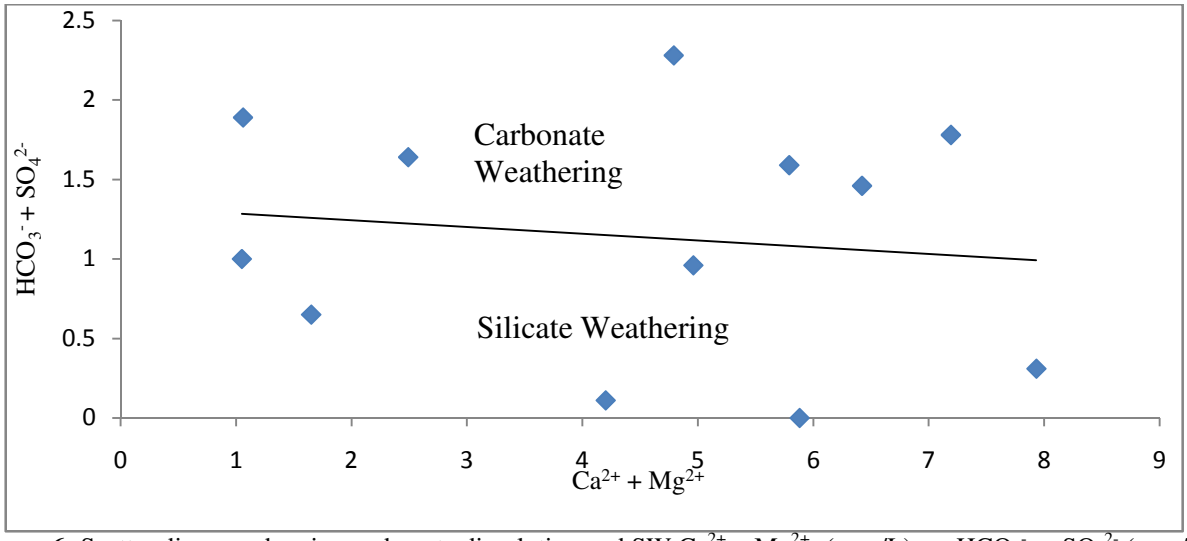

Figure-6: Scatter diagram showing carbonate dissolution and SW $Ca^{2+} + Mg^{2+}$ (meq/L) vs. HCO_3^- + SO_4^{2-} (meq/L).

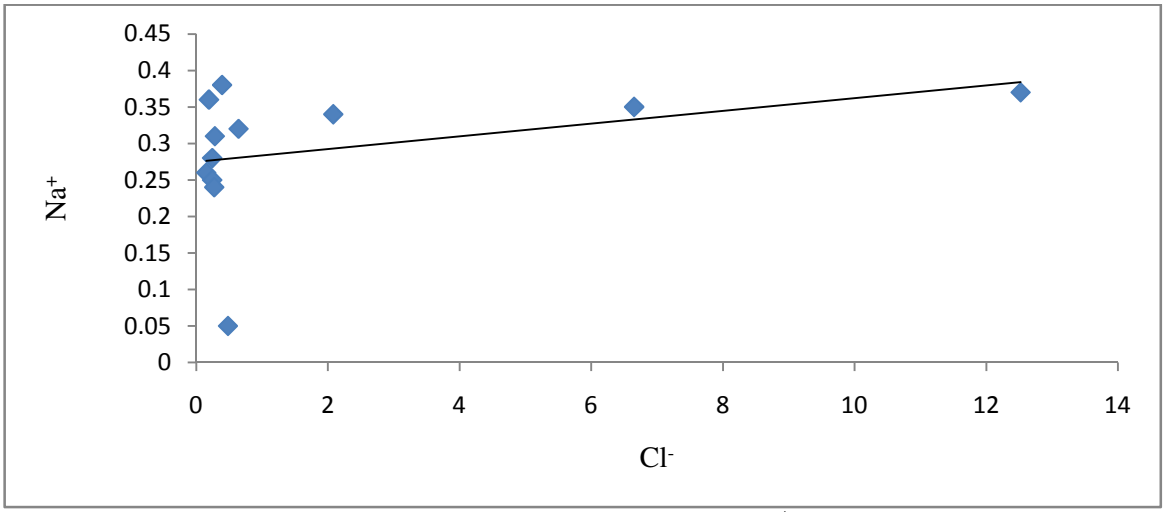

Figure-7: Showing scatter Diagram of Na^+/Cl^-.

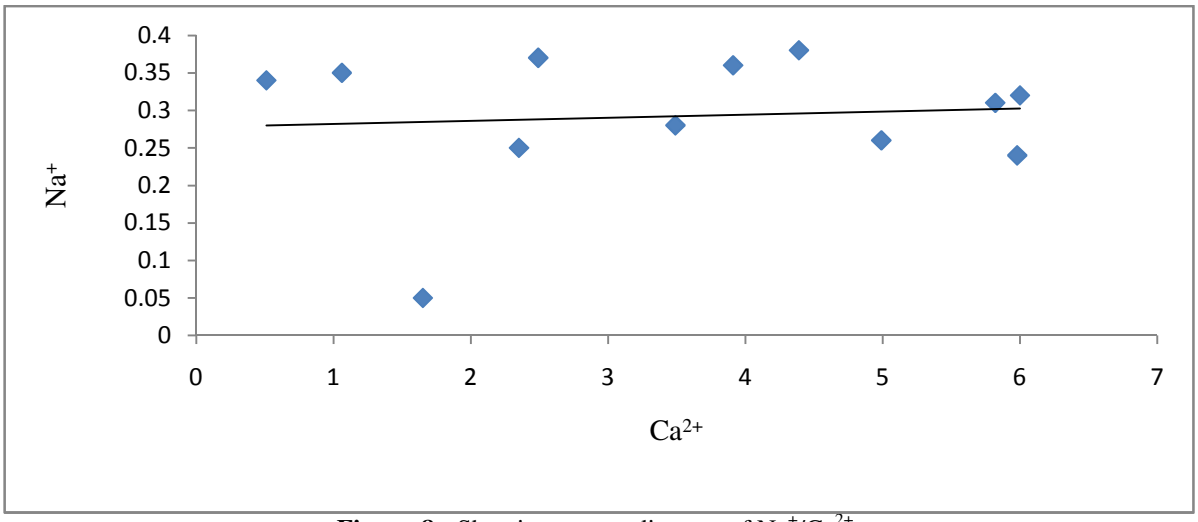

Figure-8: Showing scatter diagram of Na^+/Ca^{2+}.

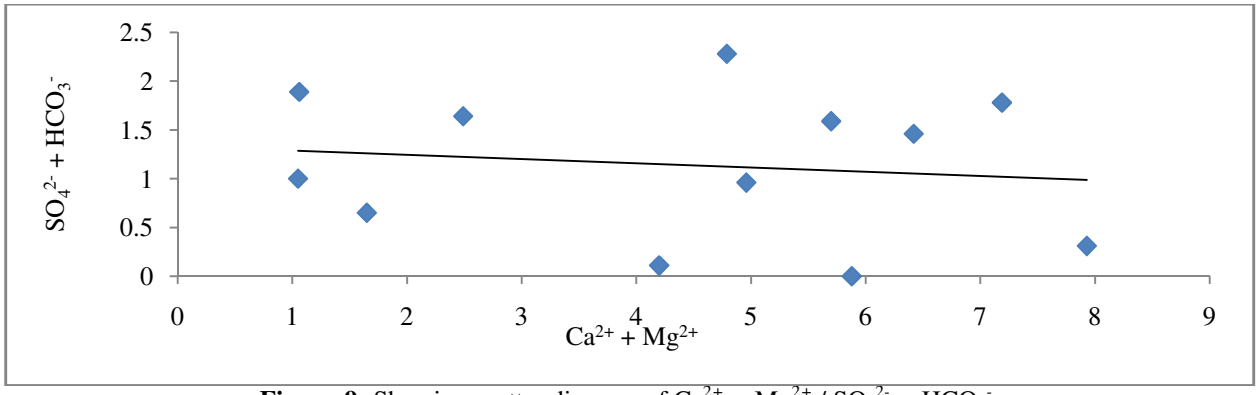

Figure-9: Showing scatter diagram of $Ca^{2+} + Mg^{2+} / SO_4^{2-} + HCO_3^-$.

Table 4: Summary of Source Rock Interaction.

Sample Code	$\frac{Na^+ + K^+ - Cl^-}{Na^+ + K^+ - Cl^- + Ca^{2+}}$	$\frac{Na^+}{Na^+ + Cl^-}$	$\frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}}$	$\frac{Ca^{2+}}{Ca^{2+} + SO_4^{2-}}$	$\frac{Ca^{2+} + Mg^{2+}}{SO_4^{2-}}$	TDS	$\frac{Cl^-}{\text{Sum of Anions}}$	$\frac{HCO_3^-}{Sum\ of\ Anions}$
UMU/01	PWU	Na^+ ODH	LDW	Ca^{2+} ODTG	VASRD	CW	SWB or E	GW
UMU/02	PWU	Na^+ ODH	LDW	Ca^{2+} ODTG	VASRD	CW	SWB or E	GW
UMU/03	PWU	Na^+ ODH	LDW	Ca^{2+} ODTG	VASRD	CW	SWB or E	GW
UMU/04	PWU	AE	LDW	Ca^{2+} ODTG	VASRD	CW	SWB or E	GW
UMU/05	PWU	Na^+ ODH	LDW	Ca^{2+} ODTG	VASRD	CW	SWB or E	GW
UMU/06	PWU	AE	LDW	Ca^{2+} ODTG	VASRD	CW	SWB or E	GW
UMU/07	PWU	AE	LDW	Ca^{2+} ODTG	VASRD	CW	SWB or E	GW
UMU/08	PWU	RW	LDW	Ca^{2+} ODTG	VASRD	CW	SWB or E	GW
UMU/09	PWU	RW	LDW	PO	VASRD	CW	RW	GW
UMU/10	PWU	RW	LDW	Ca^{2+} RIE	VASRD	CW	RW*	GW
UMU/11	PWU	RW	LDW	PO	VASRD	CW	RW*	GW
UMU/12	PWU	RW	LDW	Ca^{2+} ODTG	VASRD	CW	RW*	GW

Note: GW= Gypsum weathering, CW=Carbonate weathering, RW=Rain water, RW*=Rock weathering, SWB or E =Sea water brine or evaporate, PO=Pyrite oxidation, AE=Analysis error, Na^+ other than Halite, albite, ion, LDW=Limestone Dolomite weathering, Ca^{2+} ODTG=Calcium source other than gypsum - carbonate or silicate, Ca^{2+} RIE = Calcium remove – ion exchange or calcite precipitation, VASRD=Value above SRD range and PWU = Plagioclase weathering unlikely.

Groundwater evaluation of the study area using Gibbs Plot: The attribute of anions and cations in groundwater denote the certain physicochemical quality caused by the groundwater's interaction with soil and rock, while flowing in the aquifer[3]. Water bearing formation show the attributes of water bodies with various chemical compositions. Therefore, such attributes can be referred to hydrochemical facies of groundwater. Most times hydrochemical facies is usually affected by the rocks of the water bearing formation and the flow of groundwater. The distribution of anions (Cl^- , HCO_3^-) and cations (Na^+, Ca^{2+}) as well as the TDS value as shown in (Equation 8a and 8b) were used to plot the Gibbs diagram in other to show the dominant process that has effect on groundwater within the study area such as; evaporation dominance, rock dominance, precipitation dominance. Gibbs diagram helps in interpreting the effect of hydrogeochemical processes such as; rock-water interaction mechanism, precipitation and evaporation on groundwater geochemistry. The reaction between groundwater and aquifer minerals has a major role to play in groundwater quality which is useful to predicate the source of groundwater (Figure-10). Though previous work by Eyankware M.O.[9] stated from Chadba plot groundwater within Umuoghara fall under the alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions, that implies that the water is considered hard, but the origin of groundwater was not discussed.

For better insight on chemical attribute of groundwater and interconnection between dissolved ionic constituents, Piper diagram, Durov and Schoeller were plotted. From Figure-11, it was observed that the dominant ionic species of Piper plot is Ca^{2+}, Cl^- and SO_4^{2-}, that of Durov shows that the dominant ionic species of Ca^{2+}, Cl^- and SO_4^{2-} (Figure-12), and lastly Schoeller diagram water trend of $Ca^{2+} > Mg^{2+} > Cl^- > SO_4^{2-} > Na^+ + K^+ > HCO_3^-$ (Figure-13).

From the result, presence of Ca^{2+} in the water sources could be attributed to the water interacted with some of these minerals: amphiboles, feldspars, gypsum, aragonite, calcite, pyroxenes, dolomite, clay minerals, Cl^- could be due to water contact with sedimentary rock or igneous rock, while SO_4^{2-} could be linked to groundwater passing through gypsum or pyrite. High concentration of SO_4^{2-} in the aquifer system implies that the water interacted with mineral sources of sulphate (pyrite, gypsum, and barite). Dissolved carbon dioxide, bicarbonate, and carbonate are the major sources of alkalinity, or the capacity of solutes in water to neutralize acid. From the Schoeller plot, there is no similarity in water type between the groundwater samples, this implies that there are no similarity in geochemical processes controlling major ion chemistry in water bearing formation, therefore one can say that groundwater origin is from different source.

Soltan classification: Narsimha A. et al.[23] has clearly classified groundwater into two types, which are base-exchange indices ($r1$) and meteoric genesis indices ($r2$) as shown (Equation-9a and 9b). Where Na^+, K^+, Cl^- and SO_4^{2-} concentrations are expressed in meq/L. If $r1<1$ and $r2<1$, the groundwater sources are of Na^+–SO_4^{2-} and deep meteoric type, respectively, while $r1>1$ and $r2>1$ indicates the sources are of Na^+– HCO_3^- and shallow meteoric type, respectively[23] and also presented in Table-5. Based on Soltan classification 100% of groundwater belongs to Na^+–SO_4^{2-}.

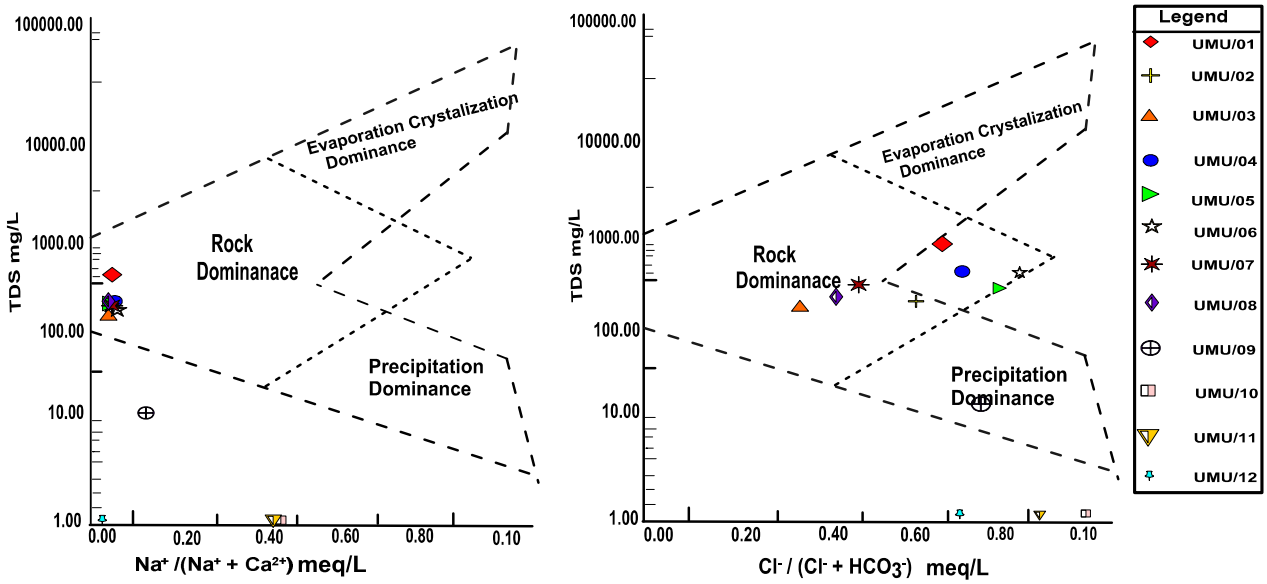

Figure-10: Gibb's Plot of Water Sampled Location of the Study Area.

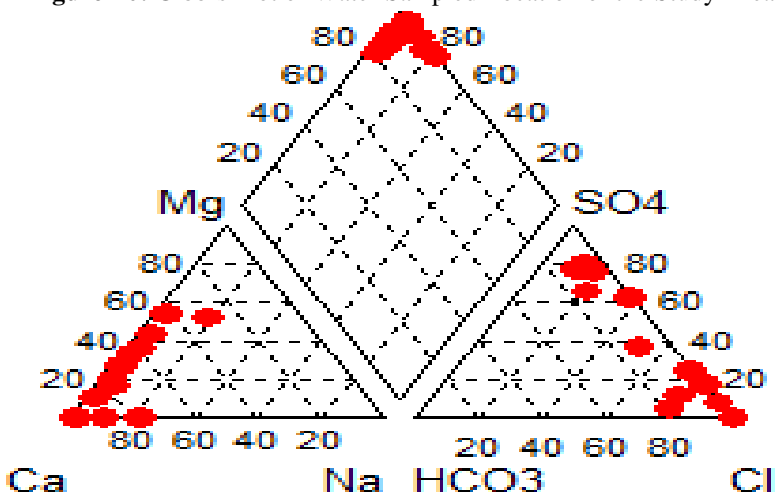

Figure-11: Piper Trilinear diagram.

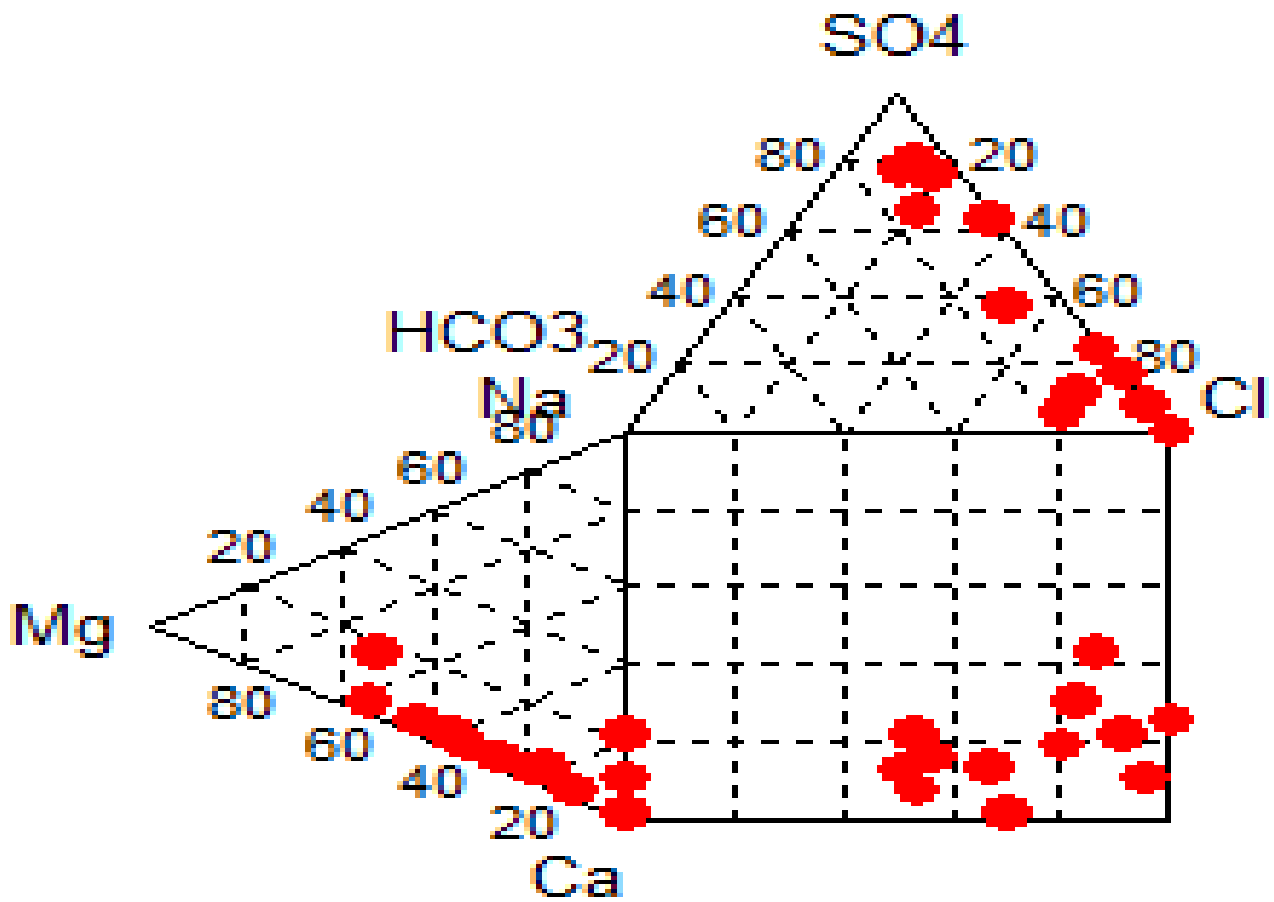

Figure -12: Durov diagram.

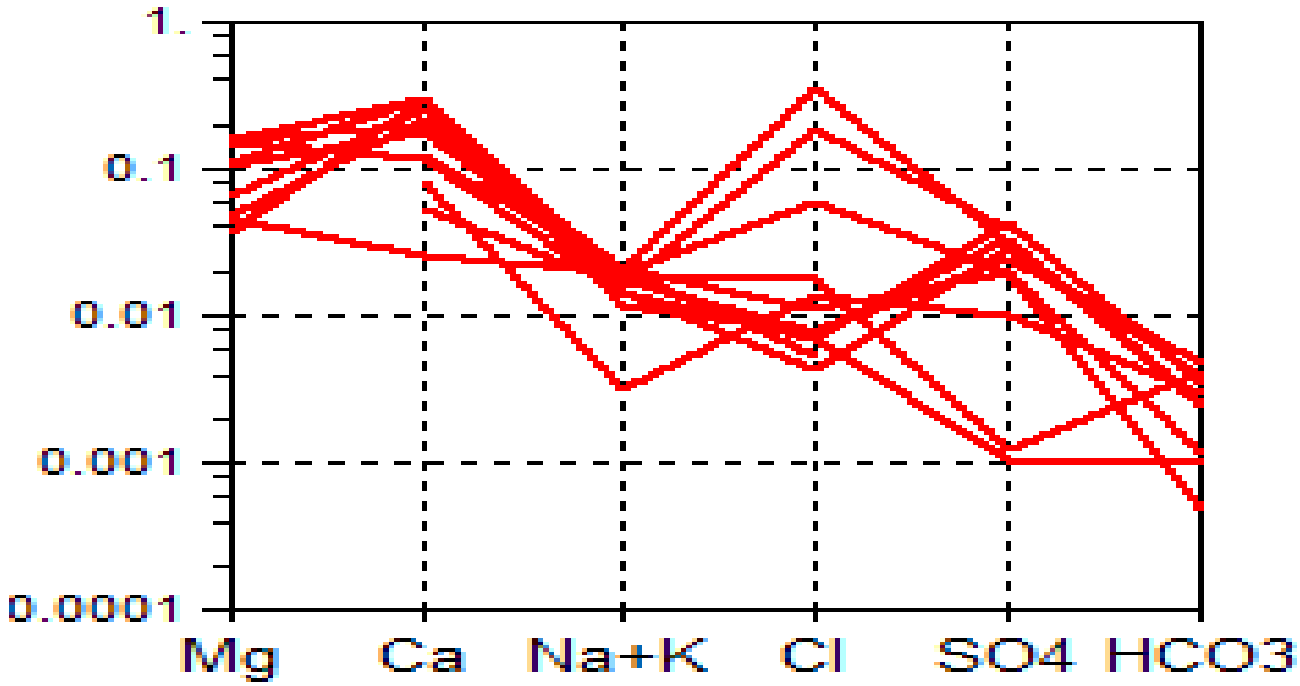

Figure-13: Schoeller Semi log diagram.

Table-5: Groundwater classification according to base-exchange (*r*1) and meteoric genesis index (*r*2) criteria modified after [23]

Sample code	r1	Water Type	r2	Water Type
UMU/01	-5.33	$Na^+ + SO_4^{2-}$	-2.83	Deep meteoric
UMU/02	0.01	$Na^+ + SO_4^{2-}$	0.12	Deep meteoric
UMU/03	0.08	$Na^+ + SO_4^{2-}$	0.17	Deep meteoric
UMU/04	0.20	$Na^+ + SO_4^{2-}$	0.10	Deep meteoric
UMU/05	0.00	$Na^+ + SO_4^{2-}$	0.01	Deep meteoric
UMU/06	-0.01	$Na^+ + SO_4^{2-}$	0.16	Deep meteoric
UMU/07	0.01	$Na^+ + SO_4^{2-}$	0.12	Deep meteoric
UMU/08	-0.02	$Na^+ + SO_4^{2-}$	0.00	Deep meteoric
UMU/09	-8.15	$Na^+ + SO_4^{2-}$	-8.02	Deep meteoric
UMU/10	-3.33	$Na^+ + SO_4^{2-}$	-3.31	Deep meteoric
UMU/11	-1.87	$Na^+ + SO_4^{2-}$	-1.66	Deep meteoric
UMU/12	-0.91	$Na^+ + SO_4^{2-}$	-0.82	Deep meteoric

Conclusion

From detailed studies, pH shows that the water is slightly basic to acidic. From SRD, it was observed that the chemistry of groundwater is influenced by the water-rock deduction such as followings: dolomite type weathering, gypsum type weathering, alkaline and alkaline type weathering. It was also observed that weathering has great influence on groundwater within the study area. While from Gibbs plot it was deduced that rock water interaction is considered to be the major hydrochemical process that has influence on groundwater within the study area. As for Piper plot the dominant ions are; Ca^{2+}, Cl^- and SO_4^{2-}, dominant ions in Durov are; Ca^{2+}, Cl^- and SO_4^{2-}, from Schoeller diagram water trend of $Ca^{2+}>Mg^{2+}>Cl^->SO_4^{2-}>Na^++K^+>HCO_3^-$. From Piper, Durov and Schoeller plot, origin of groundwater within the study area are from different source. From SRD and hydrochemical facies analysis it was observed that origin of groundwater is from different source. Soltan classification showed that 100% of groundwater belongs to $Na^+–SO_4^{2-}$ hence it can be classified under deep meteoric.

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