Characterization of Dominant Hydrogeochemical Processes in Groundwater in Onitsha Area, Southeastern Nigeria

Okolo C. M. [a], Onuora I. D. [a], Madu F. M. [a*] and Obasi P. N. [b]

[a] Department of Geological Sciences, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria.
[b] Department of Geology, Ebony State University, Abakaliki, Nigeria.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

The characterization of the dominant hydrogeochemical processes in groundwater in Onitsha area, southeastern Nigeria was carried out. This is to identify the dominant mechanisms responsible for the evolution and the chemical composition of the water sources. A total of fifteen (15) groundwater samples were collected from different locations in the study area in August 2022 and these samples were subjected to chemical analysis using standard methods. The results indicated that the water quality parameters were within the World Health Organization acceptable limits for drinking quality although turbidity in six of the samples exceeded the guideline values. The hydrochemical facies were determined using various plots. Piper diagrams indicated that Ca^{2+} - Mg^{2+} - Cl^- - SO_4^{2-} was the dominant facies with Ca^{2+} and Cl^- as the dominant ions. The Durov diagram indicate recharge water in limestone and sandstone aquifers and influenced by important ion exchange reactions. However, the Gibbs plots mainly plotted in the rock dominance zone indicating that the major processes

_____

Corresponding author: E-mail: fm.madu@unizik.edu.ng;

controlling water chemistry in the study area were water-rock interaction and dissolution of rock minerals. The ionic ratio plots were employed to determine the mechanisms and reactions prevalent in the study area that influenced the water chemistry. Na/Cl plot indicated that the excess of Cl^- over Na^+ was balanced by Ca^{2+} and Mg^{2+} while the depletion of Na^+ with respect to Clindicated ion exchange reaction which could be attributed to silicate weathering confirming the Na/Cl plot conclusions. The relative abundance of anionic facies shows that $Cl^- + SO4^{2-}$ were more abundant than $HCO3-$ and the plot of $Ca^{2+} + Mg^{2+}$ ions against $HCO3^-$ ions depict samples with excess $Ca^{2+} + Mg^{2+}$. However, $Ca^{2+} + Mg/HCO3$ ratio was less than one (<1) and indicated fresh recharge water.

1. INTRODUCTION

The use of groundwater as a critical resource can't be overstated. It an important water supply source in urban and rural areas in both developed and developing nations. It is used for domestic, industrial and agricultural purposes [1,2]. Groundwater is replenished from precipitation and surface run-off. The dominant role of groundwater is clear and its 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 geogenic and anthropogenic activities [3,4].

The groundwater chemistry depends on different hydrogeochemical processes that the groundwater undergoes over space and time. It is a function of the mineralogical structure in the aquifer, the composition of the recharge water, the residence time, the length of the flow path and the chemical processes in the environment [5,6]. Geochemical processes taking place inside the groundwater system include dissolution, percolation, precipitation, and cation exchange [7]. The interaction of these factors results in various water types [8]. Thus, hydrogeochemical composition of groundwater can be indicative of the origin and history of its spatial flow. It has been shown that the geochemical processes are responsible for the seasonal and spatial variations in groundwater chemistry [9]. Evaluation of the groundwater chemistry and delineation of various hydrogeochemical processes that are involved in the evolution of groundwater quality using various conventional graphical methods and interpreting different indices were carried out by Elango et al [10]. They reported that hydrogeochemical processes

control the chemical composition of groundwater and concluded that the character of groundwater in different aquifers over space and time is an effective tool in solving different geochemical problems. The dissolution of minerals and other anthropogenic activities have been identified as important processes controlling the hydrogeochemistry of Polar River basin [32]. Additionally, the studies of the major ions have been used to identify the hydrochemical facies of water. Also evaluation of groundwater chemistry and hydrogeochemical consideration has been carried out by various researchers by developing geochemical modelling and adopting graphical method for the interpretation of water quality parameters [11,12,13]. Thus, knowledge of hydrogeochemical processes that control groundwater chemical evolution could lead to improved understanding of hydrogeochemical characteristics of an aquifer. This could contribute to sustainable development of water resources and effective management of groundwater as a resource.

Piper [14], proposed an effective graphic procedure to segregate relevant analytical data to understand the sources of the dissolved constituents in water. The procedure was based on the statement that most natural waters contain cations and anions in chemical equilibrium. According to the location of the sample, the hydrochemical facies can be identified [15]. The facies are the diagnostic chemical aspect of water solutions occurring in the hydrologic systems. The Durov plot is a composite plot based on the percentage of major ion milliequivalents and two (optional) additional water quality parameters [16]. The Durov plot also allows for the direct comparison of two other groundwater parameters, typically pH and the total dissolved solids (TDS) or electrical conductivity.

1.1 Location and Accessibility of the Study Area

The study area is located between latitudes $6^{\circ}10^{\prime}0^{\prime\prime}N$ and $6^{\circ}7^{\prime}0^{\prime\prime}N$, and longitudes $6^{\circ}46^{\prime}30^{\prime\prime}E$ and $6^{\circ}48^{\prime}30^{\prime\prime}E$. The area includes the following communities; Fegge, Odoakpu, Woliwo, Awada, Obosi, and Okpoko all in Onitsha area. The area is easily accessible through major, minor and track roads (Fig. 1). It is located on the eastern bank of the Niger River, in Anambra State, Nigeria. It is a metropolitan city with great prospects for economic and commerce activities. Two major climatic seasons, namely the rainy and the dry season control the study area. The rainy season is from April to November, while the dry season is from December to March. The rainy season is characterized by high rainfall amount and good groundwater recharge because of good porosity and permeability of the underlying geology formations. However, the study area is underlain by alluvium deposit at the bank of the river Niger, the Ameki Formation comprising mainly Nanka Formation and Nsugbe Formation in the northern parts of the study area and the Ogwashi-Asaba Formation in the southern parts of the study area. The Nanka Formation is mainly sands and minor calcareous clay or mud with heterolith [17,18]. The Nsugbe Formation is predominantly sands with some conglomerate bands [17]. Also, the Ogwashi-Asaba Formation comprises alternating coarse sands, silts, and clays with thin to thick lignite seams [19,17].
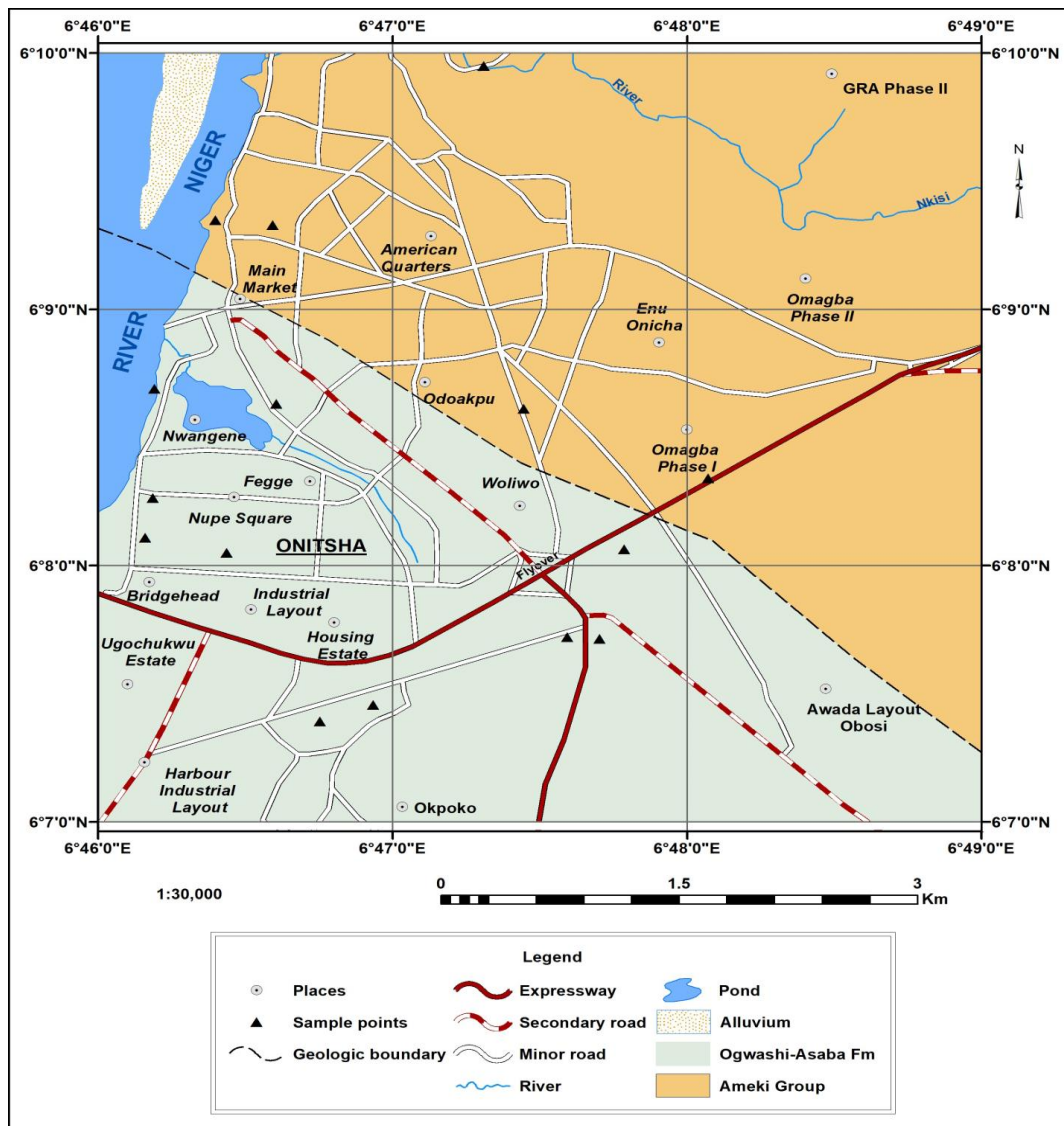

Fig. 1. Geologic and water sample location map of the study area

2. MATERIALS AND METHODS

A total of fifteen (15) water samples were collected from groundwater sources in the study area. The samples were collected in duplicates with a one-liter polyethylene bottle at every sampling point. One batch of the samples was filtered, acidified and labelled A while the second batch of the samples was neither filtered nor acidified and were labelled B. The samples labelled A were used for cation analysis and the samples labelled B were used for anion analysis. The bottles were previously washed and were later rinsed three times using the sample water before collecting the actual samples. In order to collect groundwater samples, the taps were opened and allowed to run for about five minutes to ensure that the water standing in the plumbing column were removed before collecting the sample to ensure that representative samples were collected. After collection, the sample bottles were covered with the bottle caps immediately to prevent any chemical deterioration. The samples bottles were stored in a box with ice cubes and transported to the laboratory for analysis.

The collected samples were analyzed for various physicochemical parameters using standard methods [20]. Distilled water was used in the preparation of solutions and rinsing of all equipment before use. In-situ measurements of electrical conductivity and pH, were carried out using EC meter (Model DDS-307) and pH meter (Hanna model HI991300) respectively. Argentometric method was used to determine chloride, nitrate was determined using (PD303) UV spectrophotometer and volumetric titration against ethylenediamine tetra-acetic acids (EDTA) was used for magnesium and calcium ions. Heavy metal analysis was conducted using Varian (AA240) Atomic Absorption Spectro-phometer.

The results of the chemical analysis were compared with the WHO [21] permissible limit for drinking water quality. Graphical methods such as Piper [14], Durov [16], Gibbs [22] and other ionic plots were employed in the data interpretation and assessment of the hydrogeochemical processes and mechanisms responsible for groundwater chemistry in the study area.

3. RESULTS AND DISCUSSION

The result of the chemical analysis is presented in Table 1. The physicochemical parameters are within the WHO guideline limit for drinking water quality except turbidity which exceeded the guideline values in six samples (2, 3, 4, 6, 9, and 15). The values for turbidity indicate that water sources should be filtered before use as drinking water. Turbidity may also indicate microbial presence in water sources. Farrell et al [23] noted the attachment of microorganisms to turbidity causing particles.

Table 1. The result of the physiochemical parameters in the water samples

Samples	pH	Ec us/cm	Turb NTU	NO_3 mg/l	CO_3 mg/l	SO_4 mg/l	Cl mg/l	Mg ppm	Na ppm	Ca ppm
1	7.24	44.10	2.50	5.18	22.00	41.23	20.00	0.26	1.78	3.43
2	7.18	46.60	6.50	3.26	8.00	52.47	40.00	0.12	0.77	3.86
3	7.41	33.80	17.90	11.05	30.00	65.42	113.00	0.06	0.34	5.76
4	7.23	33.70	16.70	12.33	10.00	65.35	185.00	0.06	0.49	4.88
5	6.97	54.10	3.80	6.24	12.00	54.72	47.00	0.03	0.42	4.90
6	7.01	54.20	7.20	9.55	22.00	62.47	46.00	0.10	0.37	6.75
7	7.35	54.30	4.80	5.24	16.00	70.70	39.00	0.02	0.29	7.54
8	6.98	44.70	3.40	7.83	12.00	56.17	68.00	0.11	0.23	6.38
9	6.77	45.00	5.90	4.83	16.00	44.12	15.00	0.05	0.27	4.79
10	7.22	45.10	4.40	6.06	16.00	75.76	25.00	0.10	0.26	5.88
11	6.98	55.50	3.10	12.92	10.00	45.35	35.00	0.04	0.26	6.78
12	7.55	79.55	2.30	7.35	16.00	48.23	11.00	0.04	0.29	6.78
13	6.92	68.92	2.90	4.47	8.00	64.94	95.00	0.08	0.29	6.08
14	6.93	68.93	3.20	3.31	10.00	43.70	17.00	0.03	0.26	5.74
15	7.20	79.20	5.60	5.45	18.00	63.70	132.00	0.02	0.16	6.56

3.1 The Determination of the Hydrochemical Facies and the Dominant Chemical Processes

The classification of water samples using Piper diagram is shown in fig. 2 and the interpretation was carried out according to Back and Hanshaw [24] (fig. 3). On the basis of this diagram, it was observed from the division of the triangle on the left (cation ion domain) that Ca^{2+} is the dominant cation. The order of cation distribution in water sources is $Ca^{2+} > Mg^{2+} > Na^+$. However, from the triangle on the right hand (anion domain), it was observed that 33% of the samples were located in the chloride dominant zone, 20% in SO_4^{2-} dominant zone and 47% in the no dominant ion zone. Hence, the order of distribution is no dominant ion $> Cl^- > SO_4^{2-} > CO_3^{2-}$ thus making Cl^- the most dominant ion. The observed order of distribution was also observed by Nwankwoala and Udom [25] in Port Harcourt area of River State Nigeria. The hydrochemical facies observed were Ca^{2+} - Mg^{2+} - Cl^- – SO_4^{2-} and Ca^{2+} - Mg^{2+} - HCO_3^- facies. The water type has (Ca^{2+} + Mg^{2+}) > (Na^- + $K^{-)}$), and ((SO_4^{2-} + Cl^-) > (CO_3^{2-} + HCO_3^-)). The results show that the alkaline earth metals exceed the alkali metals and the strong acids exceed the weak acids. Also, Ravikumar and Somashekar [26] reported the same trend with alkaline earth metals dominating over alkalis and strong acidic anions dominating over weak acidic anions in Varahi River basin in India. The water type indicates water that has been affected by mixing. Some points plotted in the 10% area of the diamond shape indicating Cl^- – SO_4^{2-} and Ca^{2+} – Mg^{2+} dominance. The water type is associated with permanent hardness and saline water [24].

The Durov diagram (Fig. 4) was interpreted following Lloyd and Heatcoat [27]. From the diagram it was observed that in 20% of the samples HCO_3^- and Ca^{2+} ions were dominant. However, in 80% of samples it was observed that Ca^{2+} and HCO_3^- ions were dominant. The partitioning indicate recharge water in limestone, sandstone, or many other aquifers. Also an important Na^+ + K^+ cation exchange was suspected to have taken place. The data show Na^+ replacement by Ca^{2+} or Mg^{2+} ions. A similar result was reported by Mussa and Mjemah [28].

3.2 Mechanisms of Chemical Reactions

The Gibbs diagram and other ionic plots were used to ascertain the common hydrogeochemical processes prevalent in the water sources. The Gibbs [22] plots were plotted with ionic concentration in mg/L (Fig. 5). The Gibbs plot was constructed using Na/Na+Ca against total dissolved cations, and Cl/Cl+HCO_3 against total dissolved cations. The plot was divided into three zones representing evaporation dominance, rock dominance and precipitation dominance zones. The plotted points fall in the region of rock dominance zone implying that the major process controlling water chemistry in the study area was mainly precipitation induced chemical rock weathering with dissolution of rock forming minerals to a minor extent by evaporation. Additionally, other ionic ratios were also employed to determine the processes and reactions prevalent in the study area that influence the water chemistry. It was observed that chemical weathering of rock-forming minerals is the main causative factor in the evolution of chemical composition of groundwater in the study area. It was also reported by Rao et al., [29] that the hydrogeochemistry of confined groundwater in South India is dominantly governed by natural water-rock interaction including evaporation dissolution, silicate weathering and ion exchange.

The Na^+ versus Cl^- plot was equally used in determining that evaporation was not the dominant process in the study area. Evaporation process does not affect the Na/Cl ratio. The plot of Na^+ versus Cl^- for the water sources show variations and these variations indicate that silicate weathering has a major influence on the water chemistry. Similarly, cation exchange reactions contribute to the distribution and occurrence of major ions in water. The cation exchange process can be identified by use of Na^+ and Cl^- ions. The depletion of Na^+ ions with respect to Cl^- ions is an evidence of cation exchange reaction. Rajmohan and Elango [28] made similar conclusions. Normally in ion exchange reaction, Ca^{2+} ion is retained in the aquifer material and Na^+ ion is released into the water. Excess Na^+ ion generated by the exchange reaction is not balanced by Cl^- ion but by alkalinity and SO_4^{2-} ion. Furthermore, in the reverse ion exchange reaction Na^+ ion is retained by the aquifer material and Ca^{2+} ion released into the water in a manner similar to results reported by Senthilkumar and Elango [30]. In the present study the excess Cl^- ion over Na^+ is balanced by Ca^{2+} and Mg^{2+} ions. There is a general depletion of Na^+ ion with respect to the Cl^- ion which indicates ion exchange reaction. The relative abundance of anionic facies shows that Cl^- + SO_4^{2-} were more abundant than HCO_3^-.
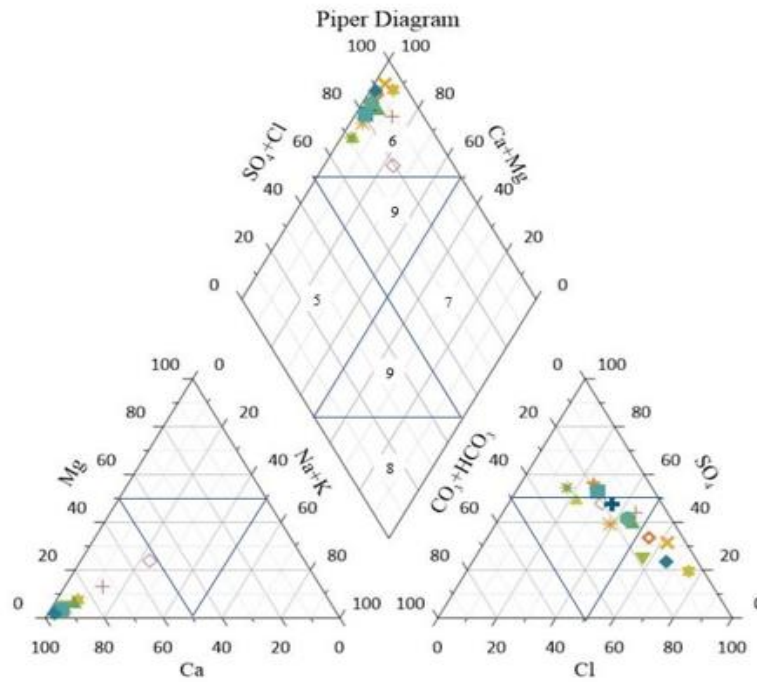
Fig. 2. Piper diagram showing the distribution of the different components of the water samples
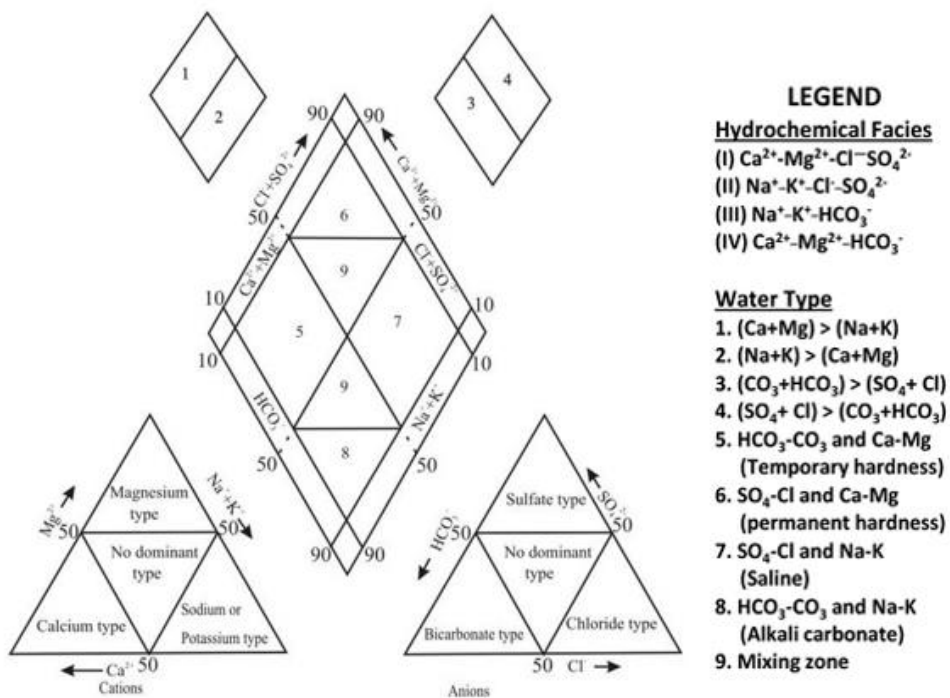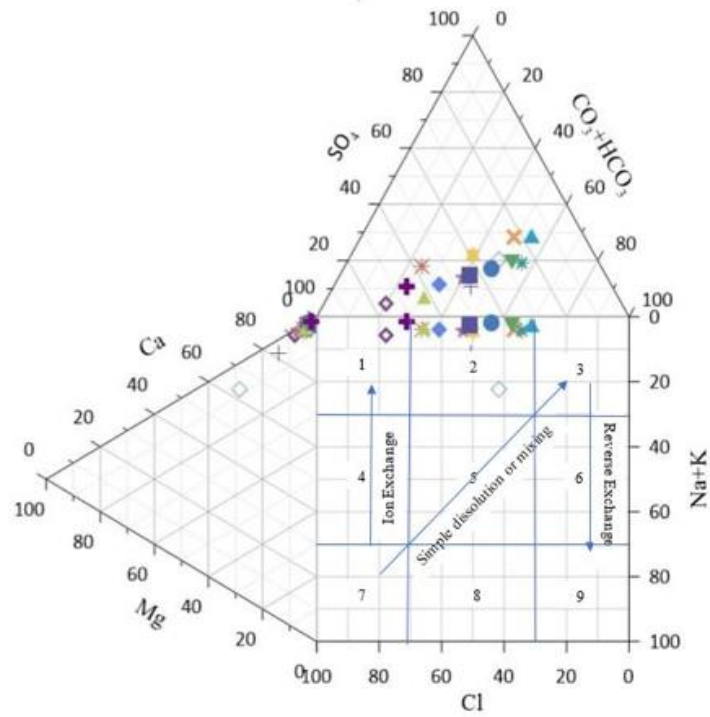

Fig. 3. Diagram showing Hydrochemical Facies [24]

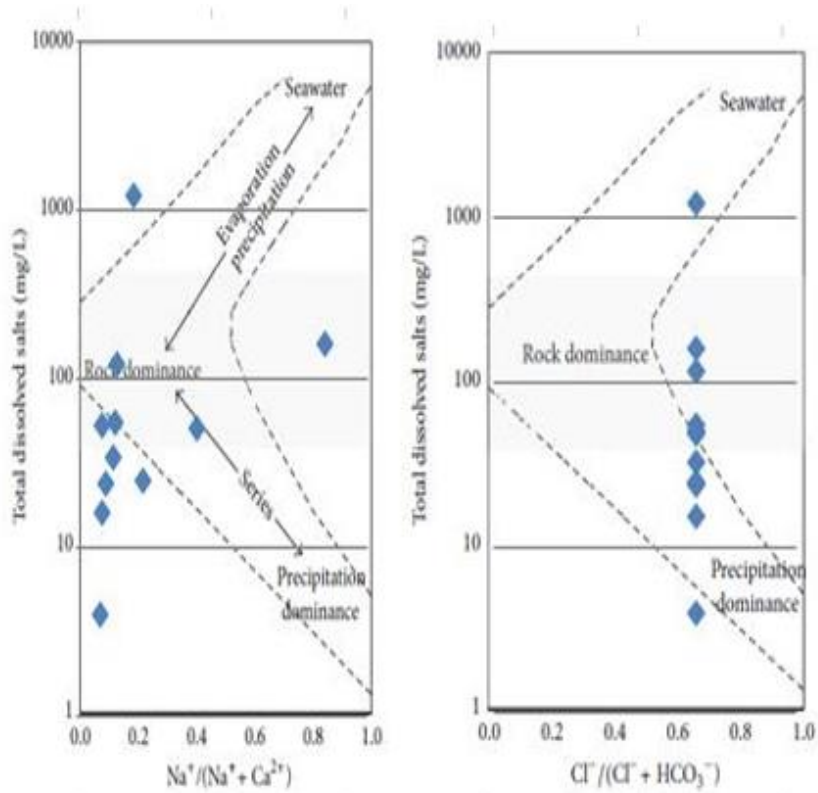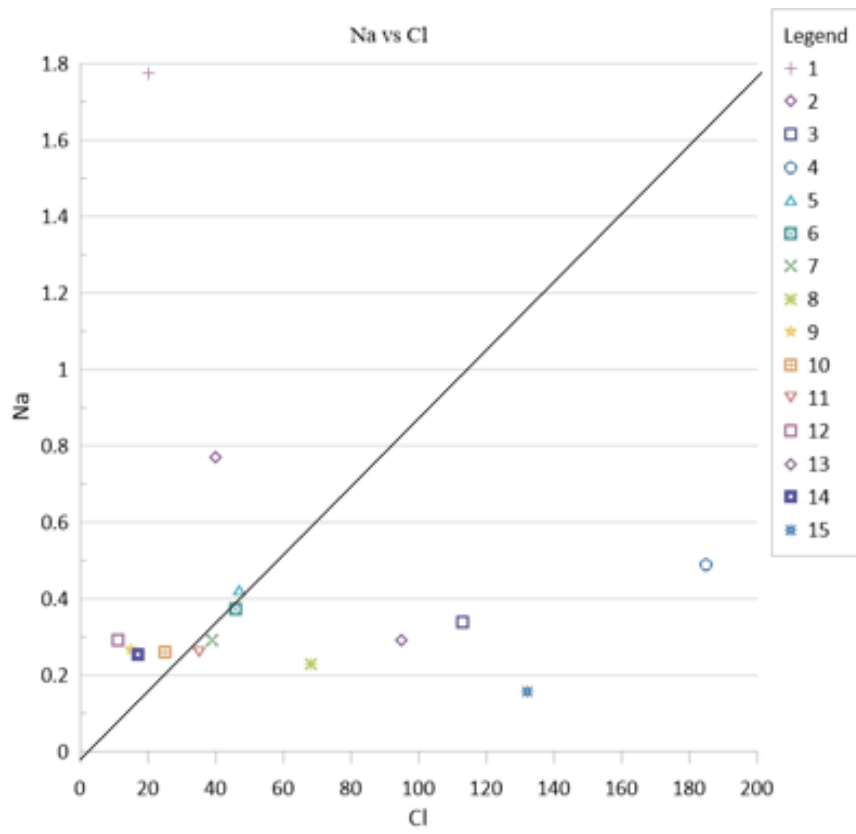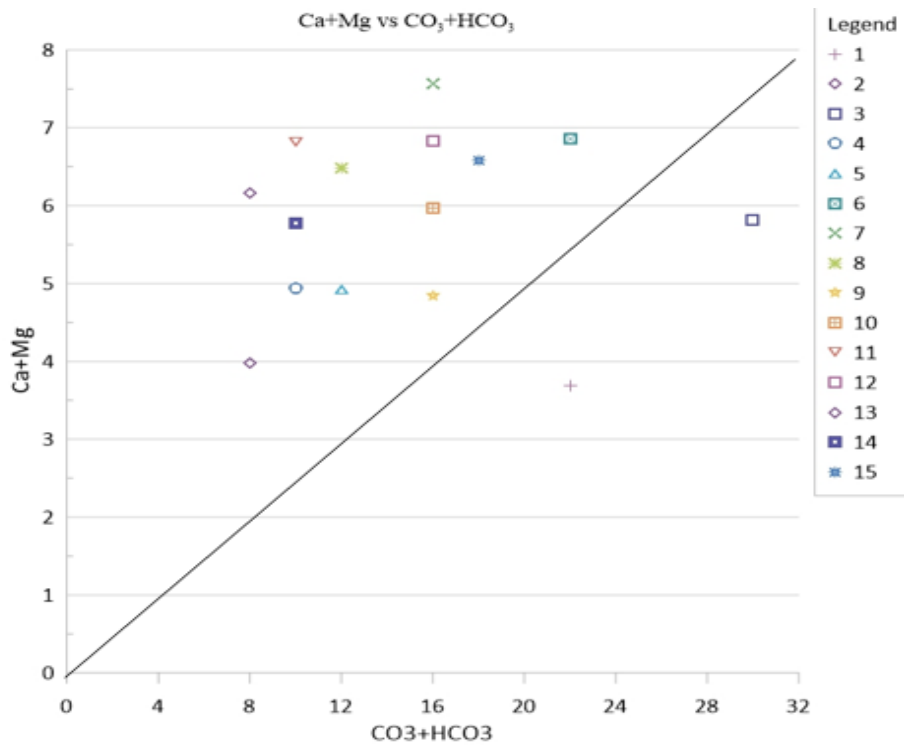**Fig. 4. Classification of water samples using Durov diagram.**

Fig. 5. The Gibbs Plots for rainy season showing the dominant hydrochemical processes
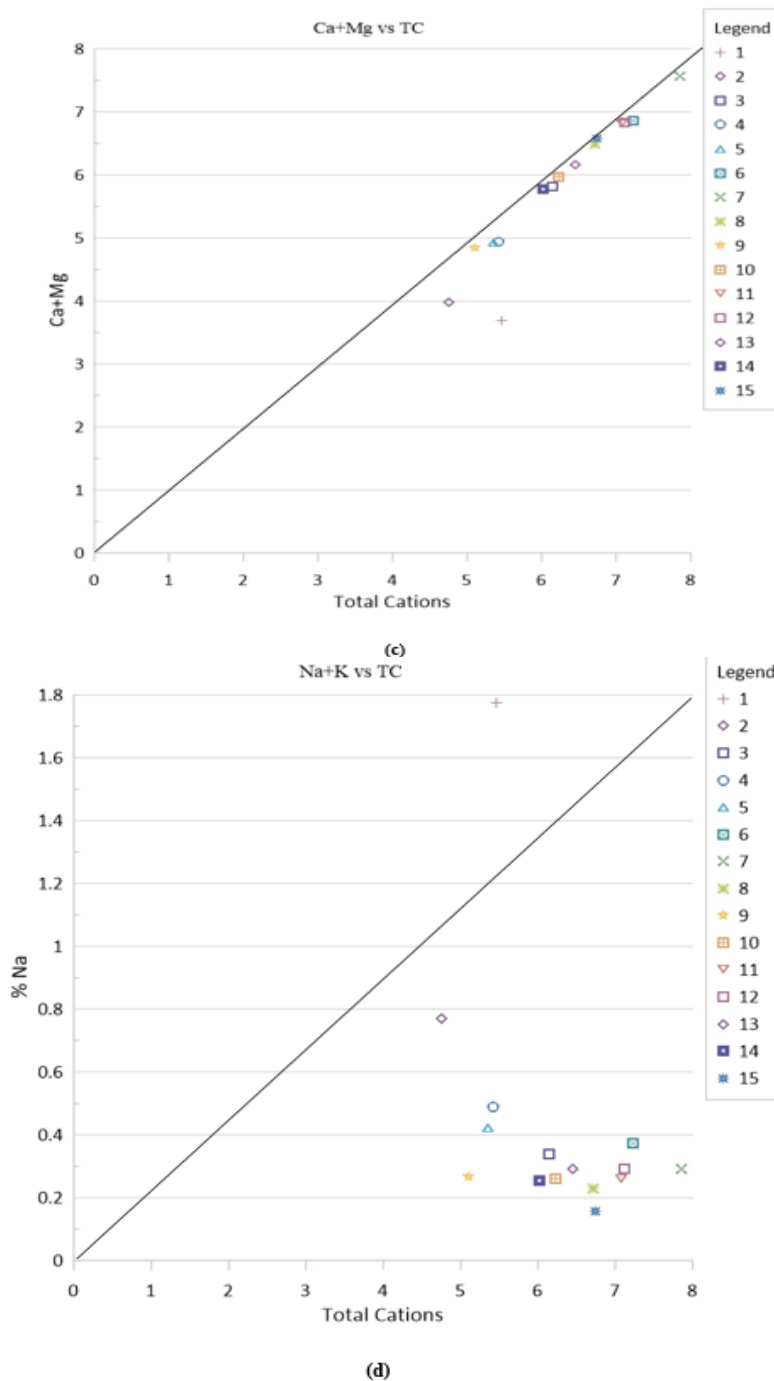
(a)

(b)

(c)

(d)

Fig. 6. Relationship between (a) Na versus Cl (b) Ca+Mg versus CO$_3$+HCO$_3$, (c) Ca+Mg versus TC and (d) Na + k versus TC

The plot of Ca^{2+} + Mg^{2+} ions against HCO$_3^-$ ions depicts samples with excess Ca^{2+} + Mg^{2+} ions. However, Ca^{2+} + Mg/HCO$_3$ ratio less than one (<1) indicate fresh recharge water thus, groundwater in the study area is mainly fresh recharge water.

The plot of Ca^{2+} + Mg^{2+} versus CO$_3^{2-}$ showed that all the plotted points are above the 1:1

equiline except one point. The data indicated excess of Ca^{2+} + Mg^{2+} ions. The plot of Ca^{2+} + Mg^{2+} against total cations (Tc) indicates that the plotted data points fall below the 1:1 equiline (Fig. 6). Additionally, the plot of Na$^+$ + K$^+$ versus Tc show that the plotted points fall below the 1:1 equiline. Therefore, the highest contribution of Na$^+$ and K$^+$ ions to dissolved cations is from silicate weathering, a conclusion consistent with

observations of Mohan et al., [31], and Rajmohan and Elango et al., [10]. However, Elango et al. [10] concluded that geochemical signatures of groundwater are effective tools in identifying the normal hydrogeochemical processes such as calcium carbonate dissolution, ion-exchange processes and silicate weathering. Some of these processes have been identified by the present study.

4. CONCLUSION

Hydrogeochemical investigation of water was carried out in the study area and it was observed that the dominant hydrochemical facies were Ca^{2+} - Mg^{2+} - Cl^- – SO_4^{2-} and Ca^{2+} - Mg^{2+} - HCO_3^- types implying water affected by mixing and simple dissolution. ''Equally, the water was observed to be fresh recharge water in limestone and sandstone aquifers and associated with important cation exchange reactions. The prominent mechanisms and chemical processes responsible for the chemical composition of the water is rock dominance and precipitation induced dissolution of rock minerals, and chemical weathering of rocks. Furthermore, there was general depletion of Na ion with respect to the Cl ion which was consistent with ion exchange reaction.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Ramkumar T, Venkatramanan S, Anitha MI, Anuradha M, Varunkumar S. Groundwater chemistry of Nagapattinam Coastal Town, Tamilnadu, India. Researcher. 2010;2(8):73-83.
2. Olayinka AI, Abimbola AF, Isibor AR. A geo-electrical – hydrogeochemical investigation of shallow groundwater occurrence in Ibadan, S. W. Nigeria. Environmental Geology. 1999;34(1-2):31-39.
3. Kurwadkar S, Kanel SR, Nakarmi A.. Groundwater pollution: Occurrence, detection, and remediation of organic and inorganic pollutants. Water Environment Research. 2020;92(10):1659-1668.
4. Okolo CM, Akudinobi BEB, Obiadi II, Okoye EI. Assessment of pollution status of the Lower Niger Drainage Area, South Eastern Nigeria using heavy metals. Journal of Basic Physical Research. 2017; 7:55-62.
5. Baghdadi ME, Zantar I, Jouider AI, Nadem S, Medah R. Evaluation of hydrogeochemical quality parameters of groundwater under urban activities—case of Beni Mellal city (Morocco). Euro-Mediterranean Journal for Environmental Integration. 2019;4(1):1–19.
6. Siddique J, Menggui J, Shah MH, Shahab A, Rehman F, Rasool U. Integrated approachto hydrogeochemical appraisal of groundwater from Sargodha District, Pakistan. Geofluids; 2020.
Available:https://doi.org/10.1155/2020/662 1038
Access on 12/12/23.
7. Ezzeldin HA. Geochemical processes affecting groundwater quality in Wadi Sidri basin South Sinal, Egypt. Egyptian Journal of Desert Resources. 2023;73(1):283-309.
8. Appelo C, Postma D. Geochemistry, groundwater and pollution. 2nd Edition,Balkema Rotterdam; 2005
9. Olea-Olea S, Alcocer J, Armienta MA, Oseguera LA. Geochemical Modelling unravels the water chemical changes along the largest Mexican river. Applied Geochemistry. 2022;137.
Available:http://doi.org/10.10161j-apgeochem-2021.105157.
Access on 18/12/23
10. Elango L, Rannan R, Senthil KM. Major ion chemistry and identification of hydrogeochemical processes of groundwater in a part of Kancheepuram district, Tamil Nadu, India. Journal of Environmental Geosciences. 2003;(10): 157–166.
11. Mondal NC, Singh VP, Singh VS, Saxena VK. Determinating the interaction between groundwater and sline water through groundwater major ions chemistry. Journal of Hydrogeology. 2010;388(1-2):100–111.
12. Wanda E, Manjerezi M, Mwatseteza JF, Kazembe LN. Hydrogeochemical appraisal of groundwater quality from weathered basement aquifers in Northern Malawi. Physics and Earth Chemistry of the Earth A/B/C. 2011;36 (14-15):1197–1207.
13. Okolo CM, Akudinobi BEB, Obiadi II. Evaluation of water resources of some satellite towns in the central part of Anambra State, Se, Nigeria. Sustainable

Water Resources Management. 2020;6(6): 102-112.

14. Piper AM. A graphic procedure in the geochemical interpretation of water analyses Eos. Transactions American Geophysical Union. 1944;25(6):914–928.

15. Nwankwoala HO, Udom GJ. Investigation of hydrogeochemical characteristics of groundwater in Port Harcourt City Nigeria: Implications for use and vulnerability. Journal of Applied Science and Environmental Management. 2011;15(3): 479 – 488.

16. Durov SA. Natural waters and graphic representation of their composition. Doklady Akademii Nauk SSSR. 1948;59: 87-90.

17. Nwagide CN. Nigerian sedimentary basin, CSS publishing house, Enugu, Nigeria, 2013;277-393.

18. Ekwenye OC, Okeke KK, Otosigbo G, Onyemesili O. A re-evaluation of the stratigraphic and palaeogeographic evolution of the Paleogene sedimentary successions of Niger Delta Jordan. Journal of Earth and Environmental Sciences. 2014;2:146–156.

19. Kogbe CA. The Cretaceous and paleogene sediment of South Eastern Nigeria. In: Kogbe CA. Edition. Geology of Nigeria. Elizabethan Publishing Company. Lagos. 1976;273-283.

20. American Public Health Association (APHA). Standard method for the examination of water and waste water 20th Edition Section 4500 B-Cl, E-SO4 2; 1998.

21. WHO Guidelines for drinking water quality. 4th Edition World Health Organization Genève Switzerland; 2010.

22. Gibbs RJ. Mechanism controlling world's water chemistry. Science. 1970;170:1088–109.

23. Farrell C, Hassard F, Jefferson B, Lerzrant T, Nocker AJ. Turbidity composition and the relationship with microbial attachment and UV inactivation efficacy. Science of Total Environment. 2018;624:638-647.

24. Back W, Hanshaw BB. Chemical geohydrology. In: Chow VT (Editor) advances in hydroscience. Academic press. New York. 1965;49-109.

25. Nwankwoala HO, Udom GJ. Investigation of hydrogeochemical characteristics of groundwater in Port Harcourt City Nigeria: Implications for use and vulnerability. Journal of Applied Science and Environmental Management. 2011;15(3): 479–488.

26. Ravikumar P, Somashekar RK. Principal component analysis and hydrochemical facies characterization to evaluate groundwater quality in Varahi River basin, Karanataka State India. Applied Water Science. 2017;7:745–755.

27. Lloyd JA, Heathcote JA. Natural inorganic hydrochemistry in relation to groundwater. An introduction. 1985;296. New York: Oxford Uni. Press.

28. Mussa KR, Mjemah IC. Using hydrogeochemical facies and signature for groundwater characterization and evolution assessment in aquifers with contrasting climate and geology in Tanzania. Applied Water Science. 2023; 13:201-226.

29. Rao NS, Sunitha B, Sun L, Spandana BD, Chaudhary M. Mechanisms controlling groundwater chemistry and assessment of potential health risks: A case study from South India. Geochemistry. 2020;80(4): 125-135.

30. Senthilkumar M, Elango L. Geochemical processes controlling the groundwater quality in lower Polar river basin, Southern India. Journal of the Geological Society of India. 2013;78:523-540.

31. Mohan G, Stokke K. Participatory development and empowerment: The dangers of localism. Third World Quarterly, 2000;21:247-268.

32. Rajmohan N, Elango L. Identification and evaluation of hydrogeochemical processes in the groundwater environment in an area of Polar and Cheyyar river basin, southern India. Hydrological Process 2004;20:2415-2427.