Geochemical evaluation of carbonate aquifers in Ngbo and environs, Ebonyi State, southeastern, Nigeria

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Abstract

The geochemical evaluation of carbonate aquifers in Ngbo and environs has been executed to ascertain the major ion chemistry and quality of waters for domestic and drinking uses. Ten water samples were gathered from pit lakes, hand dug wells, boreholes and rivers. The collected samples were analysed for pH, EC, TDS, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- and PO_4^{2-} in the laboratory using the standard methods. The results were compared with NDWQS and WHO standards. The physical parameters varied from pH (6.2–8.4), temp. (25.0–26.0 °C), electrical conductivity (4.9–102 $\mu\text{S}/\text{cm}$) and total dissolved solids (25.5–214.2 mg/l). The analysed results revealed the mean concentration of cations and anions in the following order: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Fe}^{2+}$ and $\text{HCO}_3^- > \text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{Cl}^-$, respectively. Based on the standard limits, about 90% of the waters in the study area is suitable for domestic and drinking purposes. The Piper trilinear, Stiff and Durov diagrams showed that water samples from various locations fall into mixed $\text{CaCO}_3^{2-} + \text{HCO}_3$ type. Various ionic ratio plots show that water sources are from dissolution of minerals in the aquifer media. Geochemical parameters such as Cl^- , Na^+ and K^+ show good interrelationship with positive factor loadings among the ions.

Keywords Geochemical processes · Carbonate aquifer · Hydrochemical facies · Correlation matrix

Introduction

Water is considered as fresh water exclusively if it generally contains Ca^{2+} as primary cation and HCO_3^- as principal anion. The H_2CO_3 , HCO_3^- , CO_3^{2-} , OH^- and H^+ are the major carbonic species found in water body (Panthi 2003). Most of the groundwater resources rich in Ca^{2+} ion concentrations are considered safe for drinking (Castanier et al. 1999). The deposition of limestone within an environment has been proven to be the natural source of CaCO_3 in water resources (Kile et al. 2000). However, the physico-chemical

component of groundwater in carbonate aquifers is governed by composition of water replenishment, chemical and mineralogic constitutions of the aquifer bed rocks, the residence time, hydrogeologic characteristics of the underlying rocks which govern water–rock interactions and groundwater flow, such as hydraulic conductivity and the flow regime (Moral et al. 2008).

In recent times, the chemistry of groundwater in carbonate aquifers has received considerable attention from researchers all over the world due to its heterogeneity and susceptibility to chemical pollution from human activities (Field 1988; White et al. 1995; Romanov et al. 2003). Owing to the modification in development of groundwater in carbonate aquifer, Hughes et al. (1994) stated that geological structures and hydrogeological systems within carbonate aquifers are extremely complex. On the other hand, Plummer et al. (1990) opined that dedolomitization influenced by gypsum dissolution is a major factor controlling the origin of water chemistry in the carbonate aquifers. Hanshaw and Back (1979) stipulated the geochemical changes in carbonate aquifer systems and their hydrogeological deductions. Jalali (2005) reported that the dissolution of carbonate minerals, cation exchange and weathering

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of silicates influences the chemical composition of groundwater in semiarid region of western Iran. Igwe et al. (2018) in their work on quality of natural waters in carbonate aquifers at a densely populated Odukpani area of Cross River State, Southern Nigeria stated that precipitation and dissolution of carbonate minerals within the aquifers are likely contributing to the modification of flow characteristics of the aquifer matrices.

In the study area, the understanding of various geochemical processes controlling carbonate aquifer has not been given considerable attention it required; hence, the aim of this study is to establish the hydro-geochemical process influencing modifications in the water quality.

Study area

Location

Ngbo is located in the north-western part of Ebonyi State, Southeastern, Nigeria. The area, comprising approximately 181 km², is bounded within latitudes 6°25'0" N to 6°31'0"

N and longitudes 7°58'0" E to 8°3'0" E, with estimated population density of about 234,532 people. The study area bordered with Benue State in the north, Ezza North to the South, Ishielu in the west and Ebonyi Local Government Area to the east. Figure 1 shows the geographical map of Ebonyi State showing the study area.

Topography, drainage, climate and vegetation of the study area

The area is characterized by vast low-lying plain with elevation varying from 50 to 100 m above sea level (Umeji 2000). Ngbo is drained by Ebonyi River and its associated streams, which include Ngene Ava, Nsu, Amanata and Ogurube stream. These streams are ephemeral and dry up soon after rainy season. Consequently, during the rainy season, these streams overflow its banks and cause flooding and water logged. As described by Igbozulike (1975), the study area falls within the humid rainforest region of southeastern Nigeria with annual rainfall between 1750 and 2500 mm per annum. The area is also characterized by a tropical climate with rainy and seasons. The rainy season spans from April

Fig. 1 Geographical map of Ebonyi State showing the study area

to October, whereas the dry season lasts from November to March. The average temperature in the area ranges from 29° to 30° C.

Geologic and hydrogeology

The geology and hydrogeology of the study area have been studied by various researchers at different scopes (Reyment

Fig. 2 Geologic map of the study area

Fig. 3 Pictures of rock units visited in the study area

Fig. 4 Picture of fossils imprints encountered in the study area during the field work

Table 1 Summary of sample collection

S/N	Location	Sample ID	Georeferencing	
			Latitude	Longitude
1	Lampet Mining Pit	PL 1	6°29'56.33"N	7°58'34.31"E
2	Ngbo Borehole	BH 1	6°27'4.19"N	7°58'6.11"E
3	MBC Daniel Mining Pit	PL 2	6°29'44.46"N	8°0'31.54"E
4	Enerco Mining Pit	PL 3	6°30'7.46"N	8°0'16.70"E
5	Stone Pile Mining Pit	PL 4	6°26'4.09"N	8°2'22.09"E
6	Ogwurube River	RS 1	6°27'38.32"N	8°0'55.29"E
7	Ngbo Hand Dug Well	HDW1	6°28'2.06"N	7°58'23.17"E
8	Ndeagu Amoffia Borehole	BH 2	6°30'33.43"N	8°0'35.25"E
9	Dev. Center Hand Dug Well	HDW2	6°30'33.43"N	8°2'16.16"E
10	Ngene Ava River	RS 2	6°29'17.00"N	8°0'50.09"E

Table 2 Results of physico-chemical parameters of the study area

Parameters (mg/l)	PL 1	BH 1	PL 2	PL 3	PL 4	RS 1	HDW1	BH 2	HDW2	RS 2	NDWQS (2007)	WHO (2011)
pH	7.5	6.3	8.1	7.7	8.4	6.2	7.8	6.6	8.1	6.5	6.5–8.5	6.5–8.8
Temp. (°C)	25.6	25.5	26.0	25.7	25.8	26.0	25.5	25.0	25.0	25.7	Ambient	Ambient
EC ($\mu\text{S}/\text{cm}$)	7.2	4.9	52	58	96	70	75	100	92	102	1000	1250
TDS	161.9	165.9	214.2	25.5	93.7	135.7	46.8	121.5	93.7	161.0	500	500
Ca^{2+}	47.9	102.6	86.4	112.6	62.8	108.5	100.1	68.3	74.9	47.6	75	75
Mg^{2+}	28.2	19.3	40.0	35.7	40.0	17.0	54.8	42.7	28.2	10.9	–	50
Na^+	16.08	1.62	1.02	4.81	1.43	0.96	1.05	1.62	3.81	1.02	–	200
K^+	0.98	1.56	1.23	0.27	2.07	0.98	2.11	1.12	0.37	1.41	–	–
Cl^-	1.53	1.02	0.81	1.02	1.02	9.6	1.86	3.03	4.51	0.81	250	200
SO_4^{2-}	4.9	2.6	2.6	6.8	3.4	2.9	2.9	4.1	6.9	2.6	100	200
CO_3^{2-}	6.6	19.8	24.2	10.6	13.2	5.28	36.7	40.2	19.8	6.6	–	–
HCO_3^-	30.01	20.12	60.20	80.13	20.11	10.10	20.00	20.19	18.57	25.09	–	100
Fe^{3+}	0.000	0.001	0.000	0.003	0.000	0.001	0.04	0.003	0.000	0.04	–	0.3
B ($\mu\text{g}/\text{l}$)	0.002	0.011	0.002	0.007	0.022	0.026	0.001	0.007	0.020	0.002	–	–

1965; Murat 1972; Petters and Ekweozor 1982; Agagu et al. 1985; Nwajide 1990; Petters 1991; Ojoh 1992; Nwajide 2013). The major two geological formations underlying the study area is Abakaliki (Albian) and Ezeaku Formations (Turonian). These formations consisting of dark grey coloured fissile shale, reddish brown claystone interbedded with ferruginized ironstone, and flaggy grey limestone interbedded with dark coloured dolomite with fossil imprints like gastropoda, ammonite, pelecypoda and brachiopoda have been reported by Umeji (1984, 1993). These rocks were designated as units A, B, C and D in Fig. 2, whereas Figs. 3 and 4 show the pictures of rock units visited in the area.

Hydrologically, the area is characterized by two aquifer systems: the shallow unconfined and deep confined aquifer systems (Uma et al. 1990). The shallow unconfined aquifers as shown in Fig. 5 appeared within fractured, weathered, jointed shale and some patches of sandstone in the areas of the undertaken studies.

Materials and methods

Sampling

Ten surface and groundwater samples were collected from motorized boreholes, hand dug wells, pit lakes and streams with 1 litre polyethylene bottles (Table 1, Fig. 6). The samples bottles were soaked in 10% HNO_3 for 24 hours and rinsed several times with deionized water prior to use. At each sampling locations, the bottles were thoroughly rinsed with the water to be sampled before collection, tightly closed leaving air bubble below the stopper, labelled proper and stored in cooler. The samples were sent to laboratory for chemical analysis within the 24 hours of collection.

Sample analysis

The in-situ measurements of pH, temperature, EC, CaCO_3 and TDS were carryout in the field using multiple EXTECH (341350A) PH/Conductivity/TDS/Salinity/ORP Meter. Prior to measurement of pH, the electrode was calibrated using pH 6.88 and 4.01 buffer solutions at the same manner EC and TDS of the water samples were measured. Temperature was determined using alcoholic thermometer. The HCO_3^- and CO_3^{2-} were measured by titration using methyl orange and HCL 0.05N as indicator. SO_4^{2-} by turbidmetry using visible light spectrophotometer. Ion such as Ca^{2+} , Mg^{2+} , B and K^+ were determined in the lab using the Buck Model 210/211 AAS 220GF graphite Furnance and 220 AS Autosampler, which was calibrated by 2-point calibration using the appropriate Matrix Blank for the flame and the standard set within the calmax range for each element. The conditions which the cations were done is by Air/Acetylene Flame, $\text{N}_2\text{O}/\text{Acetylene}$ Flame, Integrated mode, Normal parameter (Sodium (Na) is done by emission mode) and the samples were digested using Nitric Acid per chloric Acid.

Geochemical interpretations

The spatial distributions and illustrations of the hydrochemical facies were perfumed using ArcGis 10.4 and Rockworks computer processing software package. However, the statistical analysis of the geochemical data was determined with the aid of Statgraphics software.

Results and discussion

The results obtained during the undertaken studies is presented in Table 2. It was found that the physico-chemical

Fig. 5 Revealed the borehole log of the area

composition of the water samples was highly different in every areas of the undertaken studies.

pH and temperature

The pH value of water samples in the study ranged from minimum 6.2 to 8.4 with the least value observed in Ogwurube River (RS 1), while the maximum value was recorded at Stone Pile Mining Pit (PL 4). The pH of the water samples indicates mildly acidic to alkaline in nature. pH was within the NDWQS (2007) and WHO (2011) acceptable level. This is consistent with the studies carried out by Ozoko (2015) in the study area. The alkaline pH values obtained may have been as a result of partial neutralization of the bed rocks by the amount of dissolved CO₂, carbonate and bicarbonate in

water (Ghandour et al. 1985). The temperature ranged from 25.0 to 26.0 °C with the least value observed at Ndeagu Amoffia Borehole (BH 2) and Dev. Center Hand Dug Well (HWD 2), while the maximum value was recorded in MBC Daniel Mining Pit (PL 2) and Ogwurube River (RS 1). The temperature values were within the applicable regulation which requires ambient levels.

Electrical conductivity and total dissolved solid

EC varied from 4.9 µs/cm to 102 µs/cm with average value of 65.71 µs/cm. EC had the highest concentration of 102 µs/cm at Ngene Ava River (RS 2), while the minimum value of 4.9 µs/cm was recorded at Ngbo Borehole (BH 1). The elevated value of EC at RS 2 suggests mineral dissolution.

Fig. 6 Sampling map of the study area

The electrical conductivity (EC) for all the water samples fell within the permissible limit of 1000 $\mu\text{S}/\text{cm}$ and 1250 $\mu\text{S}/\text{cm}$ set by NDWQS (2007) and WHO (2011). Similarly, TDS fluctuate between 25.5 mg/L at Enerco Mining Pit (PL 3) to

214 mg/L at MBC Daniel Mining Pit (PL 2) with average value of 121.99 mg/L. These values are in agreement with research carried out by Igwe et al. (2018). These results indicate fresh to moderately mineralized water. According to the

Table 3 Classification of water quality based on salinity values (Robinove et al. 1958)

No. of sample	TDS (mg/L)	Interpretation
10	< 1000	Non-saline
0	1000–3000	Slightly saline
0	3000–10,000	Moderately saline
0	> 10,000	Highly saline
Total = 10		

standard proposed by NDWQS (2007) and WHO (2011), the values of TDS are 500 mg/L and 1200 mg/L. TDS values fell below NDWQS and WHO permissible limits. The entire water samples are non-saline (Table 3) based on the salinity classification suggested by Robinove et al. (1958).

Calcium and magnesium

The Ca^{2+} values are generally above NDWQS (2007) and WHO (2011) permissible limit 75 mg/L, varying from 47.6 mg/L at Ngene Ava River (RS 2) to 112.6 mg/L at Enerco Mining Pit (PL 3) with average value of 81.17 mg/L (Fig. 7). The highest concentration of Ca^{2+} observed at Enerco Mining Pit (PL 3) is expected to come from main rock types in the area where limestone and dolomite are the most dominant geological units. Consequently, the acceptable limit of Mg^{2+} is 30 mg/L. The values obtained for magnesium ranged from 10.9 mg/L at Ngene Ava River (RS 2) to 54.8 mg/L at Ngbo hand dug well with average value of 31.68 mg/L with average value of 31.68 mg/L. Higher concentration of Mg^{2+} was observed at PL 2, PL 3, PL 4, HDW 1 and BH 2, respectively. The dissolution of calcite and dolomite in the carbonate aquifers in the study area generally accounts for the Ca^{2+} and Mg^{2+} concentration in the surface water and groundwater.

Fig. 7 Spatial distributions of calcium in the study area

Fig. 8 Spatial distributions of sodium in the study area

Sodium and potassium

The estimated Na content from collected water samples ranged from 1.02 mg/L at MBC Daniel Mining Pit (PL 2) and Ngene Ava River (RS 2) to 16.08 mg/L at Lampet Mining Pit (PL 1) with average value of 3.34 mg/L (Fig. 8). Most of the samples have sodium levels that are not in excess of the permissible limit of 200 mg/L stipulated by WHO (2011). However, the potassium of analysed water samples varied from 0.27 mg/L to 2.11 mg/L. The highest value of potassium was observed at Ngbo Hand Dug Well (HDW 1) with average of value of 1.21 mg/L. No health base guideline values have been derived (NDWQS 2007; WHO 2011) for potassium. The presence of sodium and potassium in the water samples may emanate from ancient sea intrusion.

Chloride and sulphate

The maximum permissible limit of chloride in potable water is 200 mg/l. In the study area, the analysed water samples,

the concentration of chloride fluctuate between 0.81 mg/L at MBC Daniel Mining Pit (PL 2) and Ngene Ava River (RS 2) to 9.6 mg/L at Ogwurube River (RS 1) with average value of 2.52 mg/L (Fig. 9). They are generally low. The chloride content of the water sample when compared with NDWQS and WHO standard showed that all samples had concentration within the permissible limit. Moreover, the acceptable limit of sulphate as stipulated by NDWQS (2007) is 100 mg/L and WHO (2011) is 200 mg/L. The sulphate content in the water samples varied from 2.6 mg/L at Ngbo Borehole (BH 1), MBC Daniel Mining Pit (PL 2) and Ngene Ava River (RS 2) to 6.9 mg/L at Dev. Center Hand Dug Well (HDW 2) as shown in Table 2. The entire samples found to be well within permissible limit.

Carbonate and bicarbonate

The availability of CO_3^{2-} and HCO_3^- in water is associated with calcium- and magnesium-rich minerals. In the study

Fig. 9 Spatial distributions of chloride in the study area

area, the concentration of CO_3^{2-} in the water samples varied from 5.28 at Ogwurube River (RS 1) to 40.2 mg/L at Ndeagu Amoffia Borehole (BH 2) with average value of 18.29 mg/L (Fig. 10). Similarly, the analysed HCO_3^- concentration from the collected water samples ranged from 10.10 mg/L at Ogwurube River (RS 1) to 60.20 mg/L at MBC Daniel Mining Pit (PL 2) with average value of 30.45 mg/L. According to WHO (2011), the maximum acceptable concentration of HCO_3^- in water for domestic purposes is 100 mg/L. All the water samples have HCO_3^- values well within the permissible limit of WHO (2011). These results obtained are mainly attributed to the weathering–dissolution of carbonate minerals in the study area.

Iron and boron

The levels of iron in the water samples are generally within the acceptable limits of WHO and NDWQS but some were unacceptable under the standard guidelines (Table 2). Iron content ranges from 0.000 mg/L (PL 1, BH 1, PL 2, PL 3,

PL 4, HDW1, BH 2 and HDW2) to 0.04 mg/L at Ogwurube River (RS 1) and Ngene Ava River (RS 2) which is very high above the standard stipulated by WHO (2011) and is due to dissolved ferrous ion (Fe^{2+}) in the water. Hem (1985) states that high concentration of dissolved ferrous iron can occur in solution at sites of either reduction of ferric oxyhydroxides or oxidation of ferrous sulphides. Furthermore, boron fluctuates between minimum of 0.001 $\mu\text{g/L}$ at Ngbo Hand Dug Well (HDW 1) to the maximum value of 0.011 $\mu\text{g/L}$ at Ngbo Borehole (BH 1) with average value of 0.01 $\mu\text{g/L}$.

Hydrochemical facies

Piper diagram

Piper's trilinear diagram (Piper 1944) was prepared to evaluate the geochemical sources and the connectivity between the underlying lithology and water chemistry of the study area. The interpretation of piper's trilinear diagram for surface and groundwaters in the study area revealed that Ca^{2+} ,

Fig. 10 Spatial distributions of bicarbonate in the study area

Mg^{2+} , CO_3^{2-} and HCO_3^- are the predominant cations and anions, therefore, suggesting equal dominance of strong alkaline earth metals; hence, the water samples are classified as $\text{Ca}^{2+}-\text{CO}_3^{2-}$ and $\text{Mg}^{2+}-\text{HCO}_3^-$ hydrochemical facies (Fig. 11).

Stiff diagram

Stiff (1951) plot was used to classify the water qualities of the study area based on their similarity in shape. Waters of uniform quality have a similar shape. The diagram plots cations on the left and anions to the right-hand side. This classification method is a complement to Piper Trilinear diagram. Water sample from PL 1, BH 1, PL 2, PL 3, PL 4, RS 1, HDW 1 and HDW 2 displays peculiar shapes, with Ca^{2+} being the dominant cations, while $\text{HCO}_3^- + \text{CO}_3^{2-}$ is the dominant anion while BH 2 and RS 2 reveal similar shapes, with Mg^{2+} being the dominant cation, whereas $\text{HCO}_3^- + \text{CO}_3^{2-}$ is the dominant anion. The distribution of

the various hydrochemical facies can be clearly seen in Fig. 12a, b.

Durov diagram

The major cations and anions of the water samples were plotted on Durov's diagram since it helps in the characterization of evolutionary trends and reveals the hydrochemical processes occurring in any surface and groundwater system. The Durov plot revealed two geochemical processes that could control the water chemistry of the area. Most of the surface and groundwater samples revealed Ca^{2+} and $\text{CO}_3^{2-} + \text{HCO}_3^-$ dominant. These usually result from ionic exchange of Ca^{2+} and $\text{CO}_3^{2-} + \text{HCO}_3^-$ rich waters or as a result of the water exhibiting simple dissolution, mixing or dissolution influences. However, other samples showed $\text{Na}^+ + \text{K}^+$ and partly Cl^- exhibiting probably mixing or uncommon dissolution (Fig. 13).

Fig. 11 Piper trilinear diagram

Geochemical process

The results of ionic ratios were used to infer the geochemical processes and factors responsible for the modification of surface and groundwater chemistry of the study area. The identified processes are interpreted in detail in the following sections. The relationships among the Na/Cl , Na/HCO_3^- , $\text{HCO}_3^-/\text{Ca}^{2+}+\text{Mg}^{2+}$, total cations/ $\text{Ca}^{2+}+\text{Mg}^{2+}$, $\text{Na}^++\text{K}^+/\text{Cl}^-+\text{SO}_4^{2-}$ and total cations/ Na^++K^+ can be used to deduce the evolution of ions and the processes prevailing in water composition (Table 4). Forward and reverse ion exchange processes often influence the origin of geochemistry of surface and groundwater systems. However, forward ion exchange process is described by the replacement of the Na^+ ion on clay minerals by Ca^{2+} and Mg^{2+} ions in surface and groundwater systems and Mg (Barzegar et al. 2018). In a similar manner, reverse ion exchange process is interpreted by the displacement of Ca and Mg ions on clay minerals by Na ion in the surface and groundwater systems (Barzegar et al. 2018). The hydrochemical data of the analysed samples are showcased on Na^+ vs. Cl^- scatter plot. However, a scattered plot of sodium against chloride as shown in Fig. 14a revealed that most of the samples are plotting above 1:1 equiline, suggesting reverse ion exchange which is chiefly controlled by water–rock interaction, most

likely derived from the weathering of silicate minerals, while few samples are plotting below 1:1 equiline, indicating forward ion exchange. At the same time, the scattered diagram of Na^+ vs HCO_3^- highlighted that all the samples lie above 1:1 equiline, suggesting the presence of calcite weathering. Only one sample lie below the 1:1 equiline showing that silicate weathering occurs (Fig. 14b). The evidence of calcite weathering can be explained by the relationship among $\text{Ca}+\text{Mg}$ versus HCO_3 (Fig. 14c). Moreover, the evaporation process would cause high concentration of all mineral species in water (Maya and Loucks (1995). The scattered plot of $\text{Ca}+\text{Mg}$ vs. total cations reveals that all the data fall on the above the 1:1 equiline, suggesting that Na and K is not the main source for the increase of TDS (Fig. 14d). Meanwhile, a scatter plot is shown in Fig. 14e illustrating that the majority of the samples lie above the 1:1 equiline suggesting that ions result from silicate weathering (reverse ion exchange), the dominant of $\text{Cl}+\text{SO}_4^{2-}$ over $\text{Na}+\text{K}$ indicates silicate weathering and also that the higher concentration of alkalis is from precipitation as reported by Garrels and Mackenzie (1971). The $\text{Na}+\text{K}$ vs. total cations scatter plot (Fig. 14f) of the study area shows that most of the sample points fall on the total cations trend. This suggests that the cations in the surface and groundwater might have been derived from silicate weathering.

Fig. 12 a, b Stiff diagram showing water type in the study area

Statistical analysis

Correlation matrix

From the Pearson correlation matrix, the values of (*r*) can be classified into positive high and low as well as negative high and low correlations. At high positive correlation, values were observed for the parameters of CO_3^{2-} – Mg^{2+} (0.73), SO_4^{2-} – Na^+ (0.45), SO_4^{2-} –pH (0.39), HCO_3^- –pH (0.37), HCO_3^- – SO_4^{2-} (0.37) and HCO_3^- –Temp. (0.31), indicating the strong relation between these variables. A low positive correlation value was observed for the parameters of CO_3^{2-} – K^+ (0.29), K^+ – Mg^{2+} (0.29), HCO_3^- – Ca^{2+} (0.28), TDS–Temp. (0.28), K^+ –Temp. (0.23), CO_3^{2-} –EC (0.22), HCO_3^- – Mg^{2+} (0.22), Ca^{2+} –Temp. (0.21), Cl^- –EC (0.19), Na^+ –pH (0.17), Mg^{2+} –EC (0.17), Mg^{2+} – Ca^{2+} (0.16), CO_3^{2-} – Ca^{2+} (0.15), HCO_3^- – Na^+ (0.14),

EC–pH (0.13), CO_3^{2-} –pH (0.12), SO_4^{2-} – Mg^{2+} (0.10), Na^+ –TDS (0.07), SO_4^{2-} –EC (0.05), SO_4^{2-} – Cl^- (0.03), Cl^- –Temp. (0.03), SO_4^{2-} – Ca^{2+} (0.02) and Temp.–pH (0.02). The second type of correlation values which is highly negative correlation observed for the parameters SO_4^{2-} – K^+ (– 0.78), CO_3^{2-} –Temp. (– 0.56), Na^+ –EC (– 0.56), SO_4^{2-} –TDS (– 0.54), SO_4^{2-} –Temp. (– 0.47), HCO_3^- – Cl^- (– 0.46), Mg^{2+} –TDS (– 0.45), HCO_3^- – K^+ (– 0.44), Na^+ – Ca^{2+} (– 0.39), Cl^- –pH (– 0.38), CO_3^{2-} – Na^+ (– 0.36), Ca^{2+} –TDS (– 0.36), K^+ – Na^+ (– 0.34), TDS–EC (– 0.34) and TDS–pH (– 0.32), which indicates the strong relation between these variables, and also the low negative correlation for Cl^- – Mg^{2+} (– 0.29), Cl^- – K^+ (– 0.29), EC–Temp. (– 0.23), Ca^{2+} –EC (– 0.22), HCO_3^- –EC (– 0.21), Mg^{2+} –Temp. (– 0.19), CO_3^{2-} – Cl^- (– 0.17), CO_3^{2-} –TDS (– 0.16), K^+ – Ca^{2+} (– 0.15), Na^+ – Cl^- (– 0.14), HCO_3^- – CO_3^{2-} (– 0.14), CO_3^{2-} – SO_4^{2-} (– 0.12), Ca^{2+} –pH

Fig. 13 Durov diagram of the study area

Table 4 Ionic ratio values

Parameters (meq/l)	Na ⁺	Cl ⁻	HCO ₃ ⁻	Ca+Mg	Total cation	Na + K	Cl +SO ₄
PL 1	0.69	0.04	0.49	4.71	5.43	0.72	0.14
BH 1	0.07	0.03	0.33	6.71	6.82	0.11	0.08
PL 2	0.04	0.02	0.99	7.60	7.67	0.07	0.07
PL 3	0.21	0.03	1.31	8.56	8.78	0.22	0.17
PL 4	0.06	0.03	0.33	6.42	6.53	0.11	0.10
RS 1	0.04	0.27	0.17	6.80	6.87	0.07	0.33
HDW1	0.05	0.05	0.33	9.50	9.60	0.10	0.11
BH 2	0.07	0.03	0.33	6.92	7.02	0.10	0.18
HDW2	0.17	0.009	0.30	6.06	6.24	0.18	0.27
RS 2	0.04	0.04	0.41	2.46	2.54	0.06	0.07

(− 0.12), HCO₃⁻–CO₃²⁻ (− 0.11), Na⁺–Temp. (− 0.08), Na⁺–Mg²⁺ (− 0.08) and Cl⁻–TDS (− 0.04) were obtained (Table 5).

Principal component analysis

The result obtained from the component analyses reveals five components of physico-chemical parameters (Table 6). The first component accounts for 25.67% total variance of eigen value. These parameters may have been enriched by same sources, most likely from weathering and leaching of

minerals from underlying lithology of the study area. The second component accounts for approximately 28.18% of the total variance. These parameters may have been enriched in both surface and groundwater of the study area by activities related to mine tailings dumped along water ways. The third component accounts for about 30.58% of the total variance. These parameters may have been enriched in the surface and groundwater systems of the area by the activities relating to leachate from mining activities.

The 2D and 3D plots of principal component analyses (PCA) as revealed in Figs. 15, 16. The 2D component

Fig. 14 Scattered plot of various ionic ratios of the study area

Table 5 Pearson correlation matrix of the physico-chemical parameters

	pH	Temp.	EC	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	CO ₃ ²⁻	HCO ₃ ⁻
pH	1.00											
Temp.	0.02	1.00										
EC	0.13	-0.23	1.00									
TDS	-0.32	0.28	-0.34	1.00								
Ca ²⁺	-0.12	0.21	-0.22	-0.36	1.00							
Mg ²⁺	0.62	-0.19	0.17	-0.45	0.16	1.00						
Na ⁺	0.17	-0.08	-0.56	0.07	-0.39	-0.08	1.00					
K ⁺	0.03	0.23	0.07	0.11	-0.15	0.29	-0.34	1.00				
Cl ⁻	-0.38	0.03	0.19	-0.04	0.32	-0.29	-0.14	-0.29	1.00			
SO ₄ ²⁻	0.39	-0.47	0.05	-0.54	0.02	0.10	0.45	-0.78	0.03	1.00		
CO ₃ ²⁻	0.12	-0.56	0.22	-0.16	0.15	0.73	-0.36	0.29	-0.17	-0.12	1.00	
HCO ₃ ⁻	0.37	0.31	-0.21	-0.14	0.28	0.22	0.14	-0.44	-0.46	0.37	-0.11	1.00

loading, pH, Mg²⁺, CO₃²⁻, EC and Ca²⁺ load close to one another exhibiting same source of enrichment. Consequently, Na⁺, SO₄²⁻ and HCO₃⁻ load close to each other also suggests the same source of enrichment. Similarly, Cl⁻, Temp. and TDS load close to each other, also suggesting same source enrichment. K⁺ appears on its own, suggesting different sources of enrichment. Also, for the 3D component plot, it is also observed that the elements plot on three sides.

Conclusion

This research demonstrated the geochemical evaluation of carbonate aquifers in Ngbo and environs via different approaches. The water quality with respect to domestic and drinking purposes was assessed. Ten water samples were collected from pit lakes, hand dug wells, boreholes and rivers, analysed and assessed for domestic and drinking water

Table 6 Principal components of ten water quality variables

	Component 1	Component 2	Component 3	Component 4	Component 5
Row	1	2	3	4	5
1	0.372	− 2.604	1.387	− 1.826	0.679
2	1.758	0.179	0.397	0.387	1.856
3	0.152	0.292	2.108	1.039	− 0.032
4	− 2.466	− 2.238	− 0.032	1.952	− 0.236
5	− 0.359	1.299	1.070	− 0.354	− 1.688
6	2.558	− 0.349	− 2.097	1.643	− 0.285
7	− 1.462	2.603	0.393	0.538	0.546
8	− 0.890	1.598	− 1.287	− 1.271	0.906
9	− 1.702	− 0.875	− 2.009	− 1.143	− 0.319
10	2.038	0.095	0.071	− 0.965	− 1.426
Eigenvalue	5.62	4.21	2.44	2.50	2.08
% of variance explained	30.23	20.08	19.41	17.73	12.55
% cumulative variance	25.67	28.18	30.58	34.23	56.11

Fig. 15 2D component loading of the area **Fig. 16** 3D component loading of the area

quality. The pH value of the water was slightly acidic to alkaline in nature. Based on TDS classification, the entire water samples are non-saline in nature. The analysis results show that the mean concentration of cations and anions followed the order: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Fe}^{2+}$ and $\text{HCO}_3^- > \text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{Cl}^-$, respectively. Based on the NDWQS (2007) and WHO (2011) standard limits, about

90% of the water samples are suitable for domestic and drinking purposes. The greater hydrochemical facies was a $\text{CaCO}_3^{2-} + \text{HCO}_3^-$ type observed using the Piper trilinear, Stiff and Durov plots. The analysis results revealed that the carbonate weathering due to calcite dissolution was the major geochemical process contributing to the cations and anions of the aquifer water.

Geochemical parameters such as Cl^- , Na^+ and K^+ show good interrelationship with positive factor loadings among the ions.

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