Hydrogeochemical Assessment of Chemical Composition of Groundwater: a Case Study of the Aptian-Albian Aquifer Within Sedimentary Basin Nigeria

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Abstract: The research was carried out to evaluate major source influencing chemical quality of groundwater within suburban area of Abakaliki. It lies between latitudes 6°15’ and 6°35’N and longitudes 7°40’ and 8°15’E. A total of twenty one (21) groundwater samples were collected and analyzed. Parameter analyzed were; EC, pH, TDS, Cl⁻, Na⁺, Mg²⁺, NO₃⁻, SO₄²⁻, Ca²⁺, HCO₃⁻, K⁺, CO₃²⁻ these parameter were analyzed using American Public Health Association standard method. Various hydrogeochemical approach and model were used to assess chemical quality of groundwater within the study area. These include; Gibbs, Mg²⁺/Ca²⁺. End-member, Diamond field of Piper and Parson plots were used to indentify major source influencing groundwater chemistry within the study. Finding, from Gibbs plot and Mg²⁺/Ca²⁺ against Mg²⁺/Na⁺ revealed that rock dominance is the major process that control groundwater chemistry, while End-member plot showed that silicate and carbonate weathering are the two weathering process that influence groundwater chemistry within the study area. Diamond field of Piper by Lawrence and Bal-Subramanian modified, revealed that groundwater fell within High Ca + Mg & SO₄ + Cl. Parson plot revealed that 65 % of groundwater fell within Ca - Mg – Cl water type, while 35 % fells within Ca - Mg - SO₄. Relationship between TDS vs TH plots showed that groundwater samples fell within soft - fresh water category. The results of the geochemical survey reveal major ionic components trend in other of Mg>Ca>Na>HCO₃>SO₄>Cl, result reveal that there is no particular trend of ions movement in groundwater.

Key words: Water-Rock Interaction · Plot · Weathering · Influence · Nigeria

INTRODUCTION

The continuous and severe increase of water demands, due to the rapid population growth, have led to over-exploitation of water bearing fractured aquifer within the study area. Recent, studies carried out within Asu River Group of Southern Benue Trough revealed that groundwater within the area is considered hard [1, 2]. Further studies, revealed that water quality is on decrease within the area, this is mostly attributed to anthropogenic activities such as improper disposal of refuges waste, leakage from septic tanks and mining related activities, these activities has rendered water quality unsafe for various use [3-9]. Although, geology formations has directly or indirectly influenced the origin and chemical constituents of groundwater in south-south and southeastern part of Nigeria [10, 11]. On a global scale, various authors has also stated that anthropogenic activities has negative influence on groundwater quality [12-14]. Domenico and Schwartz [15], Edmunds, et al. [16] went further, to state that unsustainable groundwater development, overexploitation andimproper management of mining waste, wastewater from mining areas have caused adverse impact on quality of groundwater. Decline in groundwater quality may be directly or indirectly influencedby the leaching of contaminants through mining activities as a result of rock-water interaction, during the process ofpercolation water moves through a hydrologicalecycle it transfers both inorganic and organic components from soilto water thereby decreasing its chemical quality [17]. Assessment of groundwater quality is usually based on the availability of a large amount of information concerning its chemistry [18, 19]. Its chemistry, depends on a number of factors, such as
general geology, degree of chemical weathering of the various rock types, quality of recharge water and inputs from sources other than water rock interaction. Such factors and their interactions result in a complex groundwater quality [20]. Murray [21], Rosen and Jones [22] further pointed out that the interaction of all factors has leads to various water facies. Previous studies carried out on water quality within Ebonyi state revealed that the major factor that influences groundwater quality are anthropogenic activities such as mining activities and water-rock interaction. Although various studies has been carried out on hydrogeochemical assessment of water resources in Ebonyi state for domestic and irrigation use [23]. But detailed, studies have not been carried out within the study area to evaluate factors that influence chemical quality of groundwater within the study area. The objective of this paper was to determine factors that influence chemical quality of groundwater within the area of study and to know the dominant factor that influences its chemistry.

**MATERIALS AND METHODS**

**Study Area:** The study area is located in the sub-urban area of Abakaliki, Ebonyi state, southeastern Nigeria. The area is quite accessible through a network of major roads and footpaths as shown in Fig. 1.

**Vegetation and Climate:** The study area belongs to the rainforest region of Nigeria as described by Igbozuruike, [24]. The vegetation is characterized by orchard bush of short trees with varying densities of dominant elephant grasses. Two major seasons are experienced in the area—the wet and dry season. The wet season starts from March and ends in October, while the dry season begins in November and ends in February. These two seasons are dependent on the two prevailing winds blowing across the country at different times of the year—the dry harmattan Wind, the North East Trade Wind from the Sahara Desert that prevails in the dry season and the marine wind, the SW Trade Wind, from the Atlantic Ocean which introduces the rainy season. Temperature in the dry season and rainy season ranges from 20 to 38°C and 16 to 28°C, respectively. The average monthly rainfall ranges from 3.1 mm in January and 270 mm in July. The average annual rainfall varies from 1750 to 2250 mm. The climate of the area, no doubt, favours the dispersion of the resultant pollutants from the mining activities. Eyankware, et al. [6] stated that high amount of rainfall results in surface run-off that moves the pollutants and also assists percolation. The drainage pattern of the area is dendritic.

**Geology and Hydrogeology of the Study Area:** The Benue Trough is a linear NE–SW trending trough that is divided into three parts, namely the Upper, Middle and
Fig. 2: Geology map of the study area showing groundwater sampling points

Table 1: Lithostratigraphic framework of the Southern Benue Trough showing the position Aptian and Albian Age, Lower Cretaceous

| AGE           | STRATIGRAPHIC UNIT                                      | BASIN CYCLE          |
|---------------|--------------------------------------------------------|---------------------|
| Tertiary      | Oligocene - Pliocene                                    | Niger Delta Basin   |
|               | Eocene                                                 |                     |
|               | Ameki / Aghada Formation                               |                     |
|               | Pliocene                                                |                     |
|               | Itumo/Akata Formation                                  |                     |
|               | Danian                                                 | Anambra Basin       |
|               | Nukka Formation                                        |                     |
|               | Ajaif Sandstone                                        |                     |
|               | Maastrichtian                                           |                     |
|               | Marno Formation                                        |                     |
| Upper Cretaceous| Campanian                                              | Southern Benue Trough|
|               | Nkporo Group                                           |                     |
|               | Akoko SS/Nkporo Sh/ Oweldi SS /Eguma Sh.              |                     |
|               | Santonian                                              | Tectonic uplift and folding |
|               | Unconformity (due to erosion and non-deposition)       |                     |
|               | Coniacian                                              |                     |
|               | Awgu Group                                             |                     |
|               | Turonian                                               |                     |
|               | Eze- Aku Group                                         |                     |
|               | Asamari Sandstone                                      |                     |
|               | Eze- Aku Shale                                         |                     |
|               | Cenomanian                                             |                     |
|               | Odu-arm FM                                             |                     |
| Lower Cretaceous| Albian                                                 |                     |
|               | Aptian                                                 |                     |
|               | Asu River Group                                         |                     |
|               | Abakaliki Formation                                    |                     |
|               | Mamfe Formation                                        |                     |
|               | PRECAMBRIAN BASEMENT COMPLEX                            |                     |

Lower parts [25]. Sedimentation in the Abakaliki Basin of the Lower Benue Trough started with deposition from the Asu River Group of Upper Albian age which overlies the Precambrian Basement Complex rocks disconformably as shown in Table 1. The Asu River Group consists of Abakaliki Shale with volcano clastics, sandstone and sandy limestone lenses (Benkheil 1989). The Asu River Group is overlain by the Eze-Aku Formation of Turonian age. This formation consists of flaggy, grey or black shales with sandstones and subordinate limestone [26]. An alternating sequence of thick limestone or sandstone units occurs with calcareous shales in places where the
Table 2: Methods used to analyze physicochemical parameters

| S/No | Parameters         | Analytical Method                                                                 |
|------|--------------------|------------------------------------------------------------------------------------|
| 1    | pH                 | pH meter HachsensION + PH1 portable pH meter and HachsensION + 5050 T Portable Combination pH Electrode |
| 2    | Electrical Conductivity (EC) | HACH Conductivity                                                                |
| 3    | Total dissolved solids (TDS) | TDS meters (model HQ40D530000000, USA).                                          |
| 4    | Magnesium (Mg²⁺)   | EDTA titrimetric method                                                           |
| 5    | Calcium (Ca²⁺)     | Titrimetric method                                                                |
| 6    | Chloride (Cl⁻)     | Titrimetric method                                                                |
| 7    | Nitrate (NO₃⁻)     | Ion-selective electrode (Orion 4 star)                                             |
| 8    | Sulphate (SO₄²⁻)   | Turbidimetric method using a UV-Vis spectrometer                                   |
| 9    | Potassium (K⁺)     | Jenway clinical flame photometer (PFP7 model)                                      |
| 10   | Sodium (Na⁺)       | Jenway clinical flame photometer (PFP7 model)                                      |
| 11   | Bicarbonate (HCO₃⁻) | Titrimetric method                                                                |

Eze-Aku Formation is found [28]. The hydrogeology of the study area is typified by poor aquifer conditions. This is a result of the dominant shale units (Aquiclude) which are neither porous nor permeable and do not transmit water to wells found in the area. Eyankware et al. [6] further pointed out that groundwater on a regional scale is impossible to find. However, conditions for the presence of groundwater may occur at weathered/fractured zones or at points of sandstone intercalations. The structure and hydrogeology of the fractured aquifer in the study are typical of a multilayer complex system. Obviously, due to drilling distribution on aquifer, As water bearing formation within the study area exists in fractured shale and limestone Nwachukwu, [1]. The major sources of water are stream, hand-dug well, manual borehole and motorized borehole.

Method: Twenty one (21) water samples were randomly collected from boreholes see (Fig. 2). Sampling was carried out during the dry season when there was a decrease in the water level and the concentration of cations and anions were more stable. Though the study area consists of two geology formation, groundwater sampling was carried within the Asu River Group. Precautionary measures were taken by washing the bottles with clean water and cleaning reagents and thoroughly rinsing with distilled, de-ionized water prior to collection of water samples from the site. The samples were analyzed for eleven parameters, namely pH, electrical conductivity, total dissolved solids, magnesium, calcium, chloride, nitrate, sulphate, potassium, sodium and bicarbonate following APHA, 2012 standard (Table 2).

DISCUSSION

pH: pH is a term used universally to express the intensity of the acid or alkaline condition of a solution. From the Table 3, the measured pH is found to be slightly acidic to basic and ranges from 6.3 to 7.9 with mean value of 7.15 as shown in Table 3. Various factors are responsible for change in pH value. It is important to highlight the mechanism of processes taking place in this area, When water is in equilibrium with both CO₂ from the atmosphere and carbonate containing rock, the resultant solution will be a buffer with a pH of 8.3, this is close to the pKa of the weak acid bicarbonate ion HCO₃⁻ (pKa = 8.4). This will resist further changes in pH to any added acid or base. This is a natural mechanism for balancing the considerable dissolution of lime from the underlying formation and precipitation of lime from the waterbody [29] Further studies revealed that groundwater pH varies depending on the composition of the sediments that surround the travel pathway of the recharge water infiltrating to the groundwater and also due to prolong stay in particular rock that serves as aquifer which host the water, the longer the stay, the larger the rock water interaction [29].

Total Dissolved Solid (TDS): The water samples were classified with regard to total dissolved solids (TDS). The results of geochemical analysis (Table 3) indicated that Total dissolved solids (TDS) ranged from 68 mg/L to 602 mg/L with mean value as 293.73 mg/L. Table 4 shows that sampling points within the study area were classified under freshwater category. The sources of material in TDS can come from nature, i.e. geological condition and seawater and from human activities, i.e. domestic and industrial waste and also agriculture [30-32].

Electrical Conductivity (EC): EC is one of the important water quality parameters that shows the ability of electrical current in the water. Electrical conductivity in water is due to ionization of dissolved inorganic solids minerals, salts, metals, cations or anions that dissolved in water. EC values of the water samples ranged from 72 to 1042 μS/cm with mean value of 480.04 μS/cm as shown in Table 3.
Table 3: Results of Physicochemical Parameters

| Sample No | EC µS/cm | pH | TDS mg/L | Cl⁻ meq/L | Na⁺ meq/L | Mg²⁺ meq/L | NO₃⁻ meq/L | SO₄²⁻ meq/L | Ca²⁺ meq/L | HCO₃⁻ meq/L | K⁺ meq/L | CO₃²⁻ meq/L |
|-----------|----------|----|----------|-----------|-----------|------------|------------|-------------|------------|------------|----------|-------------|
| AI/01     | 263      | 7.4| 392      | 0.38      | 0.17      | 0.09       | 0.65       | 0.49        | 0.19       | 1.02       | 0.29     | 1.03        |
| AI/02     | 1042     | 6.9| 559      | 0.11      | 1.05      | 0.14       | 0.19       | 0.01        | 0.39       | 2.49       | 0.06     | 1.58        |
| AI/03     | 291      | 7.1| 68       | 0.59      | 0.64      | 1.40       | 1.00       | 0.37        | 0.01       | 1.39       | 0.01     | 1.65        |
| AI/04     | 404      | 7.8| 103      | 0.31      | 0.03      | 0.03       | 0.25       | 1.39        | 0.29       | 0.50       | 0.13     | 1.27        |
| AI/05     | 938      | 7.0| 494      | 0.10      | 0.11      | 0.00       | 0.85       | 0.57        | 0.18       | 1.44       | 0.87     | 1.09        |
| AI/06     | 848      | 6.8| 135      | 0.25      | 0.06      | 0.17       | 0.06       | 0.03        | 0.03       | 0.92       | 0.06     | 1.51        |
| AI/07     | 72       | 7.2| 99       | 0.83      | 0.19      | 0.16       | 0.32       | 0.19        | 0.06       | 0.84       | 0.96     | 1.99        |
| AI/08     | 125      | 6.8| 569      | 0.17      | 0.04      | 0.22       | 0.05       | 0.72        | 0.28       | 1.03       | 0.18     | 1.87        |
| AI/09     | 203      | 7.5| 602      | 0.95      | 0.15      | 0.17       | 0.83       | 0.08        | 0.19       | 0.94       | 0.56     | 1.03        |
| AI/10     | 127      | 7.7| 394      | 1.43      | 0.00      | 1.40       | 0.05       | 0.35        | 0.02       | 0.99       | 0.64     | 1.59        |
| AI/11     | 1022     | 7.1| 416      | 0.09      | 0.09      | 0.04       | 0.20       | 0.01        | 0.38       | 1.03       | 0.88     | 1.83        |
| AI/12     | 293      | 7.3| 69       | 0.78      | 0.83      | 0.25       | 0.49       | 0.02        | 1.22       | 0.58       | 0.16     | 1.04        |
| AI/13     | 144      | 6.8| 91       | 0.86      | 0.27      | 0.08       | 0.55       | 0.06        | 0.38       | 1.49       | 0.71     | 1.36        |
| AI/14     | 593      | 7.4| 242      | 0.49      | 0.16      | 0.10       | 0.19       | 0.03        | 0.47       | 2.01       | 0.48     | 1.59        |
| AI/15     | 602      | 7.1| 495      | 0.70      | 0.39      | 0.04       | 0.22       | 0.01        | 0.91       | 1.49       | 0.91     | 1.89        |
| AI/16     | 1032     | 6.7| 502      | 0.14      | 0.17      | 0.07       | 0.30       | 0.17        | 0.49       | 1.92       | 0.10     | 1.08        |
| AI/17     | 149      | 7.5| 169      | 0.05      | 0.16      | 0.61       | 0.96       | 1.20        | 0.52       | 2.30       | 0.49     | 1.22        |
| AI/18     | 830      | 7.9| 304      | 0.04      | 0.13      | 0.21       | 1.42       | 0.02        | 0.48       | 1.90       | 0.22     | 1.96        |
| AI/19     | 294      | 6.9| 193      | 0.17      | 0.26      | 0.30       | 0.59       | 0.04        | 0.50       | 0.83       | 0.74     | 1.50        |
| AI/20     | 103      | 7.1| 85       | 0.18      | 0.01      | 0.17       | 0.11       | 0.19        | 0.80       | 2.11       | 0.28     | 1.99        |
| A/21      | 207      | 6.3| 92       | 0.03      | 0.02      | 0.29       | 0.43       | 0.01        | 0.33       | 1.03       | 0.05     | 1.74        |
| Min       | 72       | 6.3| 68       | 0.03      | 0.00      | 0.00       | 0.00       | 0.01        | 0.01       | 0.50       | 0.01     | 1.03        |
| Max       | 1042     | 7.9| 602      | 1.43      | 1.05      | 1.43       | 1.39       | 1.22        | 2.49       | 0.96       |         | 1.99        |
| Mean      | 480.04   | 7.15| 293.17   | 0.43      | 0.26      | 0.31       | 0.31       | 0.32        | 0.40       | 1.35       | 0.42     | 1.51        |

Major Factors Influencing the Groundwater Chemistry

Work Rock Interaction: Freeze and Cherry [33] has been used in determination of the major mechanisms controlling water chemistry and are widely used in studies of the relationships between water chemical composition and climate or geological characteristics. It is represented as plots of TDS versus Na⁺/(Na⁺ + Ca²⁺) and TDS versus Cl⁻/(Cl⁻ + HCO₃⁻) and the controlling hydrochemical mechanisms can be divided into three zones: evaporation, precipitation and water rock interaction [34]. Most groundwater samples were plotted in the middle of the diagram except for samples AI/03 and 07 that is been influenced by precipitation. (Fig. 3), indicating that rock weathering is the primary factor controlling the groundwater chemistry. In addition to the Gibbs diagram, the ratio of Mg²⁺/Na⁺ and Mg²⁺/Ca²⁺ can also be used to determine whether evaporation and rock interaction are likely to be influencing groundwater quality Li [35]. A Gibbs diagram and Mg²⁺/Na⁺ versus Mg²⁺/Ca²⁺ diagrams were applied to the data obtained in this study and the results’ area is shown in Fig. 3a, b, respectively. These diagrams suggest that rock weathering is the main mechanism controlling the chemical constituents of groundwater in the study area. An important process of water rock interaction is mineral dissolution [35] and the assessment of ionic meq/L ratios can indicate which minerals are likely to have the largest influence on groundwater quality.

Gaillardet et al. [36] used End member plot in determining rock-weathering sources related to the hydrochemical characteristics of groundwater. They further identified the following chemical composition of Ca²⁺/Na⁺ = 0.35 ± 0.15, Mg²⁺/Na⁺ = 0.24 ± 0.12 and HCO₃⁻/Na⁺ = 2 ± 1 for the silicate end member and Ca²⁺/Na⁺ = 50, Mg²⁺/Na⁺ = 10 and HCO₃⁻/Na⁺ = 120 for the carbonate end member. Fig. 4, shows that the 99.9 % groundwater chemical composition originates from the weathering of carbonate and silicate. Silicate dissolution has influence on carbonate weathering as shown in Fig. 4.
Fig. 3a: Gibbs diagram for groundwater samples of the study area.

Fig. 3b: Plot of Mg/Ca versus Mg/Na of the study area.

Fig. 4: End-member plot for groundwater samples of the study area.
Fig. 5: Classification of Hydrogeochemical Facies (Reconstructed Diamond field of Piper by [37]) of the study area.

Fig. 6: Parson’s Plot Modified (After, Othman, 2005) of the study area showing ground water origin.

Fig. 7: Plot of TDS versus TH.
Fig. 8: Piper diagram of groundwater samples of the study area

Note: Concentrations are meq/L

Fig. 9: Durov Plot of the Study area

Fig. 10: Scholler Diagram of the Study Area

The water classification of hydrogeochemical facies of Piper diagram was reconstructed by Lawrence and Balasubramanian [37] in the new reconstructed diamond field (Fig. 5). It classified water in the various zones on the basis of various reactions occurring in the groundwater aquifer system. The reconstructed diamond field shows that groundwater sample lies within High Ca + Mg + SO4 + Cl hydrogeochemical facies as shown in Fig. 5. This implies that, Ca and Mg, are the primary courses of hardness in water. Any water with high Ca + Mg is said to be hard.

From Fig. 6. It was observed that groundwater were within the three category of water type; Na - SO4, Ca - Mg – SO4 and Ca – Mg – Cl water type. That implies that groundwater is of different origin.

TDS and total hardness (TH) indicate that all the groundwater is soft, fresh and moderately hard fresh water type Fig. 7 showed that groundwater within the study area falls within moderately, hard fresh. This is in-line with previous research within the study area that stated that groundwater within the area is considered hard Eyankware et al. [3], Edeh and Nnabo [7], Ojobor and Nnabo [8].

Hydrogeochemical facies of Groundwater: Piper, [38] diagram is very useful in determining relationships of different dissolved constituents and classification of water on the basis of its chemical characters. The triangular cationic field of Piper diagrams reveals that Ca + Mg + HCO3 are the dominant ionic specie. It also reveals that geochemical zone of the groundwater in the study area are magnesium bicarbonate type and that the alkaline earth exceed the alkaline in the groundwater see Fig. 8. However, from the Scholler diagram. It shows a hydrogeochemical trend of Mg>Ca>Na>HCO3>SO4>Cl. The result also reveal that there is no particular trend of ions movement in groundwater, this implies that the groundwater is not of the same origin as shown in Fig. 9 and 10.

CONCLUSION

The presented research has helped to establish factors that influence chemical quality of groundwater within the study area and its environs, Ebonyi state southeastern Nigeria. From the analysis, it was observed that pH ranges from 6.3 - 7.9 hence, classified as slightly acidic to basic, TDS ranges from 68 - 602 mg/L, the value range shows that groundwater is of fresh water category, TH ranges from 2.8 - 73.5 mg/L, sampled points were classified as soft water category, EC ranges from 72 -1042 us/cm. Chemical quality of groundwater was evaluated using the following models; Gibbs plot, Mg2+/Ca2+ against Mg2+/Na+, End-member plot, Diamond field of Piper modified after Lawrence and Balasubramanian and Parson plot. Gibbs plot, Mg2+/Ca2+ against Mg2+/Na+ revealed that groundwater is highly influenced by rock dominance, two major that of weathering process was observed to influence groundwater, these are silicate and carbonate weathering, Diamond plots showed that groundwater is of High Ca + Mg & SO4 + Cl type, while Parson plot revealed that 65 % of groundwater were within Ca - Mg – Cl water type, while 35 % were categorize as Ca -Mg - SO4 water type. From modified Diamond plot and Piper diagrams it
was observed that groundwater(s) are of various origin. The results of the geochemical survey reveal major ionic components trend in other of Mg>Ca>Na>HCO3>SO4>Cl, result reveal that there is no particular trend of ions movement in groundwater.

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