

Origin of Dissolved Solids in Cretaceous Aquifers at NGBO, Ebonyi State, Nigeria: A Preliminary Assessment.

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Abstract:

Ngbo and environs are underlain by Abakaliki and Ezeaku Formations in southeastern Nigeria. Abakaliki Formation consists of highly jointed, fissile, dark grey shales while Ezeaku Formation is represented by a feldspathic, calcareous sandstone member. The two aquifer systems are tapped by hand-dug wells and shallow boreholes. Samples were drawn from both aquifer systems and analysed for major elements chemistry. Results showed a pH range from 6.5-7.7 which indicated an almost neutral geochemical environment. All the groundwater samples showed low solute concentrations. Anions concentrations are in the following order $\text{HCO}_3 > \text{Cl} > \text{SO}_4$. Ca and Mg account for 70% of the entire cationic concentration. Some wells have significant boron and bromide concentration. Application of ionic ratio calculations suggest that the major reactions involve carbon weathering, dolomitic dissolution, sulphate reduction and calcite precipitation. There is also an indication of geogenic contamination of the aquifers by brines.

Keywords: Ngbo; boron; bromide; ionic ratios; Hounslow's diagram

1. INTRODUCTION

The bulk chemical composition of any groundwater is the product of chemical processes and reactions between precipitation or recharge water and the minerals and gases within the aquifer. The impact of these processes or reactions will be seen not only in high solute levels but also in the unique chemical characteristics or behaviour of such a water. The ground water (and surface water) environments are therefore constantly undergoing chemical reactions. Defining the reactants and products of these reactions can be complicated because of constantly varying temperature, pressure, pH and Eh conditions. The process of interpreting a particular chemical analysis result for a water sample is therefore an attempt at defining what

reactants, processes and conditions were involved in producing such a composition.

A lot of work has been done in the field of defining the origin of a water sample. Sulin (1946) developed a method of gaining insight into the origin of brines and set up a classification scheme. Garrels and Mckenzie (1967) used the mass balance approach for the determination of the origin of chemical constituents. Their work was based on deep knowledge of rock weathering. They found that the ratios of certain elements remained fairly constant during the weathering processes. They reasoned that these ratios would remain constant in groundwater and could be used to determine the origin of a water sample. Gibbs (1970) set up a method for knowing whether a particular water composition was derived from rock weathering or sea water or evaporation. Hounslow (1995) developed an intricate flow chart for determining the source rock of a water sample based on the concepts introduced by Garrels and Mckenzie (1967). He also introduced the Hounslow diagram differentiating the origin of brines.

In Nigeria, most geochemical studies of groundwater focus on comparing elemental concentrations with maximum contaminant levels or elements prescribed by World Health Organization (W.H.O), United States Environmental Protection Agency (U.S.E.P.A) or Nigeria regulatory bodies but this is gradually changing. Agbo (1992) worked on the origin of dissolved solids of the shale regolith aquifer waters at Abakaliki. Ozoko (2006) discussed the origin of chemical composition of Ajali aquifer waters in the Nsukka area of southeastern Nigeria while Edet et al. (2011) carried out a status review of groundwater chemistry and quality across Nigeria's basins.

The present work through preliminary, is aimed at establishing the origin of the various solutes that make up the bulk chemical composition of ground waters in Ngbo and environs, Ebonyi State, Nigeria.

2. STUDY AREA

(i) Location, relief and drainage:

Ngbo and environs are located within latitudes $6^{\circ} 30'N$ and $6^{\circ} 35'N$ and longitudes $7^{\circ} 55'E$ and $8^{\circ} 00'E$ with an areal extent of about 85 square kilometres. Communities within the study area include Ngbo, Amananta, Amachi, Umuogudu Oshia, Umuogudu Akpu, Ukwu Agbu, Ndiagu Okposhi Eshi, Effium, Amoffia and Ekwassi. These are all rural communities. Figure 1 shows the topographic map of the study area and also the communities involved. Though

there are a few dissected ridges and isolated hills, the area is generally flat or gently undulating not rising more than 120m above sea level. Ngbo and environs fall within the tropical rainforest belt of Nigeria. It has two main seasons every year, a rainy season beginning around April and ending in October and a dry season from November to March. Average annual rainfall and temperatures range for the area are 1850mm/year and $25^{\circ}C$ to $36^{\circ}C$ respectively (Ofomata, 1985). The area is dissected by Nsu River which has Amananta and Ogurube Rivers as tributaries. A number of ponds exist in the area as a result of rock quarrying activities by various companies.

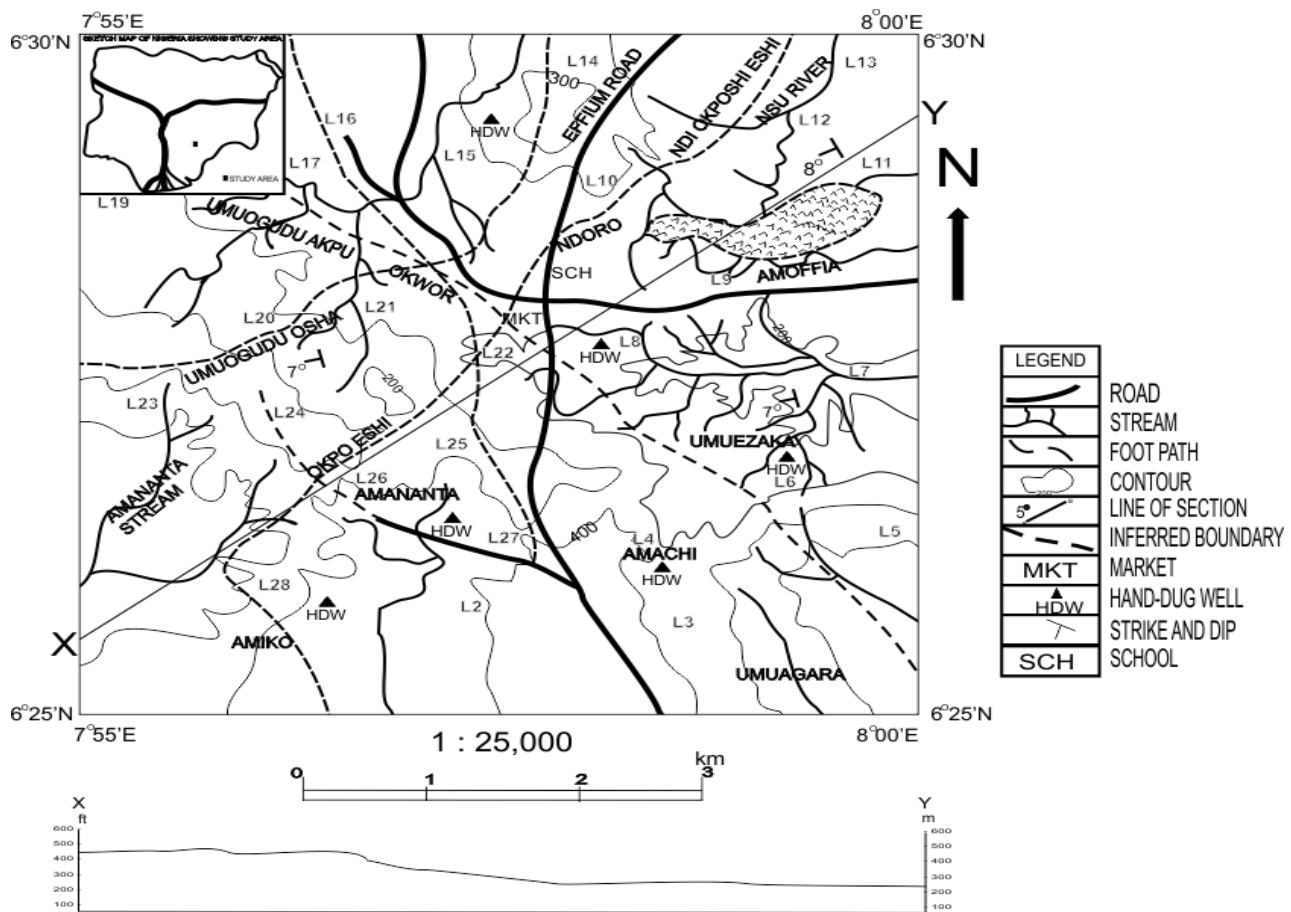


Figure 1: Topographic map of Ngbo and environs.

(ii) Geohydrologic Setting:

The rock sequence underlying the study area belongs to Abakaliki and Ezeaku Formations (Figure 2). The Abakaliki Formation outcrops in the area as highly jointed, fissile, dark grey shales that are also fossiliferous. Nwajide (2013) identified ammonites and a number of foraminifera species in them. These shales dip 7° in the southwest direction. The outcrops of the Abakaliki Formation are pronounced in the north eastern areas of the map. Figure 2 shows the geologic map. The shales are intruded into by dolerites and have evidence of being baked at its contact

with the dolerite dyke. The dyke is quite extensive in the study area. The Abakaliki Shales have been described by Reyment (1965) and Nwajide (2013) as folded shales with calcareous cements and lead-zinc mineralisation. Reyment placed its age as albian. The dolerite intrusives in the study area may be synchronous with the pyroclastics which occur in Juju hill at Abakaliki.

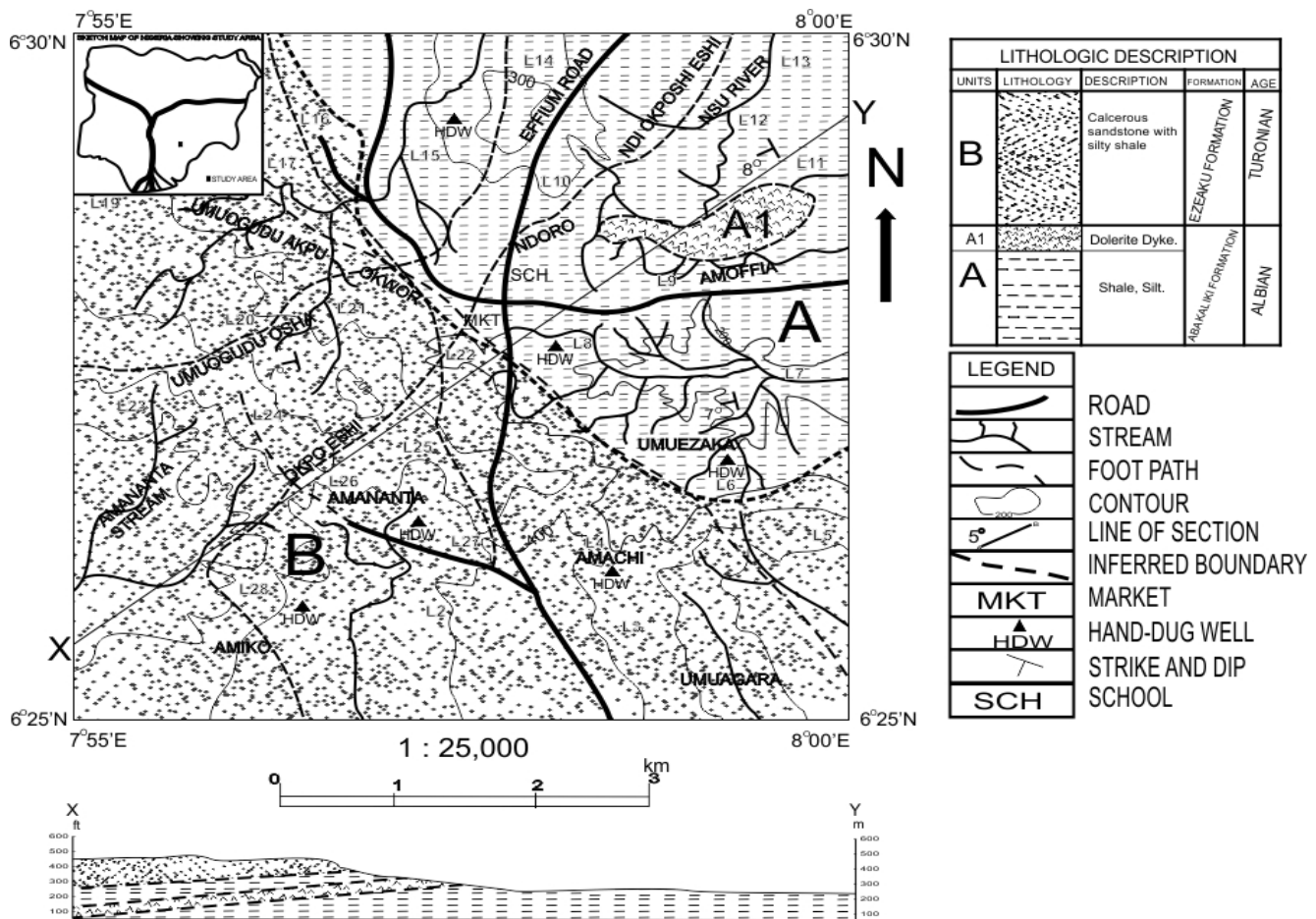


Figure 2: Geologic map of the study area.

The Abakaliki Shale Formation at Ngbo is overlain by the sandstone member of Ezeaku Formation (Turonian). This sandstone member of Ezeaku Formation outcrops at the study area in the form of light grey, highly indurated, fine grained sandstones. Towards the southeastern and southwest parts of the study area, it shows some level of being coarse grained, poorly consolidated and friable. It is feldspathic. The beds dip 6° to the northwest direction. Thin section studies indicate that the feldspars are microcline, orthoclase and sodic plagioclase (albite). The sandstone has calcareous cement in most outcrops. Outcrops of the sandstone are found in Ekwassi, UmuOgudu Akpu and Umuogugu areas which are in the northwestern part of the study area.

Two aquifer systems were identified by Uma and Onuoha (1989). These are a shallow unconfined aquifer in the fractured and weathered horizon of the Abakaliki Formation. This aquifer is tapped by several hand-dug wells and shallow boreholes in a few places. The confined aquifer occurs at depths of between 10 – 70 m but the shallow unconfined aquifer is between 1m – 15m. According to Ofoegbu (1983), several shallow boreholes which were completed in the areas of Ezeaku Formation yield small volumes of water but in the shale areas, the yield is up to $30\text{m}^3/\text{hr}$. The surface water bodies in the area include Nsu, Ogurube and Amanata rivers. They are not fit for drinking because of their high sediment load.

3. MATERIALS AND METHODS

Sampling was restricted to only groundwater in boreholes and hand-dug wells. Because of the preliminary nature of the investigation, only two hand-dug wells and three boreholes were sampled. In situ measurements of temperature, pH and electrical conductivity measurements were taken with a multiparameter water quality meter (Hanna 93103). Samples were then collected in 500ml polyethylene bottles after rinsing them with the water to be

sampled. Samples were stored in a refrigerator at low temperatures before analysis. Bicarbonates (HCO_3^-) content was determined by titrimetric method while Chloride (Cl) was determined by argentometric titration as described by Clesceri et al. (1998). Sulphate (SO_4^{2-}), bromide (Br) and Boron (B) were also determined by methods in Clesceri et al. (1998). Cations were analysed by atomic absorption spectrometry.

4. RESULTS AND DISCUSSION

Table 1 shows the results of chemical analysis for the groundwater of the study area. The pH ranges from 6.5 to 7.7 while the electrical conductivity (EC) ranges from 0.0 to $400\ \mu\text{s}/\text{cm}$. Zero values of EC indicate very dilute water in the shales. The wells penetrating sandstones have higher EC values. Total dissolved solids (TDS) are higher in the sandstone aquifers than in the shale aquifers. Calcium, Ca^{2+} and Magnesium Mg^{2+} account for more than 70% of the entire Cation concentration while bicarbonates account or more than 70% of the anions. Mg^{2+} varies from 3.26mg/l in the shale aquifer and 13.02mg/l in the sandstone aquifer. Na^{2+} has the lowest value of 2.02mg/l in one of the wells while the highest value of 5.85mg/l occurs also within the sandstone aquifer. The value of K^+ varies from 0.32mg/l in the shales to 3.70mg/l in the sandstone.

An examination of anion concentration reveal that bicarbonates (HCO_3^-) range from 40mg/l to 700mg/l while sulphates (SO_4^{2-}) vary from 0.43mg/l to 12.03mg/l and Chlorides (Cl) go from 10.37mg/l to 31.11mg/l. Values of Boron range from BDL (below detection limits) to 10.82mg/l. Danskin and Church (2005) suggests that this variation could be an important indicator of different types of groundwater. Hem (1992) maintains that boron can be toxic or plants like orange or lemon even when concentration is as low as 1mg/l. Bromide values range from BDL to 47.95mg/l. Sources of bromide in natural water have been attributed to geothermal water and anthropogenic effects (Hem, 1992).

Table 1: Result of Water Analysis in mg/l

S/N	Determination (Parameters)	L4 Confined aquifer (sandstone)	L8 Unconfined aquifer (Shale)	L10 Confined aquifer (sandstone)	L15 Unconfined aquifer (Shale)	L24 Confined aquifer (sandstone)
1	pH	7.7	6.5	7.5	6.8	7.2
2	Temperature °C	26.0	27.0	25.0	28.0	26.0
3	Electrical Conductivity, μ s	400	0.0	200	0.2	300
4	Total Dissolved Solids (mg/L)	430	30	260	40	240
5	Bicarbonates, mg/L	700	40	500	60	30
6	Sulphates(SO ₄ ²⁻) mg/L	0.89	2.79	0.43	12.03	3.12
7	Chlorides (Cl) mg/L	31.11	10.37	11.21	14.23	10.95
8	Sodium (Na ⁺) mg/L	5.85	3.70	3.43	4.21	2.02
9	Potassium (K ⁺) mg/L	3.70	0.32	2.62	2.01	3.25
10	Calcium (Ca ²⁺) mg/L	14.14	4.35	12.11	8.34	6.31
11	Magnesium(Mg ²⁺) mg/L	10.44	3.26	13.02	6.42	4.24
12	Boron (B) mg/L	BDL*	10.82	8.54	BDL	BDL
13	Bromide (Br) mg/L	BDL	47.95	26.55	BDL	BDL

*BDL = Below Detection Limits

Table 2 shows the application of ratios to the determination of the origin of dissolved solids in the study area. Ca/Mg ratios for the area range from 0.56 to 0.90 which is according to Hem (1992) a possible evidence of saltwater intrusion but since the study area is located far inland, this probably has to do with connate water or evaporation effects. Another implication of the Ca/Mg ratio is dolomite dissolution. Molar ratios for Na/Cl range from 0.29 to 0.55. This means that Na⁺ is consistently less than Cl⁻ which indicates reverse softening. Hounslow

(1995) stated that when the molar Na/Cl ratio is less than one, it means that the water is geochemically similar to oil field brine. The Br/Cl ratio or the wells is between 2.37 to 4.62. The 4.62 value is a possible indication of the onset of halite dissolution (Sonnenfeld, 1984; Hounslow, 1995). The SO₄/Cl ratio goes from 0.03 to 2.8. It is not very diagnostic geochemically. The index of Base Exchange (IBE) is from 0.45 to 0.71. It is given by Cl – Na/Cl but it was not diagnostic of any origin or source.

Table 2: Results from ionic ratio calculations or the study area

	L4	L8	L10	L15	L24
Ca^{2+}/Mg^{2+}	0.82	0.81	0.56	0.78	0.90
Na^+/Cl^-	0.29	0.55	0.47	0.45	0.29
Br^-/Cl^-	ND	ND	4.62	2.37	ND
SO_4/Cl	0.03	0.22	0.04	2.8	0.28
IBE (Index of Base Exchange)	0.71	0.45	0.53	0.54	0.71
<u>Cl-Na</u> CL					

ND = Not Determined

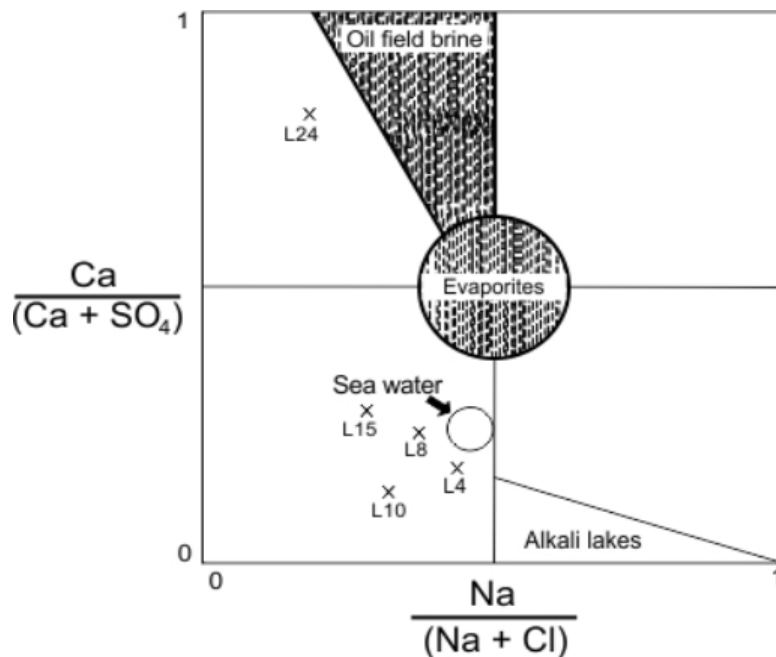


Figure3: Hounsflow's plot for the water samples.

The Hounsflow (1995) plot (figure 3) showed that most of the waters plotted close to the sea water circle. Hounsflow developed this diagram to differentiate between waters

polluted by brines and those from other origins and sources. Since all the samples plotted close to the sea water circle, it is an indication of brine contamination.

This contamination is geogenic in origin. In effect, the indicated reactions going on in these aquifers include carbonate weathering which is responsible for high levels of bicarbonates in solution and also the calcium levels. The pH range indicates an almost neutral geochemical environment (pH range: 6.5 – 7.8). In this type of geochemical environment, bicarbonate is often the main anion (Hounslow, 1995). Ca and Mg would also be the main cations. Solution cavities would be common in the rocks – which is the case in the study area. The low values of sulphates in L4, L8, L10 and L24 may be an indication of sulphate reduction but there were no traces of hydrogen sulphide being released as a result. The precipitation of calcite may be accompanying sulphate reduction and thus be a factor in providing cementation of tiny joint cracks or sandstone.

CONCLUSION:

This preliminary investigation of the origin of dissolved solids in the aquifers at Ngbo indicates that more work needs to be done. The next stage of the work would require sampling of surface water bodies like rivers and quarry ponds; sampling of the colloids and sediments carried by these rivers and a more elaborate sampling of the two aquifer systems. Results from this preliminary study shows that the groundwaters are in neutral geochemical environment with dominance of Magnesium and bicarbonate ions respectively. Application of ionic ratios suggest that the major reactions involve carbonate weathering or dolomite dissolution, sulphate reduction with calcite precipitation. There is also indication of reverse softening or geogenic contamination of the aquifers by brines.

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