**Abstract:**
This study focuses on hydrogeochemistry characteristics assessment, aimed at determining the level of water quality in Amansiodo and environs. Geologically, the area is underlain by cross-beded, friable, whitish, poorly sorted Ajali Sandstone which is overlain by heterolithic units of shale, siltstone intercalation, mudstone, latareric sandstone and ironstone of Nsukka Formation. A total of ten (10) water samples; hand-dug wells (3), springs (3) and boreholes (4) were collected from different locations within the study area and analyzed for their physicochemical parameters (pH, EC and TDS), cations (Ca, Na, Mg and (K), anions (Cl, HCO₃, NO₃, PO₄ and SO₄²⁻), trace metals (Cr, Fe, Pb, Cu, Ni, and Zn) and microbial constituent (E-coli). Wissenschaftlich Technische Werkstatten conductivity/TDS meter, HACH pH Sension meter, Jenway PFP7 flame photometer, HACH DR/4000 spectrophotometer and Bulk BGV Atomic Absorption Spectrophotometer (AAS) were used for the analysis. However, the total pH value ranges from 3.8 to 5.3 Oforugwu borehole and Imezi-Olo handdug well respectively, which are below the WHO and NSDWQ permissible drinking standard of (6.5 to 8.0), indicating acidic water. The EC ranges from 007 to 137mg/l in Onuta spring and Afor-Oghe borehole respectively, which are below the permissible limit of WHO and NSDWQ. The TDS ranges from 004 to 074mg/l and are below the WHO and NSDWQ permissible limit. The heavy metals analysed were below the permissible limit by WHO. The iron content ranges from 0.01 to 0.05mg/l in Afor-Oghe bore and Onuta spring respectively which are also below the WHO desired limit (0.3). The E-coli also ranges from 0.0017 to 0.0034mg/l in Imezi-Olo handdug well and Ogheke Spring at Ugwuetiti respectively, as well below the permissible limit of WHO (1 per 100mg/l). Chloride indicates a very high value range from 368 to 1048mg/l and are above WHO standard. The Dissolve Oxygen in the analysed sample equally detect a high range from 188 to 360mg/l which are also above the permissible WHO and NSDWQ limit. It is an indication that the water is less in contamination with organic waste. Furthermore, a pipet and stiff diagram were plotted with the aim to classify water sample analyzed, it shows that all the samples fall within the calcium-chloride type of water, which is an indication of gypsum groundwater being deduced from a single source of contamination. The water in the area needs to be treated before consumption due to excess contents of chloride and presence of bacteriological contamination that must have resulted from anthropogenic activities.

**Keywords:** Hydrogeochemistry, characteristics, water quality, Amansiodo, Ezeagu, Enugu State

1. Introduction
The need for the quality and availability of water resources has always been the primary concern of the society. According to Ngaje et al.(2010) problem of acid mine drainage have been reported in some areas, especially the coal mining areas in Enugu. Fetter (1993) pointed out that groundwater contamination may cause various diseases and other problems. Hence, there is need to assess the sustainability of water used for domestic purposes and need to assess the groundwater quality based on location and time. On the outlook of groundwater, Nwobodo et al. (2015) investigate the spatio-temporal variation of groundwater quality in Udi-Ezeagu watershed with the view to determining the physical, chemical and microbiological characteristics of groundwater samples in space and time. They further in exploration to ascertain the quality of groundwater using the parameter in comparison with WHO permissible limits. At the course of their study, they found out that mineral treatment is required in the study area and recommend continuous assessment of the groundwater supply to keep the quality in check. A More exposition on nature of groundwater, Onwuka et al. (2010), did a detective work by examining the application of chemometric technique in the assessment of groundwater quality in Udi and environs, South-Eastern Nigeria. They opined that the quality of groundwater depends on several factors, including climate, soil characteristics, manner of circulation of groundwater through the rock type and topography of the area. Furthermore, Aniebone (2015) worked on hydrogeochemistry and quality assessment of some groundwater samples from Enugu and environs, South Eastern Nigeria and after the analysis of 10 samples he expound that the groundwater was very acidic in some areas like the Onyeama mine, slightly acidic in few and within the WHO acceptable limits in most places. The quality of groundwater in the study was impaired by sea water intrusion and rock water interaction processes. The high concentration of iron of range 0.12 to 8.60mg/1 for groundwater is above the maximum...
permissible level of water for domestic use (WHO 1997). Acid mine drainage is an important form of environmental degradation in Enugu (Egboka and Uma, 1985). Based on the Electrical conductivity, the water is very fresh in nature and the geochemistry parameters such as Cl\(^{-}\), SO\(_4^{2-}\) and NO\(_3^{-}\) show good correlation with positive factors. From the foregoing, we can deduce that the reviewed studies are remarkably of similar approaches from the current study. The selected literatures, show the dimensions of the attentions already paid on groundwater quality in different environments within the study area and thereby projecting the uniqueness of the present study which had spring water in addition as the major source of water to the inhabitants.

2. Study Area

The study area is located in Ezeagu local government area of Enugu State, Nigeria (Figure 1). It is bounded by latitudes 06° 26’N to 06° 31’N and longitudes 07° 15’E to 07° 20’E with an area extent of about 85.56km\(^2\). The major towns and villages within the area include:- Akama Oghe, Afor Oghe, Amankwo, Iwollo Oghe, and Imezi Olo. The area lies within the south eastern Nigeria sedimentary basin. The topography is controlled mainly by the geology of the area, marked with two major units A and B as shown in figure 4 below. The unit B occurs as an outlier and forms most of the ridges and hills in the area which rises to about 325ft above sea level while unit A forms the lowland and rises to about 150ft above sea level as shown in figure 2 below. The drainage pattern of the study area is typically dendritic with low drainage density. At several locations there were presence of contact spring water seeping out between the interface of Nsukka Formation and the upper section of Ajali Sandstone. The springs served as source of water for domestic use in the area.

3. Regional and Local Geology

Regionally, the study area falls within the Anambra basin which is in the Southern Benue trough, being that the trough itself is a continental large scale intra – plate tectonic mega structure, which is part of the mid – African rift system initiated in the latest Jurassic to early Cretaceous and it is related to the opening of central and south Atlantic ocean...
The Southern Benue trough comprises the tectonically inverted Abakaliki anticlinorium, Afikpo and Anambra basin flanking the anticlinorim to the east and west respectively.

The Ajali Sandstones which is about 330m thick is an extensive stratigraphic unit conformably overlying the Lower Coal Measure (Mamu Formation) and Nkporo Formations that are 400 and 200m thick, respectively and underlying the Upper Coal Measure (Nsukka Formation) in the Maastrichtian (Reymert, 1965; Obi, 2000 and Nwajide, 1990). The Ajali Formation is typically characterized by white coloured sandstone (Reymert, 1965) while the Mamu Formation is essentially composed of sandy shale and some coal seams; the Nkporo Formation consists mainly of grey-blue mudstone and shale with lenses of sandstone (Obaje, 2009). According to Reyment (1965), the prevailing unit of Ajali Formation consists of thick, friable, poorly sorted sandstone.

Locally, field data from twenty one (21) locations indicates that the study area is underlain by two major rock units which are described as unit A and B (figure 7). Unit A consists of cross bedded, friable, whitish, poorly sorted Sandstone which indicate Ajali Formation and it is the oldest formation in the study area. It is Upper Maastrichtian. Unit B is the younger heterolithic Shale, Siltstone intercalation, Mudstone and Ironstone which indicates Nsukka Formation and it is Danian. The features observed in the field from the Ajali Formation includes planner cross beds and laminations, trough cross beds and Ophiomorpha burrows. Some of the exposures were thoroughly logged.

Figure 3. Litholog and Plate Showing Some of the Outcrop Locations of Ajali and Nsukka Marked as Unit A and B
4. Materials and Methods

A total of ten (10) water samples; hand dug wells, (3) springs (3), and boreholes (4) were collected and analyzed for their physicochemical parameters (pH, EC and TDS), cations (Ca, Na, Mg and K), anions (Cl, HCO$_3^-$, NO$_3^-$, PO$_4^{3-}$ and SO$_4^{2-}$) trace metals (Cr, Fe, Pb, Cu, Ni, and Zn) and microbial constituent (E-coli). The laboratory analyses were carried out at Simuch Scientific Analytical Laboratories, Nsukka, Enugu State. Figure 5 above shows the sampling location map.

Electrical conductivity (EC), Total Dissolved Solids (TDS) and pH were measured immediately in the field, with the aid of field probes because of their transient characteristics; the electrical conductivity (EC) and pH value of the water samples were measured with already calibrated *Wissenschaftlich Technische Werkstatten* conductivity/TDS meter and HACH pH *Sension* meter respectively. The EC meter was calibrated before use with potassium chloride solution (0.01M), having a conductivity value of 141.3 mS/cm at 25°C (APHA, 1995) while the pH meter was calibrated with standard buffer solutions pH 7.01 and 4.01.

Total Suspended Solids (TSS) was determined photometrically with the HACH DR/2010 Spectrophotometer at the wavelength of 810nm. The instrument was zeroed with deionised water (the blank) while the sample was mixed well before placed in the sample holder and measured. Total Solids (mg/L) = TSS (mg/L) + TDS (mg/L)

Alkalinity (bicarbonate HCO$_3^-$, carbonate CO$_3^{2-}$ and hydroxide OH$^-$) was determined titrimetrically with standard solution of Sulphuric acid solution (H$_2$SO$_4$). The sample was titrated with the 0.1N H$_2$SO$_4$ using phenolphthalein and methyl orange indicators. A 100ml water was measured into a conical flask. 3 drops of phenolphthalein indicator were introduced, when the sample remained colourless indicating in all cases that phenolphthalein alkalinity was zero. Few drops of methyl indicator was later introduced, the titre value was noted when the first perceptible colour change from yellow to orange was noticed. Alkalinity (HCO$_3^-$) as mg/L CaCO$_3$ = Vol of 0.1N H$_2$SO$_4$acid used (ml) x 50. While OH$^-$ and CO$_3^{2-}$ were obtained from standard alkalinity table using the individual value of HCO$_3^-$ in the respective sample.

Turbidity was determined spectrophotometrically at wavelength of 450nm on the HACH DR/4000 Spectrophotometer. The instrument was zeroed with filtered deionised water (the blank) while the turbidity of the sample measured.
The total hardness was determined titrimetrically using standard 0.01 N teta sodium salt of Ethylene Diamine Tetra Acetic acid (EDTA) solution. A 50ml water sample was put in the conical flask. 1 ml of buffer hardness solution was added followed by 2 drops of a solution of Erichrome Black indicator. The water sample was immediately titrated with continuous stirring using the standard EDTA till the end point when some blue colouration was observed. Total hardness as \( \text{CaCO}_3 \) (mg/L) = Volume of 0.01M EDTA (ml) X 1000 Volume of water sample taken (ml).

Calcium Hardness; the water sample was titrated using 0.01N EDTA solution. A 50ml water sample was placed in the conical flask followed by 2 ml 10N Sodium Hydroxide and 3 drops of Calcicon indicator. The end point was taken when the colour changes. Calcium hardness as \( \text{CaCO}_3 \) (mg/L) = Volume of 0.01M EDTA (ml) X 1000 Volume of water sample taken (ml).

Magnesium Hardness; Total hardness as mg/L \( \text{CaCO}_3 \) = Magnesium hardness as mg/L \( \text{CaCO}_3 \) + Calcium Hardness as mg/L \( \text{CaCO}_3 \). Thus, Magnesium hardness = Total hardness as mg/L \( \text{CaCO}_3 \) Calcium Hardness as mg/L \( \text{CaCO}_3 \).

Chloride: A 25ml water sample was placed in a conical flask followed by 1ml of a solution of potassium chromate indicator. The sample was titrated with a standard solution of silver nitrate. The end point was when the colour changed from yellow to dirty brown. Chloride (Cl) (mg/L) = Volume of silver nitrate solution used(ml) x 1000 Volume of water sample taken (ml).

The nitrate was determined on the HACH DR/4000 spectrophotometer by the principle of the cadmium reduction (NitraVer 5 nitrate reagent powder pillow) method. The instrument was zeroed with a fresh sample and the nitrate measured at a wavelength of 450nm while placing the treated sample in the sample holder.

The sulphate was determined on the HACH DR/4000 spectrophotometer by the principle of turbidimetry (SulfaVer 4 Sulphate reagent powder pillow) method. The instrument was zeroed with a fresh sample and the sulphate measured at a wavelength of 450nm while placing the treated sample in the sample holder.

The phosphate was determined on the HACH DR/4000 spectrophotometer by using the ascorbic acid (Phosver 3 reagent powder pillow) method. The instrument was zeroed with a fresh sample and the sulphate measured at a wavelength of 890nm while placing the treated sample in the sample holder.

Heavy metals (Cr, Fe, Mn, Cd, Zn, Co, Cu, Pb and Ni) were determined in the water samples with the aid of the Bulk BGV Atomic Absorption Spectrophotometer (AAS).

Potassium and Sodium were determined with the aid of a flame photometer, the Jenway PFP7 flame photometer. Culturing and Isolation (E-coili): As preparation of the media, potato agar was weighed on an electric balance and mixed with distilled water. Then the solution was subjected to heat. The petri dishes to be used were rinsed and dried and numbered according to the total number of samples represented. The potato agar solution was allowed to boil. The boiled solution was poured into the petri dishes and allowed to cover the agar coating. This culture is left for 5 days. On the fifth day the colonies formed are numbered according to the total number of samples represented.
The results of the field measurements and laboratory analysis are presented in the (table 1) above.

- **pH**: The average value of pH of the analyzed water samples shows acidic value of 4.15. Among the samples about 99% record lower than the minimum value (6.5) as prescribed by WHO and NSDWQ standard. Low pH in the study area can be attributed to the influence of acid mine drainage, acidic laterite, farming activities, fluvic and humic soils.

**TDS**: According to WHO (2006), the desired limit of TDS is 500mg/l while the maximum allowable limit is 1500mg/l, from the samples the TDS value ranges from 0.04 to 0.74mg/l which indicate values below the desirable limit and indicate good water quality free from pathogens and pollutants. Therefore can be classified as fresh (Hem, 1970). Suspended solids can be removed by water filtration, or sedimentation followed by disinfection which renders pathogens effective.

Iron and Manganese: Iron is of course a common component of acid mine drainage which can have a very detrimental effect on aquatic life, water uses and man-made structures. In this study, all the samples were below WHO and NSDWQ permissible limit (0.3mg/l). Excessive concentration of iron cause undesirable taste and stains on plumbing and laundry. Manganese is another heavy metal and it can be represented in many forms and compounds. In the study area,

| Sample no (Mg/l) & Locations | Coordinate | Depth (ft) | pH | EC (μS/cm) | TDS | DO | BOD | Na | NO₃ | Mg | Turbidity | Cl |
|------------------------|-----------|-----------|----|------------|-----|----|-----|----|-----|----|-----------|---|
| St Mary Ch Borehole (9) | 06°26'12.9" & 007°19'07.4" Elev: 276m | 520 | 4.2 | 074 | 053 | 360.00 | 152.00 | 0.01 | 1.00 | 8.65 | 12.00 | 9813.00 |
| Afor-Ogbe Borehole (10) | 06°26'35.3" & 007°18'17.4" Elev: 255m | 500 | 3.8 | 137 | 029 | 360.00 | 48.00 | 0.00 | 2.00 | 3.71 | 3.00 | 716.00 |
| WHO (2007) | -- | -- | 6.5 - 8.5 | 1000 | 500 | 5.0 | -- | 200 | 50 | 50 | -- | 200 |
| NSDWQ (2007) | -- | -- | 6.5 - 8.5 | 1000 | 500 | 5.0 | -- | 200 | 50 | 50 | -- | 200 |
| Imezi-Olo HDW (1) | 06°26'11.3" & 007°15'19.2" Elev: 166m | 35 | 0.02 | 0.00 | 0.2 | 2.03 | 0.01 | 0.00 | -- | 0.02 | 248.00 |
| Imezi-Olo HDW (2) | 06°26'11.5" & 007°15'17.4" Elev: 160m | 30 | 0.03 | 0.01 | 0.2 | 1.38 | 0.01 | 0.00 | -- | 0.06 | 188.00 |
| Imezi-Olo HDW (3) | 06°26'10.5" & 007°15'18.2" Elev: 158m | 40 | 0.06 | 0.01 | 0.5 | 0.18 | 0.01 | 0.01 | -- | 0.04 | 216.00 |
| Ovukuwu Spring (4) | 06°26'26.3" & 007°17'17.0" Elev: 260m | - | 0.04 | 0.01 | 0.7 | 0.74 | 0.01 | 0.00 | -- | 0.07 | 248.00 |
| Onuta Spring (5) | 06°26'21.7" & 007°17'19.1" Elev: 263m | - | 0.04 | 0.01 | 1.0 | 2.12 | 0.00 | 0.01 | -- | 0.12 | 360.00 |
| Ogba-Eke Spring (6) | 06°26'30.47"&007°17'21.1" Elev:117m | - | 0.03 | 0.00 | 0.2 | 1.75 | 0.00 | 0.00 | -- | 0.04 | 280.00 |
| Obiano Borehole (7) | 06°26'38.4" & 007°19'46.7" Elev: 260m | 460 | 0.03 | 0.00 | 0.1 | 0.55 | 0.00 | 0.00 | -- | 0.05 | 312.00 |
| Oforugwu Borehole (8) | 06°26'20.2" & 007°19'18.8" Elev: 279m | 500 | 0.03 | 0.00 | 0.2 | 1.38 | 0.00 | 0.00 | -- | 0.06 | 264.00 |
| St Mary Ch Borehole (9) | 06°26'12.9" & 007°19'07.4" Elev: 276m | 520 | 0.04 | 0.00 | 0.5 | 0.18 | 0.01 | 0.00 | -- | 0.08 | 360.00 |
| Afor-Ogbe Borehole (10) | 06°26'35.3" & 007°18'17.4" Elev: 255m | 500 | 0.03 | 0.00 | 0.0 | 1.85 | 0.00 | 0.00 | -- | 0.03 | 360.00 |
| WHO (2007) | -- | -- | 10 | 0.05 | 0.3 | 1.3 | -- | 250 | 3 | 1 | 2 | -- |
| NSDWQ (2007) | -- | -- | 0.01 | 0.05 | 0.3 | 1.3 | -- | 100 | 3 | 1 | 2 | -- |

Table 1: Results of Hydrochemical Data of the Study Area

The results of the field measurements and laboratory analysis are presented in the (table 1) above.
Manganese concentration ranged from 0.10 to 0.96mg/l. The later value is greater than WHO/NSDWQ (0.4) permissible limit.

Calcium and Magnesium: calcium originates naturally from decomposition of amphiboles, feldspar, gypsum and clay mineral. Calcium and magnesium combine with fatty acids in soap to form suds. The concentration of calcium in the study area ranges from 13.0 to 49.10mg/l which is all below the permissible limit of WHO/NSDWQ (75-200).

Sulphate and Electrical conductivity: Sulphate concentration in all the locations is generally less than permissible limit of WHO/NSDWQ (250mg/l). The EC value is normally high in saline water than in fresh water. The specific EC ranges from 0.07 to 137mg/l which is not a saline water.

Bicarbonate (HCO₃ & E-coli): Major source may be limestone or dolomite. Bicarbonate may be combined with calcium and magnesium to form a crust like scale of scale of calcium carbonate that retards flow heat through pipe and restricts flow in pipes. Water containing large bicarbonate is undesirable. In the study area the value of HCO₃ ranged 0.19 to 0.35mg/l. E-coli value of all the sample is below the WHO(1/100mg/l).

Potassium, Sodium, Chlorine & DO: K results from the chemical dissolution of the feldspar. It may also result from the dissolution of mica and clay minerals. The concentration of potassium in the area ranges from 0.02 to 0.12mg/l, which is below the permissible WHO(12). Sodium natural sources are in feldspar, clay minerals, evaporites and industrial waste. Na ranges from 0.00 (sample7, 8, 5, 10) to 0.03(sample 1), which is below the WHO(200) maximum limit. Chlorine may be dissolved from soil and rock or through man's activities such as dumping of industrial waste. Cl ranges from 368 to 1048mg/l, which is above the permissible WHO/NSDWQ (200mg/l) limit. DO is a measure of the amount of oxygen level in a water body. It is affected by pressure, temperature and salinity. The DO ranges from 188 to 360mg/l which is also above the permissible WHO and NSDWQ (5.0mg/l) limit.

The hydrochemical facies using piper diagram as a graphical representation of the chemistry of the water samples. The cations and anions are shown by separate ternary plots. The apexes of the cation plot are calcium, magnesium and sodium plus potassium cations. The apexes of the anion plot are sulfate, chloride and carbonate plus hydrogen carbonate anions. The two ternary plots are then projected onto a diamond. The diamond is a matrix transformation of a graph of the anions (sulfate + chloride/ total anions) and cations (sodium + potassium/total cations). The diagram divides water into four basic types according to their placement near the 4 corners of the diamond. From the diagram (figure 6), the water samples all plots at the top of the diamond, which is an area high in Ca²⁺ + Mg²⁺ and Cl⁻ + SO₄²⁻.

From the piper diagram below, all the water samples fall within the Ca-Cl water type and this is as a result of the high concentration of Calcium and Chlorine in the water samples analysed. This water type indicates water of permanent hardness.

A Stiff diagram, or Stiff pattern, is a graphical representation of chemical analyses, first developed by H.A. Stiff in 1951. It is widely used by hydrogeologists and geochemists to display the major ion composition of a water sample. A polygonal shape is created from four parallel horizontal axes extending on either side of a vertical zero axis. Cations are plotted in milliequivalents per liter on the left side of the zero axis, one to each horizontal axis, and anions are plotted on the right side. The size of the pattern is approximately equal to the total ionic contents. Stiff patterns are useful in making a rapid visual comparison between water from different sources.

From the stiff diagrams (figure 7) below, it can be seen that all the stiff plots assumes same shape and style which shows that all the water samples are from the same origin. The whole water samples are of Gypsum origin. This implies that the aquifer of their origin is gypsum.
6. Conclusion

In the water analysis carried out, the pH is mainly acidic and ranges from 3.8 to 5.3 in Oforugwu, borehole and Imezi-Olo handdug well respectively which are below the WHO/NSDWQ permissible drinking standard (6.5 to 8.0) and indicates the water of the area is not safe for consumption due to very low pH. The Total Dissolved Solid (TDS) ranges from 004 to 074mg/l which is generally within the permissible limit of fresh water. The heavy metals in the study area were discovered to be below the WHO/NSDWQ standards, the iron for instance ranges from 0.01 to 0.05mg/l in Afor-Oghe bore and Onuta spring respectively which is below the WHO/NSDWQ desired limit (0.3), E-coli also indicate that the water is free from bacteria and pathogens with a range from 0.0017 to 0.0034mg/l in Imezi-Olo hand dug well and Ogbeake spring at Ugwuotiti respectively which proved below the WHO standard limit of 1 count per 100mg/l. Based on the high concentration of calcium, the water is considered to be permanently hard. Chloride indicates a very high value ranging from 368 to 1048mg/l in sample Imezi Olo handdug well and Onuta Spring of Amansiodo respectively which is above the permissible WHO limit. Also DO indicate a high range from 188mg/l to 360mg/in sample Imezi-Olo handdug well, Onuta spring, and Afor-Oghe borehole respectively which are also above the permissible WHO and NSDWQ limit. This therefore means that the water is not safe for consumption due to bacteria, excess rate of chloride and excess dissolved oxygen which can cause external bubbles (emphysema) a rare occurrence that affects the skin and other tissues (Kumar et al., 2007). It is therefore good that the water in the area be boiled and treated before consumption to avoid outrage of health diseases.
The use of fertilizers should also be minimized especially the use of NPK fertilizer to avoid infiltration into the groundwater. Pit latrines should be sited far from water borehole site to avoid contaminations.

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