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Hydrochemical Evaluation of Water Resources of the Ohaozara Areas of Ebonyi State, Southeastern Nigeria.

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Abstract
Hydrochemical investigation of Okposi and Uburu Areas of Ohaozara and Environs of Ebonyi State has been carried out. The study area lies within the Imo – Cross River Basin province of southeastern Nigeria. The Asu River Group and the Ezeaku Shale, (Albian and Turonian respectively) underlie the area. Results of hydrochemical analysis revealed that Ca2+, Mg2+, Fe2+, Na+ and SO42-, NO3-, HCO3- are the major geochemical constituents while Al3+, MO2+, Ba2+, Ag+, Mn2+ I- and No2- are the minor constituents. Concentration of Cl- and Mn2+ ranges between 0.62 – 927 mg/l and 0.060 – 40.85mg/l respectively and are above the recommended standard for drinking water in most places. Implications of these high concentrations and the consumption of water of poor quality by the inhabitants of these areas may lead to poor health conditions. The variations in chemical constituents are attributed to non-uniform mineralization and ion exchange. There is variation in dissolved chemical constituents between the salt lake areas and other areas.
Keywords: Hydrochemical, Chemical constituents, Ion exchange, Mineralization.

1.Introduction
Water is an essential part of the ecological system. Geographically, water covers about 71% of the entire area of the earth's surface and it is found in oceans, streams, seas, rivers, lakes, ponds, springs and underground (Ogunji et al, 2004). Biologically, water makes up a large proportion of the total body fluid system of living things. An average water consumption rate of ten (10) litres per person per day has been recommended for small rural communities (UNICEF, 1989). This value is very small, compared to World Health Organization (WHO) standard of at least twenty litres per day per person (WHO, 1984). Despite this, WHO (1998) estimated that only 61% of urban dwellers in developing countries have access to safe water supply sources. It is also estimated that 1.2 billion people around the world lack access to safe water, and close to 2.5billion are not provided with adequate sanitation (Third World Water Forum, 2003). In Nigeria, about eighty percent (80%) of the total population live in rural areas, and less than fifty percent (50%) have access to potable water.
Salt Water pollution resulting from artificial and natural sources is among the various problems militating against municipal, rural and general water supply in Nigeria (Champman and Kimtach, 1989). The pollutant sources have either been from improper refuse disposal, salt water intrusion or contaminants from the host rock (Egboka and Uma 1985). This is pertinent, as water during its movement and storage in aquifers, tends to dissolve minerals in their host rocks. Higher concentrations of these constituents above toloratable standards tend to render the water unwholesome for certain type of use (Freeze and Cherry, 1979).

2.Description of the Study Area
2.1 Location
Okposi and Uburu are rural communities in Onicha and Ohaozara Local Government Areas of Ebonyi State, Nigeria (Fig 1.0). Geographically, the study area is located between latitudes 6°00I'N and 6010IN, and longitudes 7042I50IIE and 7052I50IIE. The area is richly endowed with saline springs and salt lakes: This includes the Okposi salt lake (060 02" 23' N, 0070 48" 337' E) and the Uburu salt lake (060 02' 971" N, 0070 44" 799" E). The study area is part of the tropical hinterland climate (Illoeje, 1979), with an average monthly rainfall of about 222mm, and mean annual temperature of about 290c (FARM Unit, EBSU, 2009). It has a relatively longer rainy season (March-October) and a shorter dry season (November to February). The origin of the saline groundwater is not yet known. However, Egboka and Uma (1984) suggested that possible sources of this salinity include one or a combination of the following,

a)Soluble salts in the matrix of sedimentary strata that now exists in the zone of active groundwater flow in the bedrock.

b)Ocean water intruded into the bedrock aquifer under present hydrological conditions

c)Brines that flow upward from deep (> 100m) sedimentary zones

The hydrochemical evaluation of water resources around the salt lake areas and to determination the extent of salinization of the salt lakes forms the basis for this study. Possible sources and causes of these chemical constituents are suggested.

2.2 Geological Setting

Regionally, the area lies within the lower Benue Trough, the evolution of this trough has been suggested differently by different authors (Burke et al, 1972; Uzuakpunwa 1974; Nwagide and Reigers 1996). The trough is composed of accumulation of sedimentary fill due to series of marine transgression and regressions from the Albian times. The basin is also characterized by the Santonian tectonism which resulted to major folding, faulting, fracturing, volcanic intrusion and Ld – Zn mineralization. These fold structures stretch NE – SW especially in the southern area of Abakaliki. The area is underlain by the Asu River Group and Ezeaku Formation. The area is predominantly underlain by shale, sandstone sandy shale and thin lenses of highly calcareous limestone lithologies.

2.3 River System / Drainage Pattern

Surface drainage in the area is irregular and consist mainly of a number of small ephemeral streams and rivers which tends to dry up during the dry flow in the north – south direction (see fig 2.0) into the Asu River, which is about 15km south of the area. Saline spring and lakes occur within a relatively narrow belt, which extends in a northeast - South West direction. This includes the Okposi salt lake (06° 02' 23" N, 007° 48' 337" E) and the Uburu salt lake (06° 02' 971" N, 007° 44' 799" E). Others are river Asumgbom, Atte, Azuu, Ovum, Enu and Oshi which has characteristic salinity.

3. Method of Analysis

Twenty-eight (28) water samples were randomly collected over the entire area from surface and groundwater sources (see Fig 2.0) and analyzed. Temperature, electrical conductivity and pH were measured using a digital meter. Laboratory analysis for the concentration of major ions comprising Ca2+, Mg2+, Fe2+, Na+, S042+, N03-, Cl-, HC03- and C032- was done using DR 2010 spectrophotometer. Trace constituents including As3+, Cr3+, Zn2+, Ni2+, Mo2+ were analysed using their special hydrochemical analysis kits.

4. Results and Discussion

The turbidity of the groundwater sample in the area ranges between 10-149 mg/l, while that of surface water ranges from 10-23(mg/l). By the WHO standard, turbidity exceeding 5mg/l is not good for domestic use. The pH of groundwater in the study area ranges from 7.3-9.6mg/l, while that of surface water ranges from 8.5-11.5mg/l. It is also worthy of note that the pH of the salt lakes are higher (more basic) than other ground and surface water samples analyzed. The pH is slightly above the WHO guideline for drinking water which is between 6.5 – 8.5 mg/L. The conductivity of groundwater samples ranges between 0.12-2.10 S cm-1 while that of surface water ranges between 0.18-527.1 Scm-1. This conductivity does not exceed the WHO standard. It is worthy of note that conductivity in the area decreases away from the salt lake areas. This is due to the high concentration of NaCl in the salt lake regions. From the analysis, the TDS in the area is very high (129,600 – 497,700mg/l) within the salt lake areas and are above the WHO standard of 500mg/l. A gradual decreases away from the salt lake areas was also observed. Ca2+ values of the study area ranges between 0.01mg/l-1.22mg/l, except in the Okposi salt lake where it increased excessively to 274.5mg/l. However, the WHO guideline recommends 75mg/l as permissible value for Ca2+. Calcium ion (Ca2+) is commonly present in natural waters, often resulting from the dissolution of calcium-rich rocks; this is evidenced in the study area. It may occur as carbonates and sulphates of calcium, as in limestone, dolomite, chert, flint and gypsum. The salts of calcium, together with those of magnesium, are responsible for the hardness of water. Iron mostly occurs in the form of ferrous bicarbonates (Fe (HC03)2), ferrous sulphate (FeS04), or ferrous chloride (FeCl2). The values of iron (Fe2+) in the study area range between 0 to 0.07mg/l, and the maximum value was recorded in the Uburu salt lake. WHO guideline indicates a permissible Fe2+ value of 0.3mg/l. This implies that water sources in the area have safe concentration of Fe2+. This analysis revealed that the magnesium ion concentration in water samples in the area ranges between 0.34-2.62mg/l for the boreholes while that of surface water is also on that average, but the Okposi salt lake is excessively high, having a value of 990mg/l. WHO standards indicate that the permissible limit is 50mg/l. This implies that apart from the Okposi salt lake, water sources in the area have low concentrations of Mg2+. Potassium (K+) and sodium (Na+) are present in natural waters. The concentrations of Na+ and K+ is high in the study area according to WHO standard. Bicarbonate ions (HCO3) and carbonate ions (CO32-) are present in natural waters and have been associated with the alkalinity and hardness of water (Hems, 1989). The major sources of these ions in water include the dissolution of limestone, dolomite, chalk, chert and other carbonate - rich rocks (Todd, 1980). The concentration of these ions ranges between 0.34mg/l-2.82mg/l for the boreholes and about the same range for the surface waters except for the Okposi salt lake with about 1204.5mg/l. This indicates a high level of hardness for the salt lake. WHO recommends a concentration of 200mg/l for potable water supply. Possible sources of this high concentration in the study area are weathering of carbonate rocks, inorganic carbon component (Co2) which arises from the atmosphere and soils; and biological activities.

Sulphate Ions ($SO4^{2+}$) are present in natural waters; mostly occur as a result of the oxidation of sulphide ores, gypsum and anhydrite. They can also occur as leachates from their ores and other minerals. Sulphate could constitute an oxygen source for bacteria, which chemosynthetically converts it to hydrogen sulphide (H_2S) in anaerobic conditions. This process causes odour in water. The concentration of sulphate in the study area ranges between 0m/l to 3.0mg/l. This is below the WHO recommended standards for drinking water, and hence permissible.
The concentration of Cl^- in the study area is excessively high in some places. This includes the Ahia Ochie boreholes (927mg/l), Okposi Ukwu borehole (822mg/l), and Ndiagu Onicha (528mg/l). Other boreholes in the area have low concentrations (between 0.62-5.6mg/l) The Cl^- concentration values in the surface water samples are also high (between 235.5mg/l– 679.0mg/l). The areas of higher concentrations are areas closer to the salt lakes, and within the fractured shale aquifer units, while those in the sandstone/siltstone aquifers are low. These high concentrations may be due to leachate from the brine loaded bedrocks and halite mineralization, which is not far from the area. The permissible concentration of chloride in drinking water is 250mg/l by (WHO, 1984) recommendations.
Nitrate is an important natural constituent of water. The concentration of N03 in the study area ranges from 0 mg/l (in many places) to 0.30 mg/l (the highest value), this is permissible for ware supply.

4.1 Salinity and Hardness
Saltwater intrusion is prominent in Uburu, Okposi, Obina, Onumaihi, and Obodoama all in the study area. Groundwater and surface water in these areas tend to show high salt concentrations during rainy seasons and low during the dry season. The result of water analysis reveals high value of NaCl salts. This is evident by the high conductivity values which ranges between 0.12 – 2.10 Scm-1 for ground water and 0.18 – 527 Scm-1 for surface water. The value of chloride ions (Cl) is also high (between 235.5mg/l – 5,160mg/l) in surface water and up to 927mg/l in some bore hole water samples analyzed. This shows high level of saltwater intrusion. Agricultural sources of pollution include the use of pesticides, herbicides, fertilizers and other forms of manure to increase agricultural yields. This is prominent in the study area. All these inputs commonly find their way into groundwater as leachates into the soil. Nitrates and phosphates, from fertilizer constitute important pollution in soil and water. Mining sources of pollution from lead/zinc and sylvite mineralization, which occurs in the Enyigba area of Abakaliki are also significant. Result of water analysis reveal that concentration values of Na^+ + K^+ are above 50mg/l(up to 92mg/l) in groundwater samples and above 1000mg/l in some surface water samples. Values of phosphorus ranges between 0.11mg/l to 29.0mg/l in some places. Although the analysis reveals low concentration of nitrites (between 0.00 – 0.130mg/l) this value tends to be highest where movement of groundwater is least. Salinity can be expressed as mg/l Cl^- x 1.65 (Dalton et al, 1978). Primary salinity results from sodium chloride (NaCl) and sodium tetraoxosulphate (iv) (Na_2SO_4), while secondary salinity results from calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), calcium sulphate(CaS04), and magnesium sulphate (MgS04) (Drever, 1982).

This analysis reveals that the boreholes (groundwater) have low and permissible salinity concentration and can be classified as fresh water. The salt lakes have excessively high salt concentration, (Okposi salt lake, 497, 900mg/l and Uburu salt lake, 129, 600mg/l) and hence classified as brine water. Hardness is the characteristic inability of water to leather with soap, thereby forming scum. Hardness results from the presence of divalent metallic cations, predominantly calcium and magnesium. These ions react with soap to form precipitates, and with certain anions present in water to form scale. The hardness in water is derived from the solution of carbon dioxide, released by bacterial action in the soil, in percolating rainwater. Low pH condition develops and leads to the solution of insoluble carbonates in the soil and in limestone formations to convert them into soluble bicarbonates. The total hardness recorded in the study area reveals that both the surface water and groundwater show low concentration of hardness (between 0.34mg/l – 4.24mg/l), except the Okposi salt lake which, is excessively high (1204.5mg/l). This is above the recommended drinking water standards (WHO, 1980). Using Todd's (1980) water classification based on hardness, all the water sources in the study area could be classified as soft water except the Okposi salt lake classified as very hard water.

5.Summary and Conclusion
Hydrochemical investigation of Okposi and Uburu areas of Ohaozara and Environs of Ebonyi State was carried out. The area lies within the Imo - Cross River Basin province in the saline belt of southeastern Nigeria. The study led to the following conclusions:
The concentration of the major cations such as Ca^{2+}, Mg^{2+}, Fe^{2+}, K^+, Na^+, and anions such as SO_4^-, HCO_3^-, CO_3^{2-}, Cl^- , and NO_3^-. Cl^- falls above the WHO recommended standard. This is linked to the high salinity of

water resources in the area.
There is high concentration of Ca2+ and HCO3-, low concentrations of TDS, Mg2+ and SO42- in the recharge areas, while high concentration of Na+, Cl-, K+ and HCO-3 predominate in the discharge areas.
Trace values of Al3+, Br-, CO2+, Cu2+, F-, I-, NO-2, Zn2+, As3+, Ag+, Mo2+ and Ni2+ are observed, but high concentrations of Mn2+ and Ba2- in both surface water and groundwater exist.
Most chemical parameters, (especially Cl-, Na+, Ca2+, Mg2+, SO42-, HCO3-) maintain high concentration within the salt lake area, with the values declining away from the salt lakes.
Physical parameters like PH, electrical conductivity, colour, turbidity, and TDS reveal that the water resources are slightly neutral to basic in most places. The turbidity and TDS are far above the WHO recommended standard for drinking water. The high electric conductivity is due to high concentration of NaCl in the salt water.

6. Recommendations

Water quality is as important as its quantity. Ground water and surface water in the study area contains chemical constituent which are high and indicate high level of salinity. Proper sewage disposal system should be provided and upheld in the study area. This will minimize the rate and distribution of chemical constituents in ground water. Geochemical investigation should be conducted before bore holes are sited in these areas, this is to reduce incidence of highly saline groundwater in boreholes.

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TABLE : CONCENTRATION OF CHEMICAL CONSTITUENT IN WATER SAMPLE ANALYZED

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13	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
14	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

KEY: U – [illegible]

O – [illegible]

N – [illegible]

C – [illegible]

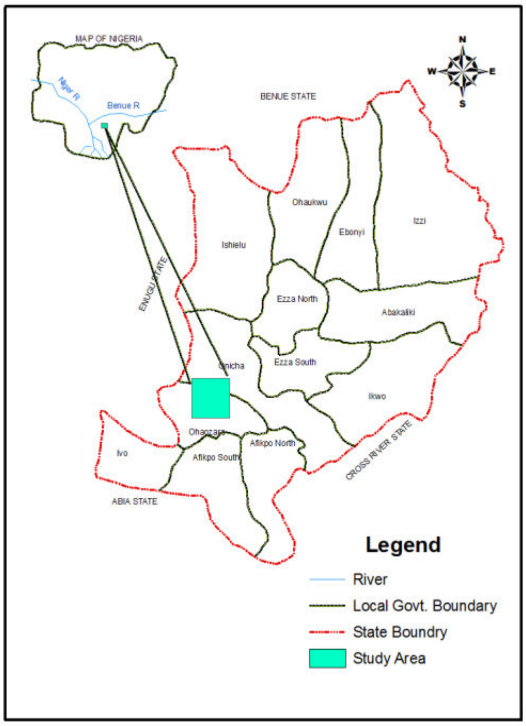

Fig 1.0 Map of Ebonyi State showing the study area

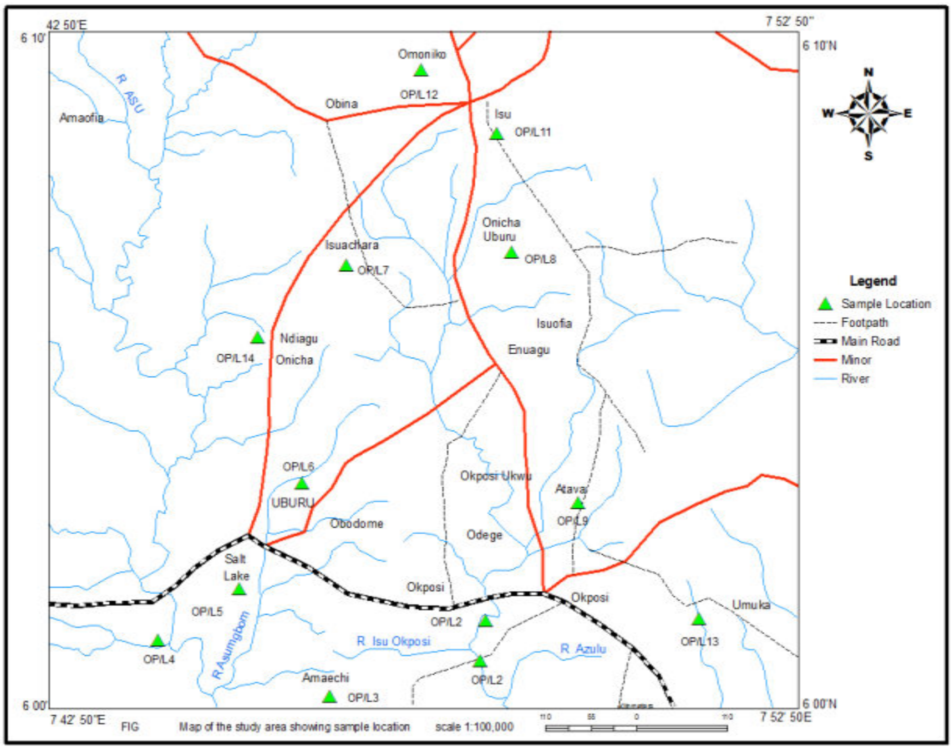

Fig 2.0: Showing River System and Sample Location