

Hydrogeochemical Characteristics and Groundwater Quality Evaluation in the Core Littoral Communities of Akwa Ibom State, Nigeria

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Abstract: The upsurge in anthropogenic activities in the littoral communities of Akwa Ibom State has taken a heavy toll on the ecological equilibrium of the entire natural ecosystem of the region. Consequently, depletion of the groundwater resources is gradually assuming an alarming proportion. To make matters worse, there is a spectre of hydrochemical events in the subsurface also contributing in no small measures to the groundwater quality degradation. Given this scenario, it has become imperative that groundwater quality in these new economically active communities be subjected to regular quality tests in order to determine the extent to which this all-important resource is being influenced by both human and natural activities in the zone. Hence the study investigated the groundwater quality in the afore-mentioned communities with a view to determining its usability for domestic, agricultural, industrial and other water-based applications. Groundwater samples were evaluated based on the World Health Organization (WHO, 2006) standard. The results of all samples analyzed revealed that the characteristics and concentrations of both physical and chemical parameters varied from one sample to another with majority falling within the WHO permissible limits. The values for P^H , electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO) and total hardness (TH) ranged from 5.6 - 6.4; 9.25 - 81.50 mg/L; 4.77 - 41.20 mg/L; 2.77 - 3.85 mg/L and 13.00 - 82.00 mg/L respectively. The concentrations (mg/L) of the cations of major alkali and alkaline earth metal were: Na^+ (26.97-47.85), K^+ (1.83-2.65) and Ca^{2+} (2.50-101.82), Mg^{2+} (0.97-41.36), while those of the common anions: HCO_3^- (9.04-50.51), Cl^- (14.04-22.00), NO_3^- (0.39-1.71) and SO_4^{2-} (0.004-0.24). The trace metals contents ranged from 0.31-1.58, 0.33-1.03, 0.001-0.05 and 0.57-1.42 for Cu, Fe, Mn and Zn respectively. The contents of major ions in the samples is in the following order of dominance: $Ca^{2+} > Na^+ > Mg^{2+} > K^+ = HCO_3^- > Cl^- > NO_3^- > SO_4^{2-}$. The graphical exposition of the data based on Piper Trilinear and Schoeller diagrams four hydrochemical facies: $CaNaHCO_3$ (mixed), $CaMgCl$ (mixed), NaCl and $CaHCO_3$. $CaNaHCO_3$ water type is the dominant facies which represents water of recharge zone while $CaMgCl$, NaCl and $CaHCO_3$ are the least. The parameters are well within the permissible limits, with the exception of pH (5.6 - 6.4) and Fe (0.33-1.03 mg/L) which are above the WHO standard of 6.5-8.5 and 0.03 mg/L. In the same vein an isolated case of high calcium content of 101.82 mg/L was recorded for one of the samples investigated. The above results when juxtaposed with the quality indices set by various health regulatory organizations, suggest that the groundwater in the area is fairly usable in its present state for agro-based activities but will require iron (Fe) and pH remediation to improve its quality for portability and industrial application.

Keywords: Akwa Ibom State, anthropogenic activities, groundwater quality, littoral communities

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I. Introduction

Water ranks as the second most essential need for the existence of all forms of lives after air. And availability of good quality source of water is not only an essential prerequisite for sustenance of all forms of lives on the planet earth, but also one of the most pivotal environmental and sustainability issues of the twenty-first century [1]. However, of 37 Mkm³ of freshwater available on earth only about 22% or 8.14 Mkm³ exists as groundwater constituting roughly 97% to 98% of all fresh water available for human use [2]. In other words about one fifth of freshwater used worldwide is derived from groundwater [3]. Groundwater is the major source of water for general usage in the littoral communities of Akwa Ibom State, South Eastern Nigeria. The subsurface water is usually available in great abundance since the aquifers are largely made up of the continental alluvial and upper coastal plain sands of the Benin Formations with approximate thickness of 2000m. This porous and permeable formation is underlain by high density delta-front sands of Aghada Formation consisting of paralic siliciclastics of over 3700m thick. The upper portion of this hydrocarbon bearing formation being

mostly dense sands with impervious shale interbeds[4] can prevent groundwater from further percolation once the aquifers are recharged [5]. While the lower segment of the formation serves as the major hydrocarbon reservoir in the Niger Delta basin. Another factor attributed to the abundant groundwater in the area is the prevalent equatorial climate characterized by heavy rainfall which keeps aquifer adequately recharged [6]. However, aquifers replenishment according to [7] occurs majorly from yearly atmospheric precipitation either directly by rainfall or indirectly from rivers and lakes which (in response to the gravitational pull) percolates through cracks and deep porous zones into the aquifers. It is pertinent to note here that this phenomenon by which aquifers are recharged with water from outside the geological formations is arguably a huge source of groundwater quality depreciation, considering the amount of hazardous substances dissolved by the surface waters before infiltrations into the aquifers. For instance surface runoff into the streams, rivers and porous zones may be contaminated with nitrate and phosphates fertilizers, and acid based herbicides such as 2,4-D (2,4-dichlorophenoxyacetic acid) in local areas where application of these agro-chemicals is grossly abused due to inadequate guides or lack of adherence to safety protocols.

Frequent oil spills and indiscriminate discharge of industrial effluents such as hazardous materials from spent drilling fluids containing heavy metal complexes and lignosulfonate compounds by the marginal oil field operators are also responsible for water quality depletion in the littoral communities. Other human-induced or anthropogenic sources of groundwater contamination include, leaky septic tanks, landfills etc. And using contaminated water is one most common causes hazards to public health through spread of disease [8]. Subsurface water quality degradation may also occur as a result of over-exploitation or groundwater mining [9] - a phenomenon occasioned by groundwater withdrawal in quantities beyond natural recharge rates thus paving the way for saline water ingress or intrusion, especially in the shallow coastal aquifers with high porosity and permeability. This phenomenon has been extensively studied by several authors including [10-12]. Although the anthropogenic activities are accountable for a large percentage of groundwater depletion, geogenic events such as mineral and rock weathering, decomposition of the soluble products and changes with respect to travel and residence time according to [13] also influence the quality of groundwater. In the same vein ion exchange reactions from dissolution of calcite, dolomite and gypsum in diverse acidic environments coupled with redox reactions mediated by micro-organisms[14] are still some of the natural processes having significant influence on the groundwater chemistry. It is pertinent to note that once water bodies are contaminated it becomes unusable and the clean-up program may require a huge capital outlay. The Ogoni hydrocarbon clean-up project in Rivers State is a case in point. In the light of the foregoing [15] foresees a worsening scenario if sustainable freshwater resource monitoring/management framework is not put in place, considering rapid population growth, upsurge in urbanization, increasing agriculture and industrial activities around the globe.

Although groundwater is found in great abundance in the littoral communities, it might still be unfit for human consumption, considering the vast array of afore-stated factors engendering its vulnerability. Whilst quantity depletion due to over-exploitation of the aquifer recharge as noted by [16] can be easily noticeable wherever it occurs, only little is known about the enormity of hazards associated with using water of degraded quality, for whatever purpose. In other words not much is known about groundwater resource with regards to its increasing level of quality depreciation occasioned by a combination of both human and natural activities in the area. Hence, to create the required awareness there is the need for regular monitoring of the groundwater chemistry for the safety of all forms on earth if the much talked about sustainable water development goal must be actualized. This work is therefore an attempt to key into this scheme in favor of the littoral communities Akwa Ibom State in particular, and by extension those of Niger Delta in general. A number studies bordering on the upsurge of groundwater pollution and its implication on the environment have been carried out by many researchers. These include work by [17] on water resources of Nigeria; assessment of ground water across Delta State [18]; work on urban groundwater pollution [19], to mention but a few.

1.1 Physical Setting and Location of the Study Area

The southern end of Akwa Ibom State occupies southeastern part of Niger Delta situated in the Gulf of Guinea. The study area is the littoral communities of the State lying between latitudes 4°29' 30'' and 4° 49' 20''N and longitudes 7°30'20'' and 8° 20'40''E. Akwa Ibom State has a near-triangular geometry covering a total landmass of about 6,900 square kilometers, encompassing the Qua Iboe River Basin, the western part of the lower Cross River Basin or the Calabar Flank and the eastern part of the Imo River Basin. The State has an ocean front spanning a distance of 129 kilometers from Ikot Abasi in the west to Oron in the southeast cutting across the five core littoral Local Government Areas (LGAs). However, the study also captured the five neighboring LGAs, by reason of their proximity to the ocean front, summing up to ten LGAs as the present study area (Fig. 1). The study area is largely drained by Imo River, Kwa Iboe River and Cross River together with their tributaries. The area is a flat lowland plain whose main landforms are mangrove swamps and floodplains with recent alluvial accumulations, beach ridges and mangrove mudflats [20]. The aquifer recharge in the study area is usually high all year round due to high rainfall of about 2000mm annually [21]. The vegetation and climate of

the area can be delineated to have two distinct seasons namely the dry and wet season. The dry season occurs between November and March, while the rainy season sets in between April and October. However, over the last couple of decades, it has become very difficult to create a clear-cut distinction between the two periods due to the yearly fluctuations occasioned by climate change. But in spite of these anomalies the high temperatures, humidity and annual precipitations of the area favor steady plant growth thus engendering a vegetation cover characterized mainly by mangrove trees in the core littoral settings, while landward communities are marked with luxuriant foliage of the rainforest belt of Nigeria. However, anthropogenic activities such as urbanization, agriculture, exploration and exploitation by the marginal oil and gas field operators in the area have resulted in deforestation of parts of the study area.

1.2 Geological Setting and Hydrogeology of the Study Area

The knowledge of the physical characteristics of the sub-surface rocks is an important element in understanding their influence on the hydrogeochemical processes of the groundwater system. The study area as earlier mentioned is part of Niger delta basin which according to the recent report by the United States Geological Survey (USGS) covers about 300,000Km² out of which 56,000 Km² is on land whilst 244,000 is in water (Fig. 2). The basin proper began developing in the Eocene (60million years ago) accumulating sediments that is presently about 10,000 meters in thickness. Niger Delta is a three unit lithostratigraphic basin- ranging from the oldest marine Akata Formation, a turbidite reservoir overlain by the paralic Agbada Formation, a deltaic reservoir which collectively constitute the Tertiary Niger Delta (Akata-Agbada) Petroleum System[22]. The Niger Delta basin is current hub of hydrocarbon exploration and exploitation activities. Overlying the Agbada Formation is the Coastal Plain Sand - the Benin Formation in which the aquifer (1500-2000m) thick, made up mostly of coarse grained, pebbly and poorly sorted sands with minor clay intercalation is located. Thus every borehole drilled in the study area derives its water from the you Benin formation at the flow rate of about 300m³ per hour at a penetration depth of between 130-150m [23].

Based on reports by[23-25]. The littoral setting of Akwa Ibom belongs partly to the coastal plain sands, beach ridge complex and alluvium of Quaternary Period and consists of freshwater dryland, freshwater swamp, coastal brackish water swamp, and beach ridge complex. The alluvial deposits largely composed of fine to very coarse grained sands and ranging in color from greyish to light brown occur along banks of major rivers.. The floodplain muds and clay are light grey. The freshwater swamp belt is landward of brackish water swamp zone and gradational to it. While brackish water zone is landward of beach zone and the mangrove swamp belt [25].

II. Methodology

2.1 Field Study and Sample Collection

A total of 22(twenty-two) water samples were collected, 2 from each of the ten communities. The two samples from each community or Local Government Area (LGA) were then blended into one sample giving a total of 10 samples from the 10 LGAs. At each sampling location the well was pumped for at least 5 minutes to ensure the water sample was fresh and direct representative of the aquiferous fluid - bearing all its physicochemical attributes. Each sample was placed in a 1 litre brand new LDPE plastic bottle pre-treated with a 1 molar solution of trioxonitrate(V) acid (HNO₃) and thoroughly washed with high-grade de-ionized water, then finally rinsed severally with water to be sampled. The sample containers were labelled using the first three letters of the LGA's name viz: IKO ⇒ Ikot Abasi; EAS⇒ Eastern Obolo; MKP⇒ Mkpato Enin; ONN ⇒Onna; EKE⇒ Eket; ESI⇒Esit Eket; MBO⇒ Mbo; UDU⇒ Udung Uko and ORO⇒ Oron. All the fast changing physicochemical parameters were determined in-situ and thereafter the sample containers were stoppered and safely transported under 4°C to the laboratory where trioxonitrate (V) ions (NO₃⁻) content was immediately determined before addition of a drop of conc. trioxonitrate (V) acid to all the samples in order to prevent the formation of complexes with various metallic ions in the samples. The samples were then preserved in the refrigerator for the determination of other parameters. Reagents used included: Erochrome Black-T (EBT), Brucine sulphate, Ethylene Diamine Tetra-acetic Acid (EDTA), Silver nitrate, Potassium tetraoxochromate(VI), Hydrochloric acid, Tetraoxosulphate(VI) acid, Ammonium hydroxide, Ammonium chloride, etc, were either sourced from Chemistry Department Laboratory, Akwa Ibom State University where most of the analyses were carried out, or purchased from Standard Chemical Stores and they all conformed to analytical grades. The groundwater quality evaluation samples was carried out strictly in accordance with the prescribed analytical procedures of American Public Health Association [26] and World Health Organization [27].

2.2 Sample Analysis

As earlier mentioned, the unstable parameters such as pH, temperature and electrical conductivity (EC), total dissolved solids (TDS) and dissolved oxygen (DO) were determined in the field. The pH was measured with pre-calibrated digital pH meter (Model Ohaus Starter 2100). Temperature, EC and TDS were determined by means of a triple function digital conductivity meter (Model DDSJ-308A) with a calibrated probe. DO was

measured by means of a DO Meter (Model JPSJ-605 DO Analyzer), Sulphate ions were determined using the analytical instrument- Accu Vac Ampul (Model 685 Sulfate AMMV) and the readings were confirmed via Sulfaver 4 powder in another Analytical instrument Model Hach DR3800. Nitrate content was determined using an acidified solution of Brucine sulfate and the medium analyzed by means of the UV-Visible Spectrophotometer (Thermo Scientific Helios Y). Total alkalinity based on the concentration of hydrogen trioxocarbonate (IV) ions (HCO_3^-) was determined titrimetrically using 0.02M HCl as titrant and methylorange as indicator. Total hardness based on the concentration of calcium and magnesium ions (Ca^{2+} and Mg^{2+}) was evaluated via digital titrimetric instrument in which 0.01MEDTA buffered with NH_4Cl at pH of 10 was as the titrant and Erochrome BlackT as indicator. Chloride ions (Cl^-) concentration which is the sum total of chlorine (Cl) forming salts with the first two most abundant alkali elements (Na and K) was determined via classical titrimetric using AgNO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ as the titrant and indicator respectively. The concentration Ag^+ ions consumed was used to quantify the amount of chloride and in turn that of sodium and potassium ions in the samples. Finally, the determination of the concentrations of heavy metals (As, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were achieved by the use spectrophotometer Model SOLAAR 969 at the Akwa Ibom State Ministry of Science and Technology located at Obio Imo Street, Uyo.

III. Results and Discussion

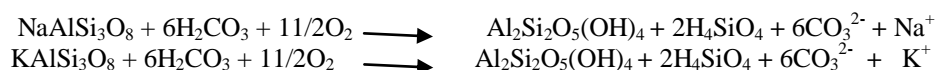
3.1 Physicochemical characteristics of the water samples

Hydrogeochemistry gives an insight into the processes or events occurring in the subsurface reveal the how the events affect the groundwater vis-à-vis its quality and suitability for human consumption, agricultural, industrial and other water based applications. Again, it helps infer what changes are taking place in the water system due to rock-water interaction as well as anthropogenic influences.

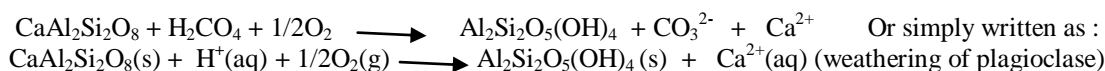
Field study revealed that temperature which is one of the few physical parameters used for groundwater evaluation ranged between 26.5 °C to 26.7 °C across the zone. Although the [27] has no set limit for water temperature, apparently due to its spatial variations, study by [28] indicates that temperature is a key factor affecting the number and kinds of species in aquatic environment. In the same vein [29] noted that water temperature plays a vital role in Schistosome (Bilharzia) transmission in permitting a suitable snail population to flourish and in controlling the length of the incubation period of the parasite in the snails. In the light of the foregoing there is need to set a temperature regime (minimum and maximum) for sake of such aquatic organisms, spatial variations notwithstanding. The pH values of all the groundwater samples in the area ranged from 5.6 to 6.4 (ave. 5.95), as opposed to the permissible range of 6.5 – 8.5. This is an indication that the water the area is fairly acidic. In other words, the low pH value depicts the presence of free hydrogen ions and acidic cations of metal like iron (Fe) and aluminum (Al) which maybe anthropologically or geogenically released into the groundwater flow system when Fe(II) disulfide (FeS_2) mineral especially pyritic clay undergoes chemical weathering by oxidation to generate tetraoxosulphate (VI) acid into the groundwater by oxidation shown: $\text{FeS}_2 + 1/2\text{O}_2 + 4\text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + \text{Fe}^{+2} + 2\text{H}^+$. In addition, low pH may result from acid rains caused mainly by acid gas (SO_2 , H_2S and CO_2) polluted air occasioned by incessant gas flaring, acidic industrial emissions and discharges which dissolve in rain drops and leach through the permeable and porous soil into the aquifers. Electrical conductivity (EC) - the second chemical parameter after pH that was determined in-situ. This parameter has a direct bearing with pH since water becomes more conductive in the presence of positively charged species. Consequently, the higher the acidity of groundwater, the higher the electrical conductivity (EC) and total dissolved solids (TDS); though, relatively high TDS in water might be attributed to increased residence time of the water in the aquifer which allows longer interaction with the minerals. The longer the time of mineral and rock-water interplay the more the dissolution of those solids and the higher the value of TDS and EC. This observation is more or less reflected by the results presented in table 2, with EC range of 9.25-81.50 $\mu\text{s}/\text{cm}$ giving the average of 50.71 $\mu\text{s}/\text{cm}$ (Tables 1 & 2).. While TDS values vary from 4.77 to 41.20 mg/L giving an average of 21.87 mg/L as presented on tables 1 & 2, and succinctly demonstrated on the Durov Plot (Fig.3) and on the Cross Plots (Figs.4a & b). According to the study by [30] on water classification TDS < 1000 mg L⁻¹ is for freshwater; TDS > 1000 mg L⁻¹ (brackish water); TDS > 10,000 mg L⁻¹ (saline water) and TDS of 100,000 mg L⁻¹ is for brine. In the same vein [31] also puts the TDS for freshwater at (< 1000 mg/l). Based on those reports all the water samples in the study area are fresh since their TDS values are by far lower than those set by the two reports and are also consistent with [29] standard of 1500 mg/L.

The dissolved oxygen (DO) values in the samples varied between 2.77 mg/L to 3.85 mg/L which is 3.60 mg/L on average. Samples with values lower than 3.0 mg/L may be due to high temperature or the presence of organic impurities. Oxygen dissolves faster at low temperatures than at high temperatures. For instance at 25 °C its solubility of oxygen is only about 8.30 mg/L; whereas at 4 °C, it is as high as 13.30 mg/L. Without adequate levels of DO in water aquatic lives can be adversely affected. [32] noted that the DO level lower than 3.0 mg/L is stressful to most aquatic organisms. Total alkalinity is a measure of the capacity of water to resist lowering of its pH and expressed as the amount of CaCO_3 present in water. The values ranged between 14 mg/L

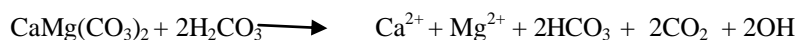
and 82mg/L(ave.29.88mg/L).This average is well within allowable limit of 50mg/L. Hardness of the water is the property mainly attributed to the presence of the two alkaline earth metal ions (Ca⁺ and Mg⁺). The total hardness (TH) is an essential prerequisite of water quality whether it is meant for domestic, industrial or agricultural purposes. It is a measure of the tendency of water to resist foamability with soap. The TDS of the water samples in the study area varies between 23 and 167 mg/ L (ave.70.11 mg/L). According to TH classification models [28] and [29], all the water samples in the stud area are within the soft water TH (<60mg/L to moderately hard (75–150 mg/ L) category. The low to moderate values of TDS, EC and TH obtained for the water samples in the area depict a minimal to fairly mineralized soft groundwater system with limited residence time. On the cations chemistry of the groundwater, the results show dominance of Sodium ions (Na⁺) over its counterpart alkali metal - potassium (K⁺) with the average concentrations of 54.65mg/L and 6.52mg/L respectively. The dominance of the former over the latter is probably based on their natural abundance but under a given environmental conditions both of them are released mainly from their silicate minerals (sodium and potassium aluminum silicates commonly as albite and muscovite) into the groundwater system via chemical weathering. Represented below are the chemical transformation involved in the weathering of the two silicate minerals.



In the same vein, the presence of the two major alkaline earth metals, Calcium (Ca²⁺) and Magnesium (Mg²⁺) in the groundwater samples with Ca⁺⁺ (39.55mg/L) dominating over Mg⁺⁺(15.83mg/L) is possibly in line with their ranking on the scale of natural abundance. In any case, Ca⁺⁺ may have been released from the weathering of a plagioclase (anorthite) during which the felspartic mineral is transformed via acid hydrolysis into a clay mineral (kaoli- nite) as shown below:



The above reaction appears to be major source of calcium ion(Ca²⁺) while the secondary contribution may have come from the dissolution of hydrated calcium sulphate, gypsum (CaSO₄.2H₂O) and calcium magnesium carbonate, dolomite (CaMg(CO₃)₂), which of course may have been the main source of magnesium ion(Mg⁺⁺) in the groundwater system. Below is the reaction leading to the formation of the aforementioned ions:



On the the ground ware chemistry, the dominance of bicarbonate over all other anions indicates the contribution of silicate and carbonate for chemical weathering. Whereas the relatively high value of Cl⁻ is due to the impact of saline water and base ion exchange reaction[32]. The nitrate and sulphate concentration are quite low and well within the[27] permissible limits ((Tables 1&2; Figs 6,7and 8). On whole the major cations chemistry of the groundwater system in the study area based on the mean values is the order of concentrations : Na⁺ > Ca²⁺ > Mg²⁺ > K⁺. , the anion chemistry of groundwater in the area is dominated by hydrogen trioxocarbonate (IV) ions (HCO₃⁻) and Chloride ions (Cl⁻) with the mean concentrations of 20.364mg/L and 17.468vmg/L respectively. While trioxonitrate(v)ions (1.217mg/L) and tetraoxosulphate (Vi) ions (0.0423mg/L) are present as secondary anions. Thus the anions abundance is in the order HCO₃⁻ > Cl⁻ > NO₃⁻ > SO₄²⁻. The presence of the four(4) minor/ rare metals (Cu, Fe, Mn and Zn) based on their in their mean concentrations (mg/L) was in the order Zn> Cu >Fe > Mn (Table 2). While the overall presence of all the cations and anions based on their concentrations in different samples from various location as shown and table 1and demonstrated on figs.7 & 8.

3.2 Hydrochemical Facies of the Water Smaples

The hydrochemical evaluation of the aquifer system is usually based on the ionic constituents, water types, hydrochemical facies and factors controlling groundwater quality. Piper Trilinear Diagram [33] (Fig.3) is used to infer hydrochemical facies which can then be used to classify the groundwater accordingly. The diagram is made up of two triangles, one for cations and the other for anions. The cation and anion field are combined to show a single point in a diamond-shaped field, from which inferences is drawn on the basis of hydrochemical facies concept [34]. To achieve this the concentrations of ions were calculated in milli-equivalent per liter (meq/l) and expressed in percentages based on all the ions present, and the values were used in plotting the trilinear diagram. And from the plot four hydrochemical facies were delineated from the Piper trilinear plot of groundwater samples from the study area (Fig. 3), namely: CaNaHCO₃ (mixed), CaMgCl (mixed), Na(K)Cl and CaHCO₃. CaNaHCO₃ water is the dominant facies which represents water of recharge zone while CaMgCl,

NaCl and CaHCO₃ are the least. The presence of NaHCO₃ CaNaHCO₃, and CaMgCl water type shows hydrochemical processes such as ion exchange. The plot further reveals that the strong acid ions (SO₄²⁻ + Cl-) are in excess of (HCO₃⁻ + CO₃) as in Table 3. This is an indication that the chemistry of groundwater in the area is largely influenced by a number of geochemical processes which include rock-water interaction in the aquifers and the ever-increasing anthropogenic influences in the recharge zone. The Schoeller semi-logarithmic diagram (Fig.4) was also used in tandem with the Piper diagram to further elucidate the ionic character of the groundwater in the area. This tool allowe major cations and anions ions in most samples to be plotted on a single graph and from the plot samples with identical patterns can be quantitatively discriminated. Results based on the Schoeller plots revealed Ca²⁺ as the dominant cation and HCO₃⁻ as the dominant anion. It also reveals that the alkali earth (Ca + Mg) are by far dominant over the alkali (Na + K), while the strong acids (SO₄²⁻ + Cl-) are in excess of (HCO₃⁻ + CO₃) thus confirming the result of the Piper trilinear plot above.

IV. List of Figures and Tables

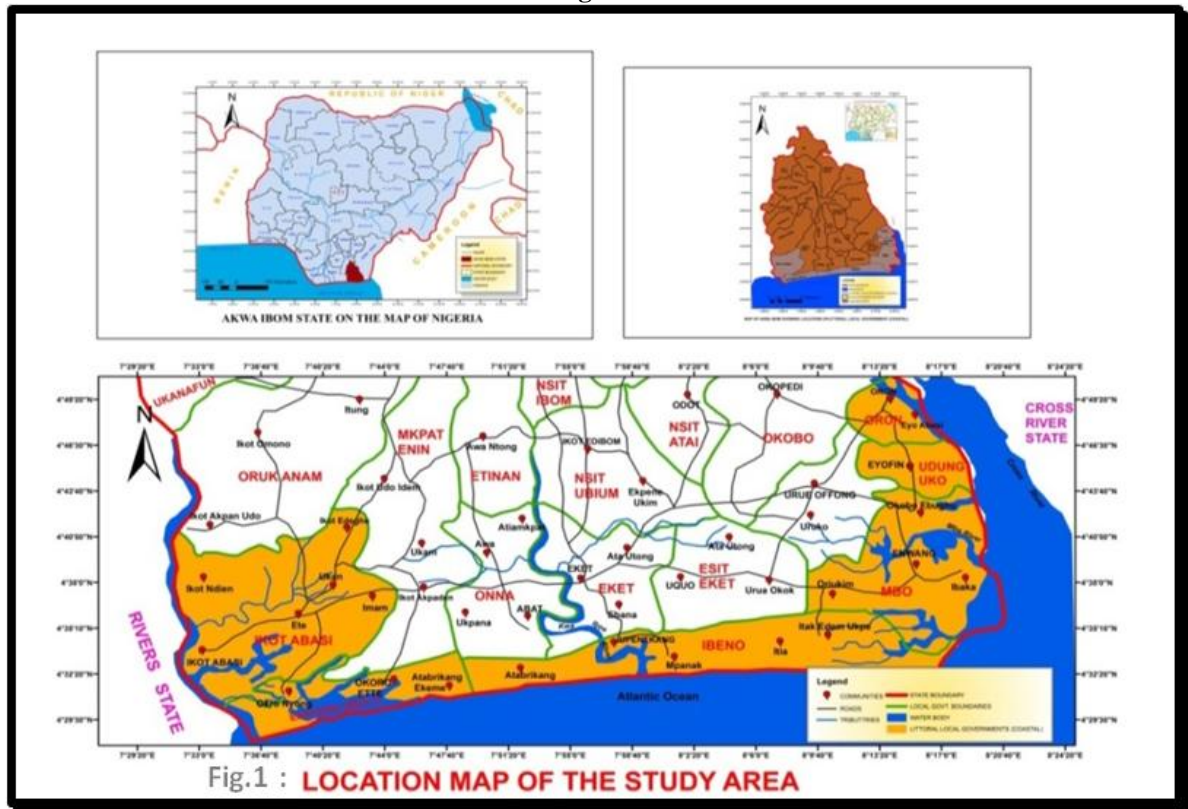


Fig.1 :

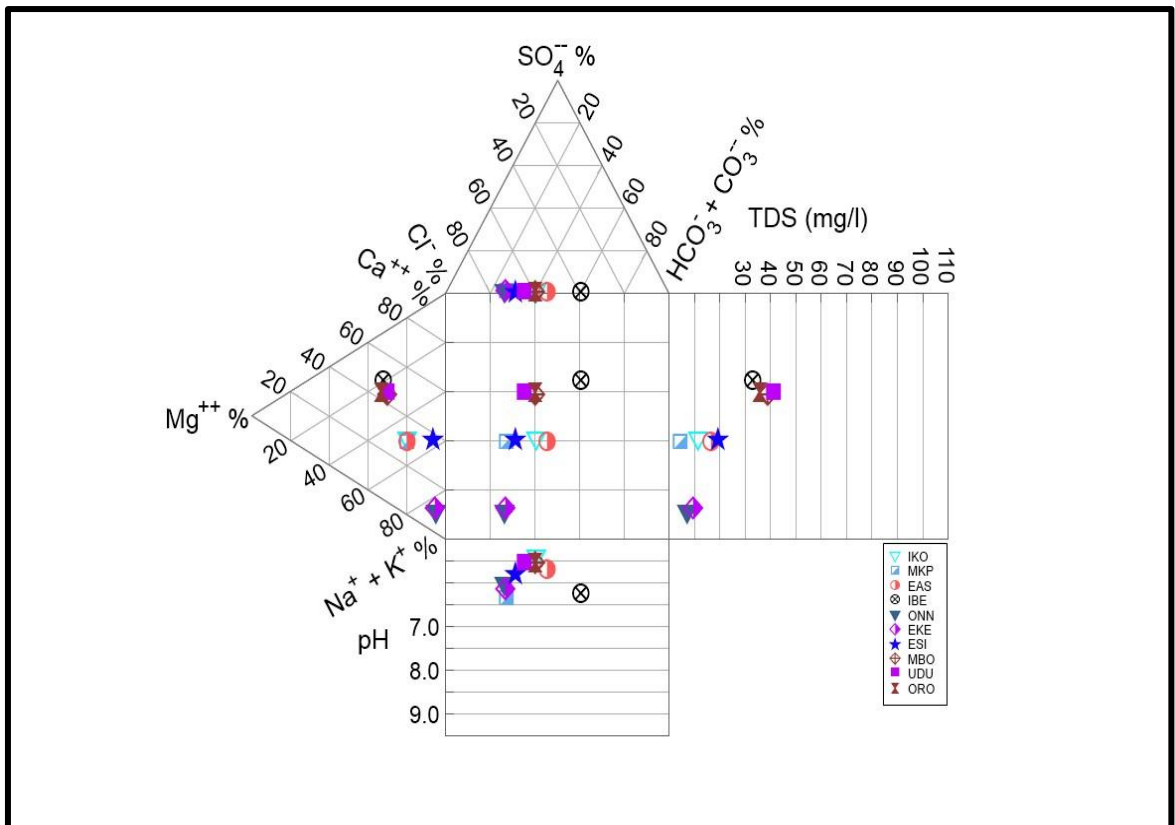
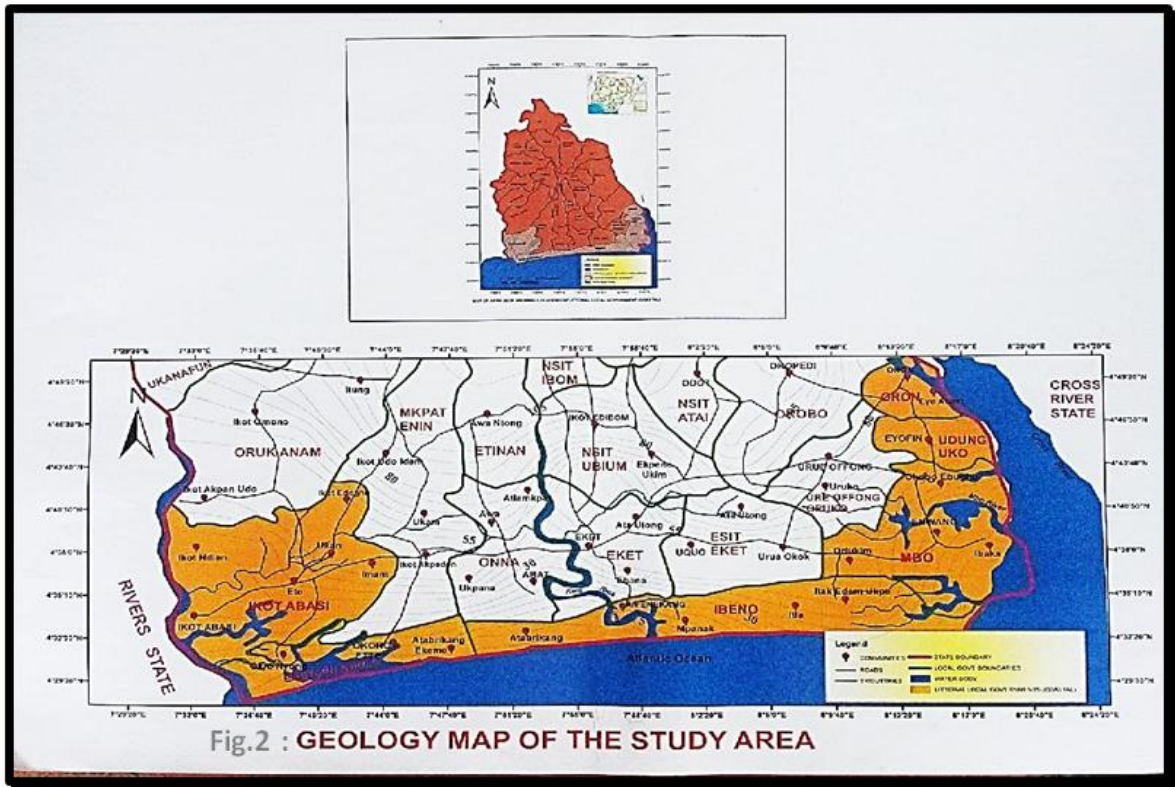


Fig. 3: Durov Plot showing relationship between TDS, pH and Ions

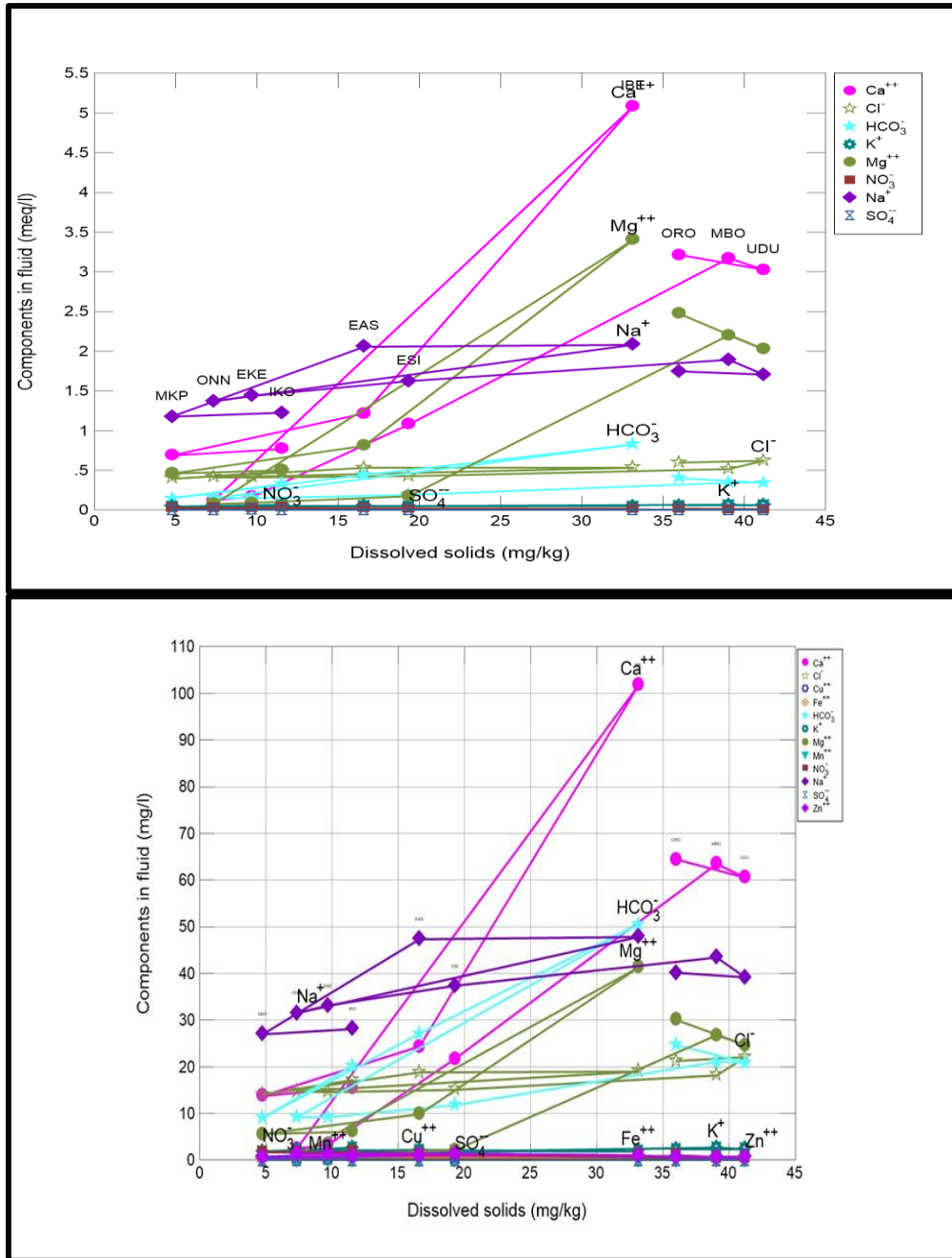


Fig. 4a:(down):Cross Plot for TDS & 4b:(up) for TDS(location specific)

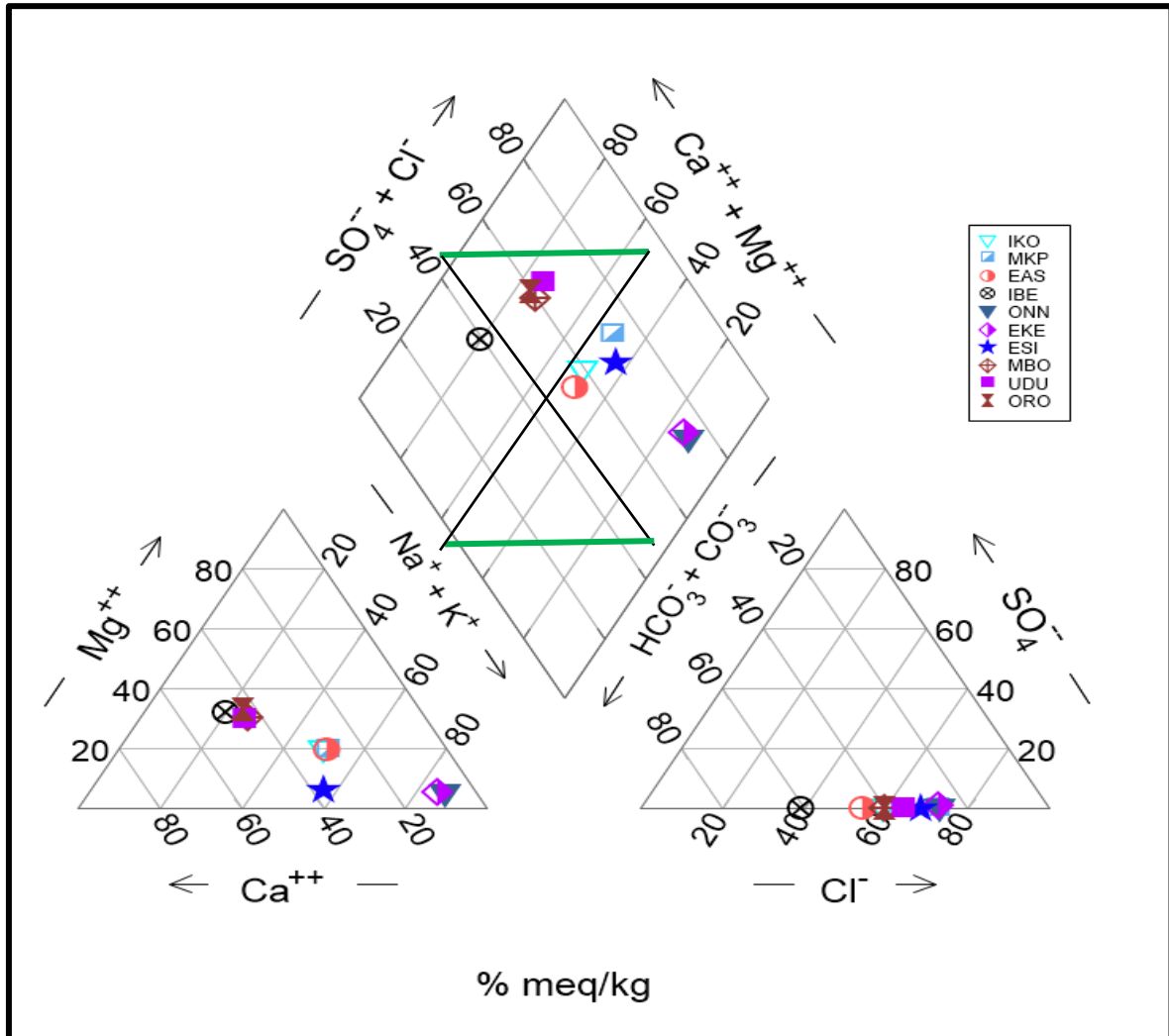


Fig. 5: Trilinear Piper Diagram for the groundwater samples

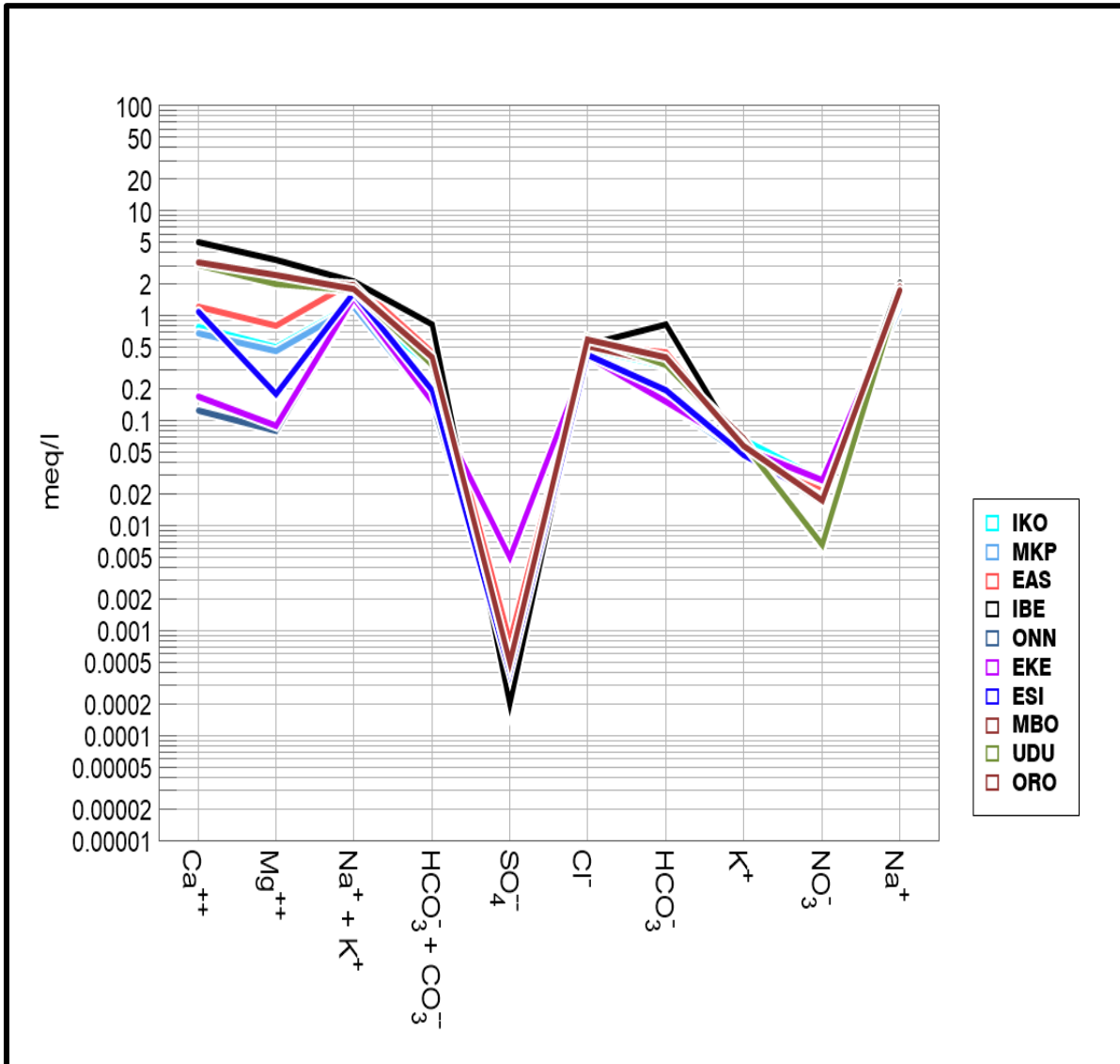


Fig. 6: Schoeller Diagram for common ions in the groundwater samples

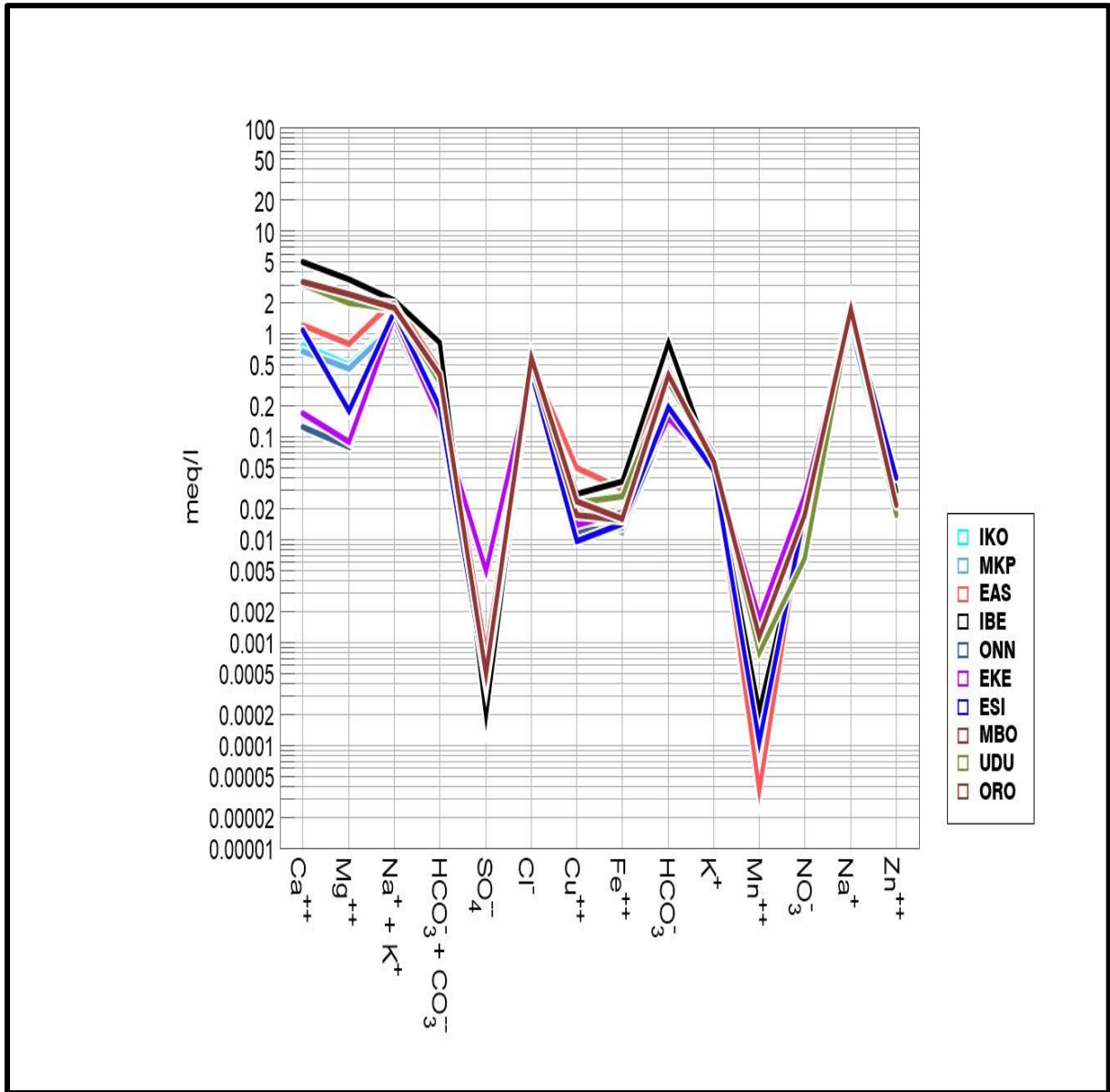


Fig. 7. Schoener Diagram for an ions in the groundwater samples

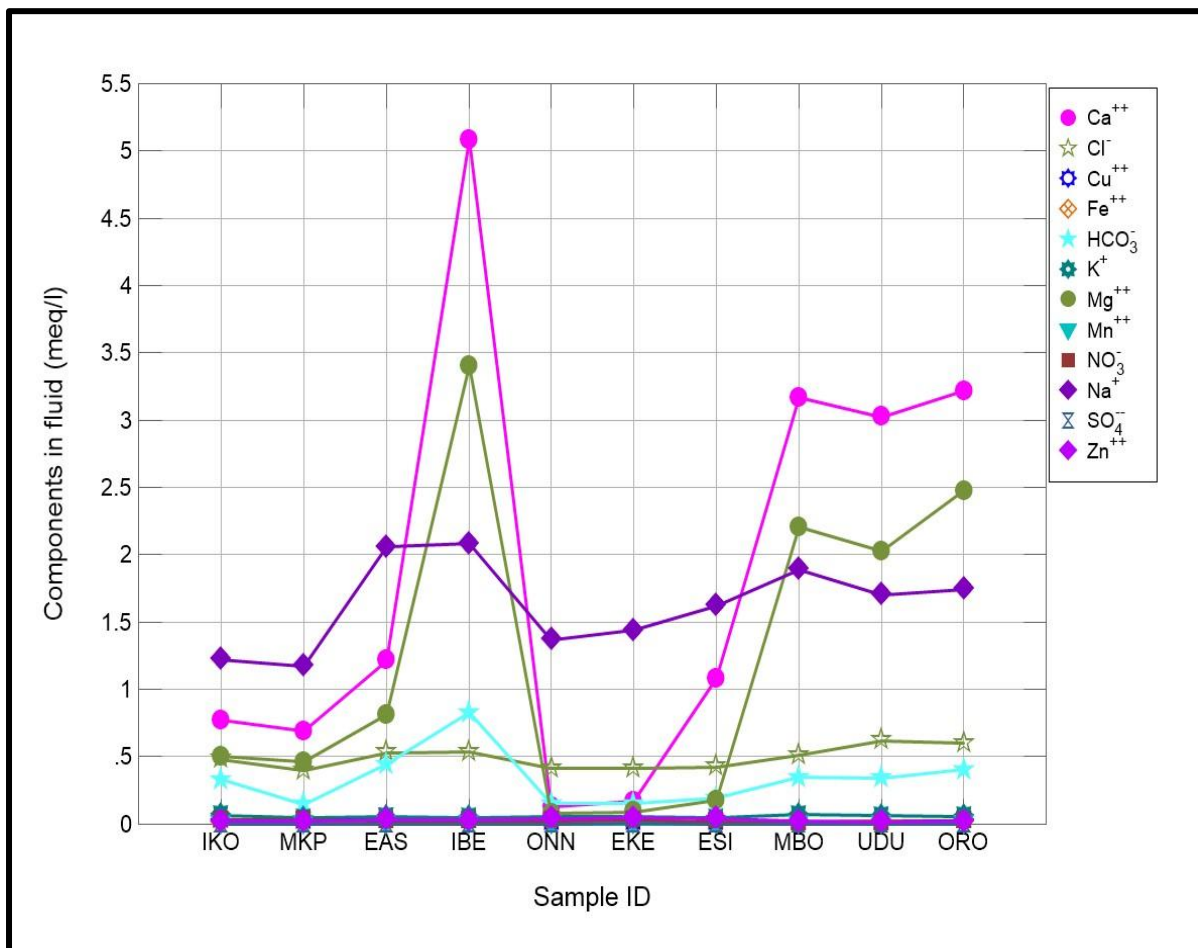


Fig.8: Series Plot showing the concentration of all ions in the groundwater samples

Table 1: Physicochemical Analysis of Groundwater Samples

PARAMETER	IKO	MKP	EAS	IBE	ONN	EKE	ESI	MBO	UDU	ORO	WHO MAL(2004/06)
TEMP.(° C)	26.5	26.6	26.5	26.7	26.7	26.7	26.6	26.5	26.6	26.6	-
pH	5.44	6.40	5.72	6.26	6.06	6.16	5.81	5.56	5.58	5.57	6.5-8.5
EC(µs/cm)	32.13	9.25	33.31	64.92	14.25	41.50	63.30	72.33	81.50	76.05	1000
TDS(mg/L)	11.55	4.77	16.60	33.16	7.35	9.71	19.34	39.05	41.20	36.00	>600
DO(mg/L)	3.71	3.57	3.82	2.77	3.85	3.77	3.70	3.81	3.50	3.45	-
T. ALK. (mg/L)	13	14	44	82	14	16	18	27	26	28	50
T.HARD(mg/L)	28	25	41	167	24	26	33	102	103	110	100-300
HCO ₃ ⁻ (mg/L)	20.17	9.04	27.10	50.51	9.18	9.22	11.80	21.06	20.90	24.66	400
CO ₃ ⁻ (mg/L)	5.16	3.40	9.34	15.33	2.08	3.22	4.30	7.26	7.10	8.76	-
Cl ⁻ (mg/L)	17.11	14.04	18.77	19.01	14.67	14.62	15.11	18.16	22.00	21.19	250
NO ₃ ⁻ (mg/L)	1.71	1.69	1.35	1.05	1.66	1.68	1.15	0.39	0.41	1.08	50
SO ₄ ²⁻ (mg/L)	0.031	0.023	0.004	0.007	0.022	0.24	0.021	0.024	0.025	0.026	250
K ⁺ (m g/L)	2.60	1.83	2.15	1.88	2.04	2.11	1.86	2.65	2.40	2.27	50
Na ⁺ (mg/L)	28.10	26.97	47.33	47.85	31.50	33.08	37.10	43.45	39.17	40.11	200
Ca ²⁺ (mg/L)	15.45	13.81	24.33	101.82	2.50	3.38	21.66	63.50	60.59	64.40	75
Mg ²⁺ (mg/L)	6.10	5.60	9.88	41.36	0.97	1.08	2.15	26.77	24.60	30.06	50
Cu ²⁺ (mg/L)	0.78	0.71	1.58	0.89	0.38	0.44	0.31	0.55	0.72	0.76	2.0
Fe ²⁺ (mg/L)	0.40	0.33	0.86	1.03	0.37	0.51	0.40	0.43	0.74	0.45	0.3
Mn ²⁺ (mg/L)	0.002	0.001	0.001	0.006	0.045	0.048	0.003	ND	0.022	0.031	0.1
Zn ²⁺ (mg/L)	0.721	0.613	1.033	0.955	1.344	1.416	1.311	0.630	0.566	0.710	3.0

Table 2: Statistical Analysis of Values Based on The Parameters Used

PARAMETER	MIN	MAX	MEAN	VARIANCE	SD
TEMP. (°C)	26.50	26.70	26.6	0.006667	0.08165
Ph	5.44	6.40	5.856	0.114716	0.338697
EC (µs/cm)	9.25	81.50	48.854	684.957	26.17168
TDS (mg/L)	4.77	41.20	21.873	198.6338	14.09375
DO(mg/L)	2.77	3.85	3.595	0.103117	0.321118
T. ALK(mg/L)	13.00	82.00	28.2	448.6222	21.1807
T H(mg/L)	24.00	167.00	65.9	2556.1	50.55789
HCO ₃ ⁻ (mg/L)	9.04	50.51	20.364	158.2517	12.57981
CO ₃ ⁻ (mg/L)	2.08	15.33	6.595	15.39221	3.92329
Cl ⁻ (mg/L)	14.04	22.00	17.468	8.035951	2.834775
NO ₃ ⁻ (mg/L)	0.39	1.71	1.217	0.25349	0.503478
SO ₄ ²⁻ (mg/L)	0.004	0.24	0.0423	0.004896	0.069972
K ⁺ (mg/L)	1.83	2.65	2.179	0.088232	0.297039
Na ⁺ (mg/L)	26.97	47.85	38.507	50.77647	7.125761
Ca ²⁺ (mg/L)	2.50	101.82	37.144	1103.278	33.21563
Mg ²⁺ (mg/L)	0.97	41.36	14.857	211.2951	14.53599
Cu(mg/L)	0.31	1.58	0.712	0.129351	0.359654
Fe(mg/L)	0.33	1.03	0.552	0.057151	0.239063
Mn(mg/L)	0.001	0.05	0.018	0.000377	0.019416
Zn(mg/L)	0.57	1.42	0.9299	0.108784	0.329824

Table 3: Distribution of ions on Piper Trilinear Diagram

sSAMPLE CODE	DATA ON CATION ▲ (%)			DATA ON ANION ▲ (%)			DATA OF ALL IONS ON ▼ (%)	
	Ca ⁺⁺	Mg ⁺⁺	Na ⁺ + K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻ +CO ₃ ²⁻	SO ₄ ²⁻ + Cl ⁻	Ca ²⁺ + Mg ²⁺
ESI	36.9	0.04	57.06	68.73	0.06	31.21	68.99	42.04
EKE	0.64	5.08	85.29	72.52	0.88	26.6	39.3	70.93
UDU	44.38	29.71	25.91	64.38	0.05	35.57	64.43	74.09
ORO	42.9	33.03	24.09	59.61	0.05	40.34	59.66	75.03
EAS	29.32	19.63	51.05	54.32	0.08	45.6	54.4	48.95
IBE	47.87	32.07	20.07	39.28	0.01	60.7	39.3	79.93
MBO	43.28	30.05	26.72	X	X	X	59.74	73.28
ONN	X	X	X	X	X	X	73.34	12.57
IKO	X	X	X	X	X	X	59.36	49.69
MKP	X	X	X	X	X	X	72.77	48.53

NB: x- analyte marker superimposed

IV. Conclusion

The results obtained from the physicochemical analysis of the groundwater samples in the littoral communities in Akwa Ibom indicate that groundwater samples in majority of the locations are barely fresh considering the low to moderate mean values of TH, TDS, EC and pH. However, the low of pH in the range of 5.44 to 6.40 falling below the permissible limit for all the samples analyzed depicts unsafe water quality for domestic use. Although low pH according to [35] is one of the attributes typical of tropical regions of torrential rainfalls and abundant flora but the groundwater acidity associated with anthropogenic activities is a matter of urgent concern. The abundant rainfall of about 2000mm experienced yearly in the study area ensures a continu-

ous leaching of sediments thereby reducing its soluble components with time. Beyond this is the significant dilution of groundwater resulting from abundant recharge by precipitation, and rapid circulation of water through the soil due to its high permeability and porosity. This scenario may probably account for the low slute concentration of groundwater in the study area. This concern calls for pH remediation in order to upgrade the water quality in the area to the globally acceptable standard. The major alkali metal chemistry of the groundwater samples in the area is largely in favor of Na against K; while that of the alkaline earth in favor of Ca against Mg. The concentrations of the two group of metals are within the acceptable limits with the exception Calcium with a high value of 101.82mg/L recorded for one of the samples in the core littoral communities. The study further revealed the HCO_3^- as the most dominant ion over Cl^- , NO_3^- and SO_4^{2-} . The entire sequence of the abundance of the major cations and anions in the area follows the trend: $\text{Ca} > \text{Mg} > \text{Na} > \text{K} = \text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$. The concentrations of minor metals detected is in the order: $\text{Zn} > \text{Cu} > \text{Fe} > \text{Mn}$ and all are within the WHO standard (0.3mg/L) with the exception of iron (Fe) for which a high concentration of 1.03mg/L was recorded in one of the core littoral communities. Barring the few cases of anomalies noted above, the groundwater quality in the littoral communities of Akwa Ibom can be considered fairly safe (within the context of the standards set by various health regulatory organizations) for domestic, agricultural, industrial and other water-based applications. However, pH and Fe remediation is strongly recommended in order to improve the water quality in the study area. Also recommended is the need to embark on water quality awareness campaign to enhance the safety standard and the quality of life in the littoral communities of Akwa Ibom State in particular and that of Niger Delta in general.

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