

## Estimation of Bivalent Iron Accumulation and the Associated Geoelectrical Footprints in Selected Transition Aquifers of Bayelsa State-Niger Delta, Southern Nigeria

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### Abstract

The variability inherent in the near surface lithology of the transition zones of the Niger Delta is also known to be associated with local variation of groundwater quality in terms of colour, odour and taste occasioned by the presence of provocative groundwater iron concentrations. Integrated hydrochemical analysis and 2-D resistivity profiling were carried out in selected transition aquifers of the Niger Delta in Bayelsa State. The aim of the study was to attempt an estimation of bivalent iron in the subsurface of the study area by identifying an electrical resistivity value range that can be used as footprints to infer the presence of iron from surface geoelectric survey. It was observed that iron (II) is better represented in the subsurface geoelectrical signature than calcium and chloride radicals, which dominate the groundwater of this locality as revealed by the trilinear plots. In conclusion, a resistivity value less than  $164 \Omega m \pm 5$  has been identified to represent groundwater iron concentration of more than 1 mg/lit in the study area.

**Keywords:** Bivalent Iron accumulation, geoelectrical footprints, hydrochemical analysis, resistivity profiling.

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### I. INTRODUCTION

When we inquire for truth, we either make attempts to match history with present observations or conduct scientific investigations to confirm existing facts. The transition aquifers of the Niger Delta have been known to exhibit what is referred to as lithologic intercalation which may vary even within a locality, this characteristic is also associated with local variation of groundwater quality in terms of colour, odour and taste (Etu-Efeotor and Akpokodje, 1990). In most cases, the variation in colour, odour and taste inherent in these transition aquifers are due to clay embodiments and inclusion of vegetative matter entrapped within clay layers found in the sedimentary succession or clay intercalation associated with the near surface lithostratigraphy of the transition Niger Delta (Rayment, 1965; Kogbe, 1989; Short and Stauble, 1967).

According to Nwankwoala and Ngah (2014), the source of the iron prevalent in the transition zones and coastal bars and beaches of the Niger Delta has not been well established, however they also suggested that it may have been emplaced by iron fixing bacteria associated with sedimentary environments of decaying vegetative matter in agreement with the position of Froelich et al., (1978). Allen(1965a and b) and Oomkens(1974) posited that the Quaternary glaciations was accompanied by eustatic lowering of the sea level such that the paeleo-strand line was at the present edge of the continental shelf, that this geologic event could have exposed the sediments and created paleo-soils rich in iron oxides. The subsequent rise in sea level would have incorporated the paleo-soil into the geologic record. It was noted that the microbial oxidation of organic compounds with the subsequent reduction of Fe (III) is an important process in a variety of subsurface aquifers. Many pristine aquifers have extensive anaerobic zones in which organic matter is oxidized with the reduction of iron (III) which can cause serious water problem. Iron (III) reduction produces iron (II) which oxidizes back to insoluble iron (III) when pumped to the surface (Lovely, 1999). Although most shallow aquifers are aerobic in the pristine state but when contaminated with organic compounds such as petroleum products or landfill leachates, anaerobic plumes can develop Anderson and Lovely (1999). Also, that these zones of iron (III)

reduction are quite extensive in contaminated aquifers and iron (III) reduction is associated with microbial removal of organic contaminants in groundwater.

According to Lovely (1991), Lovely and Blunt-Harris (1999); until this decade it was generally considered that much of the iron (III) reduction that took place in sedimentary environments was the result of abiotic reactions. For instance, it was often stated that the development of a low redox potential as the result of microbial consumption of oxygen and production of reduced metabolite could result in an abiotic conversion of Fe (III) to Fe (II). However direct evaluation of the above hypothesis shows that a low redox potential is not a sufficient condition to bring about Fe (III) reduction, rather; micro organisms which have the capacity to enzymatically reduce Fe (III) to Fe (II) are required. It was observed that the only condition that sustain a significant Fe (III) reduction is when enzymatic activity is maintained in sediments suggesting that Fe (III) reducing bacteria catalyze most of the reduction reactions in sedimentary environment Lovely (1997).

Coates et al., (1995) identified a wide diversity of Fe (III) reducing micro organisms referred to as dissimilatory Fe (III)-reducing microorganisms which fall into different phylogenetic groups e.g. *Geobacter* and *Shewanella* which are the delta and gamma subclass of the proteobacteria respectively, they are often isolated from sedimentary environments including the subsurface. When organic matter undergo oxidation, iron (III) is reduced to iron (II) by accepting electron according to Back and Barnes (1965) and Schwillie (1976). As reported by Hem and Cropper (1959), thermodynamic evidences confirm that iron (II) is the most stable form of iron under anaerobic conditions found in groundwater. The mechanism by which the oxidation of organic matter is coupled to the reduction of iron (III) has not been elucidated, but it has long been suspected that microbial activities are necessary to couple the oxidation of organic matter to the reduction of iron (III) Lovely and Philip (1987). Similar microorganisms as those identified by Coates et al., (1995) might catalyze the reduction of Fe (III) in the ancient sediments of several deep aquifers in the Atlantic coastal plain Lovely et al., (1991). However it has been demonstrated experimentally that there are respiratory Fe (III)-reducing microorganism that can enzymatically couple the complete oxidation of organic compounds to CO<sub>2</sub> with the reduction of iron (III) to iron (II) (Lovely et al., 1991; Lovely and Philip, 1987).

From the forgoing introduction, it could be seen that the accumulation of iron (II) in the subsurface seem more of a natural phenomena that occurred contemporaneously with sedimentation and diagenesis in certain sedimentary environments. In as much as it becomes problematic where concentrations are above acceptable limits, the least that could be done is to look for ways of identifying these zones of high concentration and to possibly avoid such in groundwater exploration and exploitation projects. This study is aimed at using chemical laboratory means to establish the concentrations of iron (II) in selected Niger Delta transition aquifers, and then attempting an ‘imaging’ of the footprints of Known iron (II) ion concentrations in terms of in-situ qualitative and quantitative geoelectrical resistivity evaluation.

### Study Location

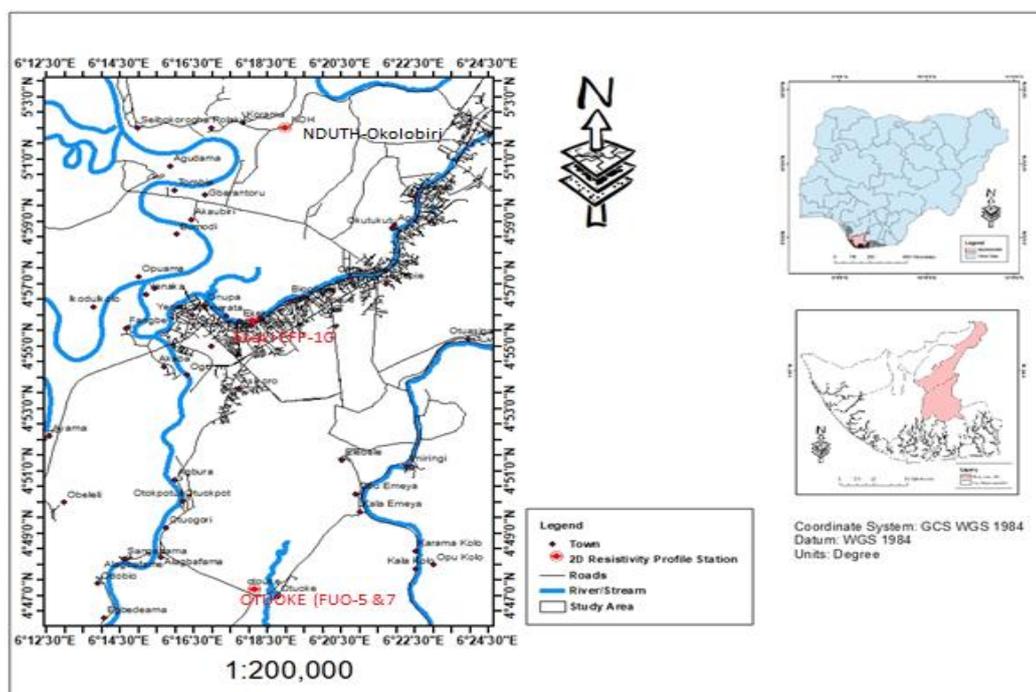


Figure 1: Map Showing Location of the Study Area

## II. METHODOLOGY

Integrated hydrochemical parameter estimation of water samples collected from freshly drilled boreholes and 2-D geoelectrical resistivity profiling of subsurface rocks/fluids was used to characterize iron (II) in groundwater (electrical resistivity footprints) derived from surface based electrical resistivity measurements that carry information about the average concentration of dissolved bivalent iron in the aquifer.

### Physicochemical Analysis: Materials and Method

1. Digital pH meter
2. Conductivity and Salinity meter
3. Total Dissolved Solids (TDS) and turbidity meter
4. UV/VIS spectrometer
5. Atomic Absorption Spectrometer (AAS)

Other apparatus used include; 50 ml Burette, Pipette 10 ml and 25 ml graduated; Beakers (100 ml, 250 ml and 500 ml); volumetric flasks (1000 ml, 500 ml and 100 ml); conical flask 250 ml.

### Chemicals and Reagents

1. Ethylene Diamine Tetra Acetic acid (EDTA); solochrome Black T indicator; ammonia/ammonium chloride buffer pH10; 0.02 mol HCl acid; 1, 10 – phenanthroline 0.1%.
2. Hydroxyl ammonium hydrochloride; 10% solution of sodium acetate; silver nitrate solution
3. Barium chloride solution etc.

While standard laboratory manuals as prescribed by W.H.O is referred for the determination of the physicochemical parameters identified in the present work, a summary of the methods used in the laboratory analysis of minerals or metal ions inclusive of iron (II),  $\text{Fe}^{2+}$  is noteworthy.

### Sample preparation

(a) the method of wet-ashing was employed wherein 100 ml of water sample was placed in a 250 ml conical flask, 25 ml of 2 M  $\text{HNO}_3$  was added to the water sample and mixed properly. This was evaporated to dryness over a six-hole water bath, cooled to room temperature and 25 ml of conc.  $\text{HNO}_3$  added to the residue in the flask, which was heated on a hot plate to near boiling point under controlled temperature until the solution is dry. The above process was repeated until the residue turned white after which distilled water was then added and the residue washed and filtered in a 100 ml volumetric flask and made up to the mark with distilled water.

(b) Determination of metals: sodium (Na) and Potassium (K) were determined by flame photometry while Calcium (Ca), Magnesium (Mg), Iron (Fe) and Manganese (Mn) were determined by AAS at their various wavelengths using Acetylene gas combination.

### 2-D Resistivity Profiling: Material and Method

- Instrument: Pasi Earth Resistivity Meter model 16GL-N
- Survey geometry: Wenner-Schlumberger Array
- Number of Electrodes: 21 electrode system
- Cable wire: four (4) reels
- Laptop computer
- Software: DiproWin

The Pasi Earth Resistivity Meter recorded resistance in ohm ( $\Omega$ ) which is multiplied by a geometric factor (K) computed from the dipole spacing 'a' and 'n' factor to obtain an apparent resistivity value ( $\rho_a$ ) which is the resistivity that would have been obtained with the same electrode spacing if the earth were to be of uniform material. Using the laptop computer, apparent resistivity recordings were then loaded onto a DIPROWin platform where inversion was done to produce the true resistivity structure of the subsurface with respect to depth of investigation.

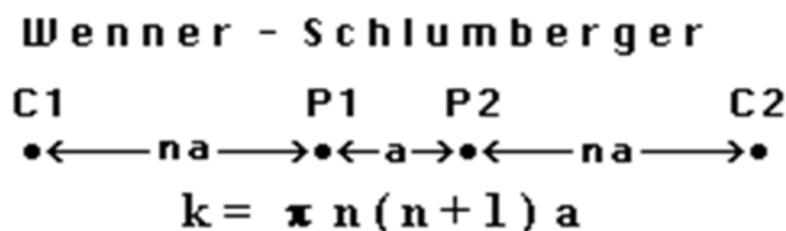


Figure 2: Schematic of the Wenner-Schlumberger Array (Loke, 2004)

The geometric factor K is given as:

$$K = \pi n(n + 1)a \tag{1}$$

Where 'n' is the spacing factor usually multiples of 'a'

### III. RESULTS

Table 1: Physicochemical Parameters of Water Sample

Physicochemical Parameters	FUO-7	FUO-5	NDTH- 1	OPS-9	EFP-10 C1	Eva H <sub>2</sub> O C2	WHO limits
Fe <sup>2+</sup> (mg/lit)	1.55	1.64	1.48	0.12	0.00	0.00	0.3mg/l
Mn <sup>2+</sup> (mg/lit)	0.09	0.12	0.05	0.03	0.00	0.00	0.2mg/l
K <sup>+</sup> (mg/lit)	2.31	2.64	2.80	2.53	2.74	1.58	--
Na <sup>+</sup> (mg/lit)	9.58	10.26	11.21	22.12	11.24	5.56	--
Mg <sup>2+</sup> (mg/lit)	4.62	5.27	5.60	11.00	5.39	2.83	30-50mg/l
Ca <sup>2+</sup> (mg/lit)	15.76	20.53	22.40	44.12	21.56	11.30	75-80mg/l
Cl <sup>-</sup> (mg/lit)	34.00	39.00	43.00	86.00	42.00	22.00	250mg/l
NO <sub>3</sub> <sup>-</sup> (mg/lit)	0.136	0.218	0.308	0.127	0.001	0.001	50mg/l
SO <sub>4</sub> <sup>2-</sup> (mg/lit)	0.546	0.066	0.371	0.738	0.034	0.004	400mg/l
HCO <sub>3</sub> <sup>-</sup> (mg/lit)	1.00	1.17	0.800	1.97	0.90	0.60	--
pH	6.22	6.27	6.67	6.52	6.78	6.40	6.5-8.5

NB. NDTH, FUO and EPF are pseudo names of data points

Table 2: Relationship between Resistivity, Lithology and Physicochemical Parameters

Lithology and Resistivity Match			Concentration of conducting mineral ions (mg/litre)									
Location/ Depth to aquifer	Lithology	Resistivity ρ (Ohm-m)	Fe <sup>2+</sup>	Mn <sup>2+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
NDUTH-1 (9-12) m	Fine- med sand	(64-104)	1.48	0.05	5.60	22.4	11.2	2.80	43.0	0.31	0.80	0.37
FUO-5 (10-12) m	Fine-med sand	(116-164)	1.64	0.12	5.27	20.5	10.3	2.64	39.0	0.22	1.17	0.07
FUO-7 (10-15) m	Fine sand	(76-119)	1.55	0.09	4.62	15.8	9.58	2.31	34.0	0.14	1.00	0.55
OPS-9 (7-10) m	Medium sand	(230-292)	0.12	0.03	11.0	44.1	22.1	2.53	86.0	0.13	1.97	0.74
EFP-10 (5-10) m	Medium-coarse sand	(273-377)	0.00	0.00	5.39	21.6	11.2	2.74	42.2	.001	0.90	.034

Table 3: Mean and Standard Deviation of Major Mineral Components of Borehole Water Samples

Data point	Manganese (Mg/lit)	Magnesium (Mg/lit)	Calcium (Mg/lit)	Sodium (mg/lit)	Potassium (mg/lit)	Chloride (mg/lit)	Nitrate (mg/lit)	Bicarbonate (mg/lit)	Sulphate (mg/lit)
NDUT-1	0.05	5.6	22.4	11.21	2.8	43	0.308	0.8	0.37
FUO-5	0.12	5.27	20.53	10.26	2.64	39	0.218	1.17	0.066
FUO-7	0.09	4.62	15.76	9.58	2.31	34	0.136	1	0.546
EFP-10	0	5.39	21.56	11.24	2.74	42	0.001	0.9	0.034
Mean	0.065	5.22	20.05	10.57	2.62	39.5	0.166	0.97	0.25
SD	0.004	0.22	2.59	0.69	0.19	3.5	0.24	0.14	0.21

Piper Diagram of Borehole Water Samples

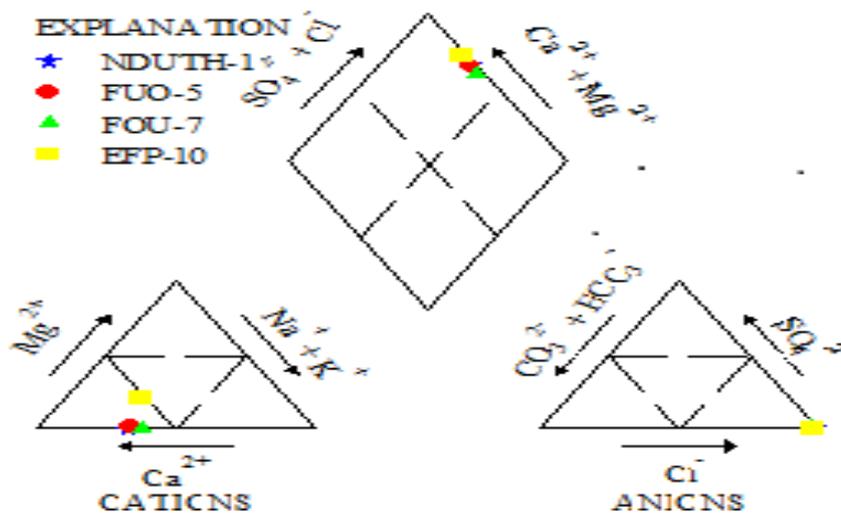
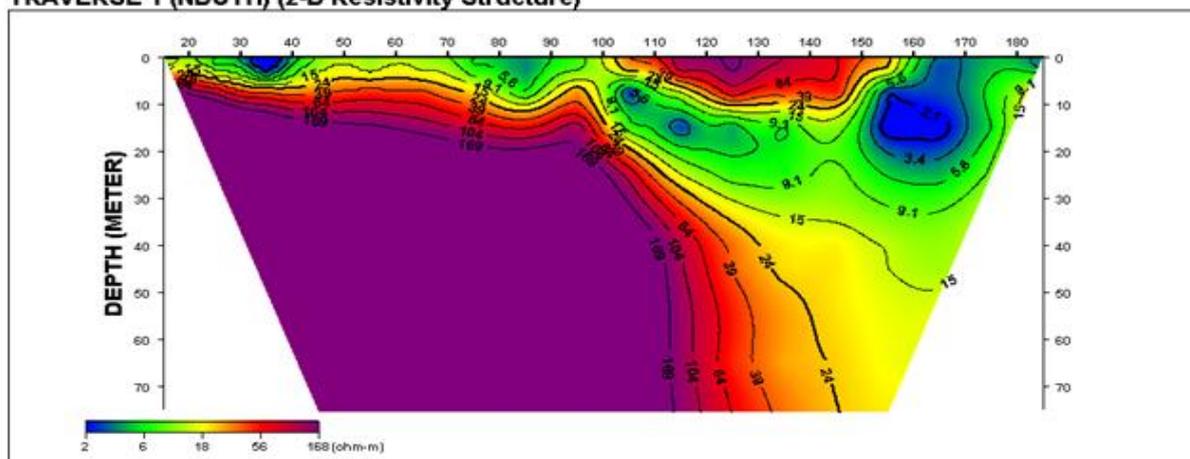


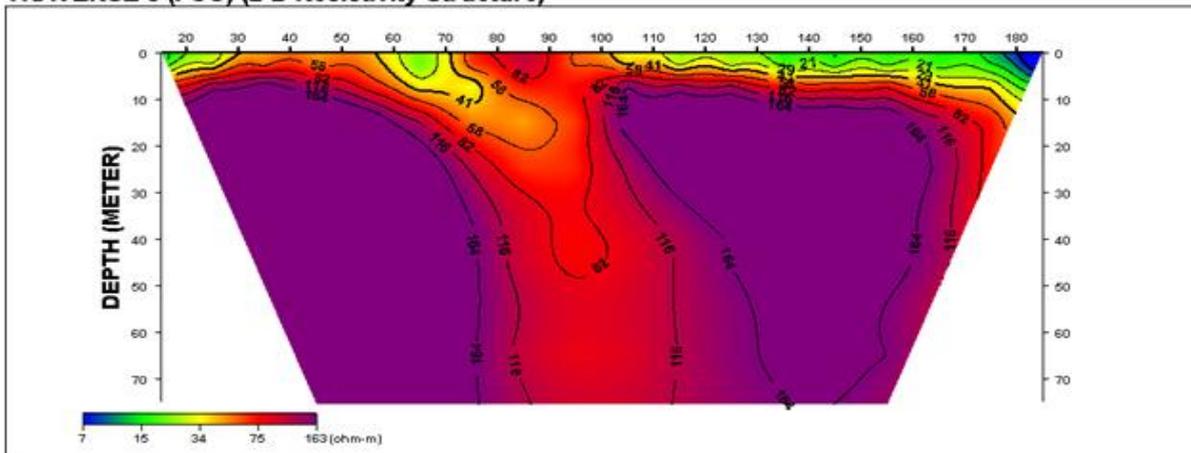
Figure 3: Trilinear Plot Showing Hydrochemical Facies of the Study Area (Piper, 1994).

TRAVERSE 1 (NDUTH) (2-D Resistivity Structure)



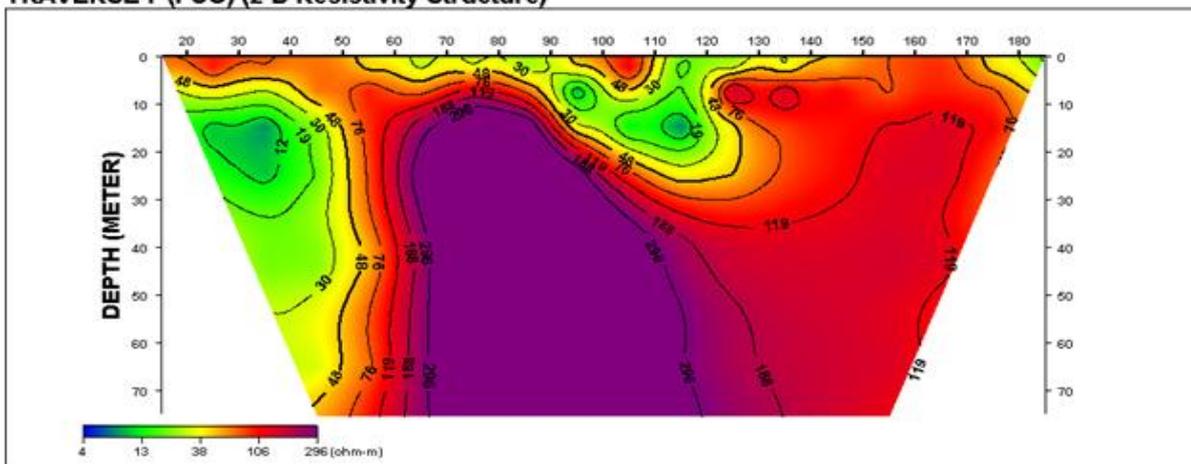
(a)

TRAVERSE 5 (FUO) (2-D Resistivity Structure)



(b)

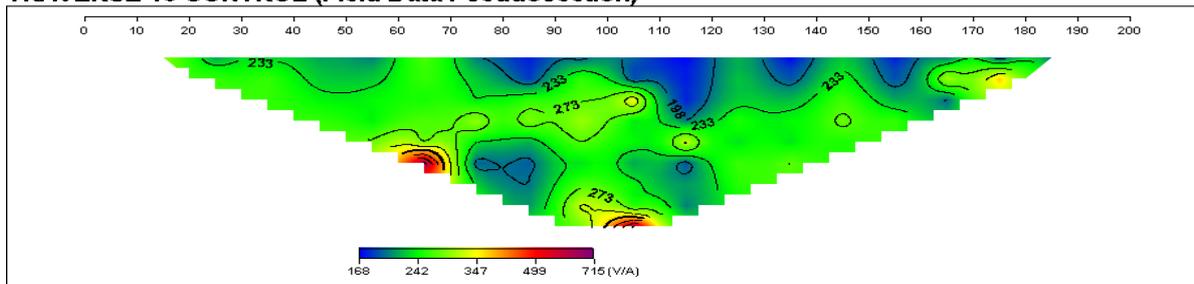
TRAVERSE 7 (FUO) (2-D Resistivity Structure)



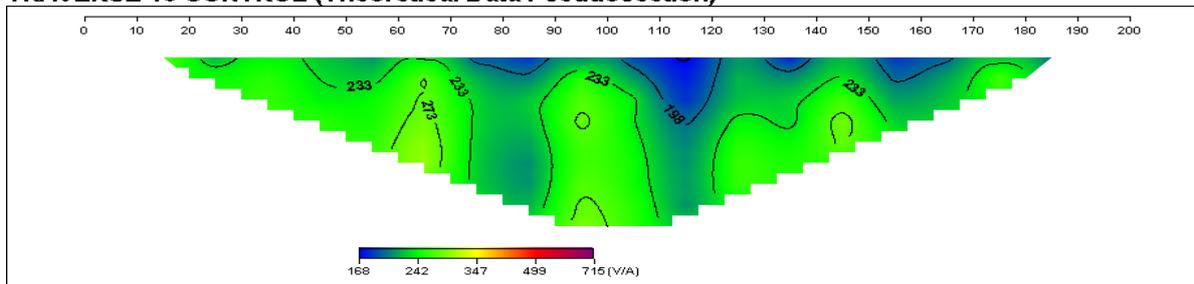
(c)

Figure 2: 2-D Resistivity Profiles of the Study Area.

TRAVERSE 10 CONTROL (Field Data Pseudosection)



TRAVERSE 10 CONTROL (Theoretical Data Pseudosection)



TRAVERSE 10 CONTROL (2-D Resistivity Structure)

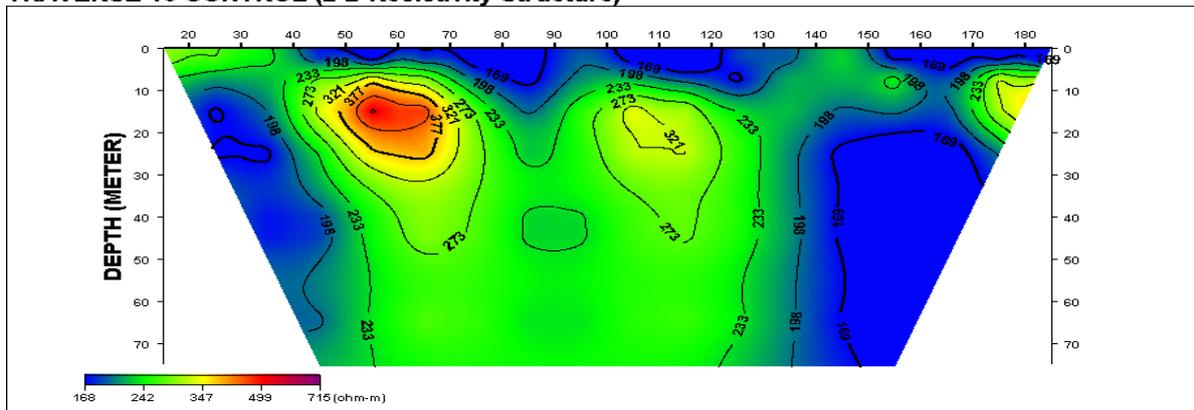


Figure 3: Resistivity Profile EFP-10 (Control)

IV. DISCUSSIONS

Table 1 shows the physicochemical parameters of water samples with WHO limits. Major cations captured are Iron ( $Fe^{2+}$ ), manganese ( $Mn^{2+}$ ), potassium ( $K^+$ ), sodium ( $Na^+$ ), magnesium ( $Mg^{2+}$ ) and calcium ( $Ca^{2+}$ ), while the anions are chloride ( $Cl^-$ ), nitrate ( $NO_3^-$ ), sulphate ( $SO_4^{2-}$ ) and bicarbonate ( $HCO_3^-$ ). The concentration of iron ( $Fe^{2+}$ ) varies from a maximum of 1.64 mg/lit at FUU-5, 1.55 mg/lit at FUU-7, 1.48 mg/lit at NDUTH to 0.00 mg/lit at EFP-10 (control). Manganese ( $Mn^{2+}$ ) also followed the same trend recording a maximum of 0.12 mg/lit at FUU-5 and 0.00 mg/lit at EFP-10. The highest concentrations of potassium ( $K^+$ ) were recorded at NDUTH-1 and EFP-10 with values 2.80mg/lit and 2.74 mg/lit respectively, while sodium ( $Na^+$ ) and magnesium ( $Mg^{2+}$ ) had their highest at OPS-9 with concentrations 22.12 mg/lit and 11.00 mg/lit respectively. Calcium ( $Ca^{2+}$ ) also recorded its highest at OPS-9 with a value of 44.12 mg/lit while chloride ( $Cl^-$ ) had a concentration of 86 mg/lit. Nitrate ( $NO_3^-$ ), sulphate ( $SO_4^{2-}$ ) and bicarbonate ( $HCO_3^-$ ) had their maximum concentrations at NDUTH-1, OPS-9 and EPF-10 with concentrations of 0.308 mg/lit, 0.738 mg/lit and 0.90 mg/lit respectively.

Table 2 shows the link between hydrochemical parameter and subsurface resistivity of the horizon of interest, it calibrated the aquiferous zone with observed/estimated electrical resistivity and hydrochemical parameters. At NDUTH-1, it could be seen that a depth range of 9-12 m with lithology of fine – medium sand was associated with a resistivity range of 64 – 104  $\Omega m$ , while iron ( $Fe^{2+}$ ) concentration averaged 1.48 mg/lit. While groundwater iron concentration of 1.55 mg/lit corresponded to a resistivity of 76 – 119 $\Omega m$  at FUU-7. Also, a resistivity range of 273 – 377  $\Omega m$  was recorded against a lithology of medium – coarse sand at depth of 5 – 10 m corresponds to a 0.00 mg/lit iron ( $Fe^{2+}$ ) concentration at EFP-10 which served as control. The Piper diagram indicated that groundwater in the study area is of the calcium chloride type, and the concentrations of all

other major anions and cations tend to cluster around common value ranges as seen from the dispersion analysis (table 3). For instance, the concentration of magnesium in all four boreholes, cluster within the range 4.6 – 5.6 mg/lit, the same observation holds good for all the major ions in all three locations aside sodium and chloride ions. A computation of their Standard Deviation (SD) across the four data points (table 3) showed small Standard Deviation (SD) values in comparison with their statistical means. It could be inferred that the data are less dispersed or tend to cluster about their mean values which makes it logical to assume that the contribution to electrolytic conductivity within the aquifers of the study area due to variation in the concentrations of major hydrochemical ions according to Piper (1994) may not have played significant role in the localized variation of electrical resistivity recorded by the 2-D electrical survey. Rather, the two observable high concentrations of iron (II) at the Niger Delta University Teaching Hospital (NDUTH) and the Federal University Otuoke (FUO) seem to have been represented in the subsurface geoelectrical signature as an increase in electrical conductivity. It could be seen that the concentration of iron presents a bolder image (footprint) when viewed with the lens of electrical resistivity wherever it occurs in excess of 1 mg/lit in the subsurface of the study area.

## V. CONCLUSION

It was concluded that within the limits of this study, geoelectrical resistivity values less than one hundred and sixty four ( $164\Omega\text{m} \pm 5$ ) corresponding to a subsurface region interpreted to be sandstone is most likely to have groundwater with bivalent iron concentration greater than 1mg/lit in the study area.

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