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Assessment of heavy metal contamination in groundwater of Agbor, Ika south l. G. A., delta state, Nigeria

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Heavy Metal Contamination of groundwater is an issue of deep concern worldwide and as such the degree to which these metals have contaminated the most valuable fresh water resource "GROUNDWATER" must be summarily understood. 10 Borehole water samples were taken from various parts of Agbor and analysis were carried out for the major anions and cations with Arsenic been the heavy metal of interest. Upon comparison with NIS and WHO standards for drinking water, the results shows that though they were measurable concentration of Arsenic in three locations but they were high enough to pose threat to human health. Nonetheless, the results were subjected to Statistical Analysis using Principal component Analysis (PCA) to standardized data sets. The results gotten was tied to graphical methods, Stiff plot and Piper diagram to obtain the water type as Ca2+-Mg2+-Cl- -SO42- and revealed the dominant ions. PCA revealed that five components control the hydrochemistry of the study area.Ammonium,Nitrate,Phosphate and TDS dominated component 1 which accounted for 41.1%,Chloride, sulphate and EC are parameters in component 2, component 3 hasCalcium, Magnesium and Bicarbonates, component 4 isdominated bypH and component 5 holds potassium and sodium accountable for hydrochemical variation. United States Environmental Protection Agency (US EPA 2012) and EU 1998 Standards were compared with parameters to ascertain the quality of the water for domestic use. pH had a value less than 6.5 for most of the sampled locations and these were out of range of US United States Environmentaal Protection Agency (EPA) and European Union Drinking Water Directives(EU DWD) standards

Keywords: Heavy Metal Contamination, groundwater, Nigeria, Delta state

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Introduction

Groundwater is fresh water that is accumulated in porous and permeable materials of the earth called Aquifer. It is not usually static but flows through the interconnected pores within the rock. This water forms part of the natural water cycle present in aquifers. The ease with which water can flow through a rock mass depends on a combination of the size of the pores and the degree to which they are inter-connected. Also, the degree of cementation of the host rock, through which groundwater is described as the main source of portable water supply for domestic, industrial and agricultural uses in the southern part of Nigeria, especially the Niger Delta, due to long retention time and natural filtration capacity of aquifers. The groundwater quality in the region is variable, depending on the types of aquifer (confined, unconfined, perched or leaky aquifer) and varied aquifer characteristics. It is of vital importance to maintain the appropriate level of quantity and quality of discharging groundwater as this has a significant impact on surface-water quality.

The W.H.O (World Health Organization), S.O.N (Standard Organization of Nigeria), F.M.E (Federal Ministry of Environment) and E.P.A (Environmental Protection Agency) set a maximum contaminant level in drinking water supplied to municipal or population. When a standard or guideline is exceeded in the municipal or community water system, the state is required to take proper action to improve water quality level including treating the water through filtration or aeration**,** blending water from several sources to reduce contaminants including inorganic chemicals such as salts, metals and mineral. These substances may occur naturally in geological structures or sometimes caused by mining, industrial and agricultural activities. When these chemicals are consumed in large amounts by human, they affect human health such as brain damage or the reduction of mental processes (GAZA *et al*., 2005) and central nervous function (BOUCHARD *et al*., 2011), Interestingly, small amounts of chemical elements (heavy metals) are common in our environment and diet, even some of them are necessary for good health, for example, living organisms require varying amounts of heavy metals such as iron, cobalt, copper, manganese, molybdenum and zinc, which are required by humans too. There are two main sources of water supply that are available to man, surface water that includes: rivers, lakes, stream, drainage areas which funnels water toward the

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holding reservoirs and subsurface or ground water which includes wells, springs and horizontal galleries.

Delta state forms a large part of the Niger-Delta estuary and the largest oil producing state in Nigeria. Consequently, the state is exposed to a large proportion of the environmental degradation and health hazards associated with exploration and exploitation of crude oil. Also road ways, location of dumpsites and automobiles now are considered to be one of the largest sources of heavy metals (ABDULLAH KANDY ROOTLE, 1972). The frequency of oil spill and untreated waste water discharge into water Bodies and the attendant negative impact on the aquatic and terrestrial ecosystem is well known and well documented over the years (NDUKA & ORISAKWE, 2009). Heavy metals enter into the environment mainly via three routes namely:

(i) Deposition of atmospheric particulate;
(ii) Disposal of metal from enriched sewage sludge, sewage effluents and solid wastes
(iii) By-products from metal mining process.

Aim of the study

The aim of this study is to assess the presence of heavy metals in the groundwater of Agbor – a town in Delta State, and attempt to determine their origin.

Location and Accessibility

Agbor is located in Southwestern Nigeria within latitudes 6°07' and 6°20'N, and longitudes 6°05' and 6°20'E, and covers an area of about 650 km² (Fig. 1). Agbor is located in Ika South Local Government Area of Delta state. It has a population in excess of 240,000, crowded and highly competitive if not more homogeneous than any other community in the region. From the shanty towns to throngs of men in vehicle on the narrow roads where multitude of well attired local shoppings at domestic markets, boutiques and stores are found.

Methodology

Sampling and Location Samples were collected from Boreholes in the study Area. Hand dug wells were not seen in the study Area because of the terrain and topography of the Area. Thus it would have been better to establish a relationship between the two water sources in terms of heavy metal contamination. 1 Litre opaque screw cap plastic bottles were used, washed thoroughly as a precaution prior to usage using mild detergent and then rewashed with the sample water before sample collection filled to the brim, tightly covered to retain the water parameters that was present in the water when the sample was taken and to avoid contamination.

Samples were then appropriately labelled with their GPS coordinates of the location from which they were collected, elevation, time of sample collection, ground elevation and location or land mark present in the area. BH was added as a suffix for samples collected from boreholes thus BH 1–10 was used for the borehole samples. Collected samples were then

Table 1: table showing sample location and their coordinates

S/N	Locations	Latitude	Longitude	Elevation
1	Yoruba Street	06^0 15’ 11.6” N	006^0 11’ 24.6” E	153m
2	Nzugbe Street	06^0 14’ 58.1” N	006^0 11’ 20.2” E	150m
3	Oshell by Okoli Street	06^0 14’ 46.09” N	006^0 12’ 20.37” E	152m
4	Obiagbena Street	06^0 14’ 50.1” N	006^0 12’ 22.25” E	152m
5	Owanta Street	06^0 15’ 4.27” N	006^0 12’ 50.02” E	151m
6	Along Obi – Ikechukwu	06^0 15’ 20.06” N	006^0 10’ 52.42” E	148m
7	Imidia by Charles Street	06^0 15’ 18.37” N	006^0 11’ 23.92” E	151m
8	Queens Street5	06^0 15’ 30.72” N	006^0 11’ 32.75” E	152m
9	Down Queens Street	06^0 15’ 21.43” N	006^0 11’ 22.6” E	155m
10	Okoh Street	06^0 15’ 21.9” N	006^0 11’ 24.4” E	155m

Table 2 Laboratory Results For Groundwater Analysis

BH	Ph	TDS	EC	Cl	HCO$_3$	PO$_4$	SO$_4$
L1	4.56	15	31	24.7	0.07	0.3	4.9
L2	4.65	108	219	21.73	0.08	0.28	4.87
L3	4.7	6	12	23.53	0.09	0.25	3
L4	4.72	9	21	20	0.092	0.17	3.36
L5	4.78	15	30	4.25	0.097	0.1	1.36
L6	4.08	109	219	23.4	0.026	0.31	3.12
L7	4	8	17	21.5	0.01	0.41	3.5
L8	4.35	50	100	16.11	0.05	0.19	2.44
L9	4.14	14	28	20	0.02	0.25	2.31
L10	4.39	32	65	10.82	0.05	0.14	1.61
Min.	4	6	12	4.25	0.01	0.1	1.36
Max.	4.78	109	219	24.7	0.097	0.41	4.9
Mean	4.437	36.6	74.2	18.604	0.0585	0.24	3.047
Median	4.475	15	30.5	20.75	0.06	0.25	3.06
S.D.	0.287481	40.1392	80.69807	6.492155	0.032018	0.092014	1.196765
Skewness	-0.36932	1.376716	1.386062	-1.48616	-0.29336	0.236397	0.336461

stored in coolers and transported to the laboratory within the specified retention time of 4hrs for further analysis. Sampling was done in good weather condition to avoid rainwater contamination, as this could affect the quality of the samples collected.

Table 2: Laboratory Results For Groundwater Analysis (Continued)

NO_3	NH_4	Ca	Mg	Na	K	Ar
0.99	0.15	8.5	3.45	2.2	0.8	0.01
0.92	0.12	8.43	3.04	2.15	0.73	0.03
0.85	0.09	6.4	3.1	2.09	0.53	0.01
0.76	0.03	4	2.15	1.2	0.18	0.02
0.64	0.01	3.64	1.52	1.26	0.23	0.01
0.95	0.15	9.86	3.11	2.18	0.79	0.01
0.8	0.11	8.5	3	2.11	0.8	0.03
0.89	0.08	5.26	2.29	1.76	0.48	0.01
0.9	0.1	6.5	2.5	2.11	0.85	0.03
0.77	0.04	4.12	1.63	1.42	0.36	0.03
0.64	0.01	3.64	1.52	1.2	0.18	0.01
0.99	0.15	9.86	3.45	2.2	0.85	0.03
0.847	0.088	6.521	2.579	1.848	0.575	0.019
0.87	0.095	6.45	2.75	2.1	0.63	0.015
0.105	0.048	2.227	0.666	0.405	0.253	0.009
204	488	397	474	211	739	944
-0.650	-0.31	0.049	-0.47	-0.82	-0.47	0.23

The sampling was done between the 19th of May through 20th of May 2017 using a Global Positioning System (GPS) Garmin 76 for taking coordinates and elevation readings at locations where samples were collected and a digital map for reference. Random sampling technique was employed in the selection of sampling points. The table below is a summary of sample location and their coordinates.

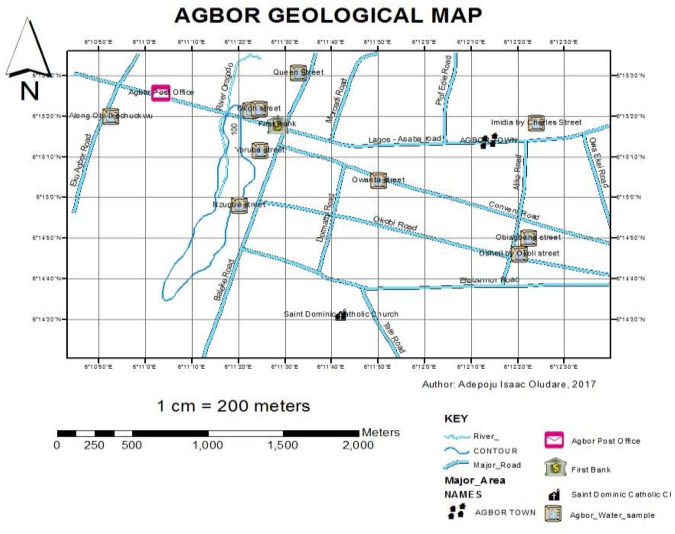

Figure 1: Map showing Sample Points and Prominent Towns in the Study Area

PH

The samples collected were measured for pH value in the field, using a pH meter (Model Ecosense). Each sample was placed in a plastic beaker, the electrode end of the meter was then rinsed with distilled water followed by the sample and inserted into the sample in the beaker. The READ button on the pH meter was pressed and the pH value at a stable pH reading was recorded. The process was then repeated and the average of the two reading obtained was recorded.

Conductivity

Electrical conductivity (EC) for the water samples were measured using an Electrical Conductivity Meter (HANNA HI 991301). The EC meter electrode was rinse with distilled water and the sample, the sample was poured into a plastic beaker. The electrode end of the meter was then inserted in the sample. The READ button on the meter was pressed and the EC value at stable meter reading was recorded.

Temperature

The temperature of samples was measure with the aid of Mercury-in-glass thermometer calibrated in degrees centigrade. The thermometer was rinsed with distilled water and then sample after which it was immersed in a plastic beaker filled with the water sample.

The thermometer was then left in the beaker for a few seconds after which the stable temperature value on the thermometer was recorded.

Methods of Field Measurement

Laboratory Analysis

S/N	Location	Tem (°C)	pH	TDS (Mg/l)	EC (µs/cm)
1	Yoruba Street	28.0	4.5	15.00	31.00
2	Nzugbe Street	28.9	4.6	108.0	219.00
3	Oshell by Okoli Street	29.6	4.7	6.00	12.00
4	Obiagbena Str	28.8	4.7	9.00	21.00
5	Owanta Street	28.8	4.7	15.00	30.00
6	Obi-Ikechukwu Str	29.5	4.0	109.00	219.00
7	Imidia Street	29.1	4.0	8.00	17.00
8	Queens Street	31.6	4.3	50.00	100.00
9	Down Queens Street	29.5	4.1	14.00	28.00
10	Okoh Street	31.1	4.3	32.00	65.00

The analytical methods used in the determination of the Heavy Metals Concentration in water are in accordance with the American Standard for Testing Materials (ASTM, 1962) and American Public Health Association (APHA, 1992)

Standard procedures. The collected water samples were preserved with Conc. HNO_3 upon arrival at the laboratory and refrigerated to 4.0°C pending analysis. Prior to this the Total Dissolved Solid measurement was performed on the water samples as prescribed by the American Public Health Association Standard Procedures.

Heavy Metals For assessment of contamination, the method of Arnold (6) was used in which heavy metals extracted by molar nitric acid is assumed to represent the amount that has been acquired through contamination.

The heavy metals of interest are Arsenic and it was determined in water samples and blanks with a Computerized Varian 220 Flame Atomic Absorption Spectrophotometer according to predetermined specifications at TUDAKA Laboratories, Jakpa Road, Warri Delta State, Nigeria.

Single elemental working standard solutions were prepared by dilution of 1000mg/l stock solutions of the element, As.The solutions ranged between 0.1mg/l to 10.0mg/l

External calibration was used by running deionised water and a suite of calibration standards for the metal. The extracted solutions and blanks were then run on the Atomic Absorption Spectrometer to obtain the absorbance values. Concentrations of the metal in the water sample were then calculated from the equations of the calibration curve.

Sample Preparation 5 mL of Conc. HNO_3 was added to 100 mL of well-mixed water sample in 125mL conical flask. The solution was then evaporated to near dryness of about 20ml on hot plate while ensuring that the sample did not boil by using low to medium heat. The content of the beaker was then allowed to cool. Another 5.0ml of conc. HNO_3 was added to the content of the beaker and the beaker was immediately covered with a watch glass.

The beaker was then returned to the hot plate and a gentle flux action of the solution was set by increasing the temperature of the hot plate (medium to high). This heating was continued with regular addition of HNO_3 as necessitated until a light colour residue was obtained which indicated that digestion was complete. Additional 10mL Conc. HNO_3 was added to the residue and washed with distilled water and filtered into a volumetric flask to remove silica and other insoluble residue. The mark was then made up to 100 mL with distilled water and the solution was stored in a 125ml polypropylene bottle.

Phosphate Ion Determination of Phosphate (P) was in accordance with the American Public Health Association (APHA) 425C. 5ml of Antimony Molybdate solution was added to 40ml of Sample and 2ml of Ascorbic acid was added. The blank solution was to the same treatment as the sample. After about 10-20 minutes the absorbance of both sample and blank solution was measured with UV – visible spectrophotometer at a wavelength of 680nm.

Chloride Ion The salinity and chloride in water was determined in accordance with the American Petroleum Institute (API-RP) 45. 100ml of sample was measure and put in a 250ml conical flask. A 1ml of k_2CrO_4 was added and titrated with 0.014N $AgNO_3$. The end point for was marked by a colour change from yellow to reddish brown.

The formula for chloride calculation is:

$$\text{Mg/L } (Cl^-) = \frac{35.5 \times Cb \times Vb}{\text{ml of sample}} \times \frac{1000}{1}$$

Where:

Cb = Concentration of $AgNO_3$ (Normality)

Vb = Volume of $AgNO_3$ (Consumed)

Nitrate Ion Nitrate in water was determined in accordance with the American Society for Testing and Materials. A number of reaction tubes in a wire rack containing 10ml of sample were set up, with blank and standard solution prepared from sodium nitrate, spacing them so that empty space surrounds each tube. The rack was set in a cool water bath, 2ml NaCl solution prepared from (300g of NaCl crystals in distilled water) was added to the sample, standard and blank solution. The set up was mixed thoroughly by swirling and then 10ml H_2SO_4 prepared from (500ml of conc.H_2SO_4 to 125ml distilled water) to each of the solution. The setup was again swirl and mixed thoroughly and allow to cool. The rack of tube were replaced to mix thoroughly and placed in a well stirred boiling water bath, that maintain a temperature of not less than 95°C and left there for 20minutes. The samples were then removed and immerse in a cool water bath. When thermal equilibrium was attained, the tubes were removed and dried with tissue paper. The standard and sample against the reagent blank at 410nm in the spectrometer was read.

Sulphate Ion The sulphate ion in water was determined in accordance with the American Public Health Association (APHA) 427C. A 70ml quantitative measure of each standard solution was added to the volumetric flask, 10ml of NaCl-HCl was then added and the content of the flask was shaken. A 10ml of Alcohol-Glycerol mixture was added and the content shaken again. 5.0g of finely divided $BaCl_2$ was then added to make the volume mark. The absorbance of the reagent blank and standard was read and a calibration graph plotted using Microsoft Excel.

Calcium and Magnesium Ion The calcium hardness of sample was determined in accordance with the American Public Health Association 122B. 50ml of sample was measured into a conical flask, with 1ml of 8.0N KOH and 4-drops of calcon indicator. This was titrated with 0.01N EDTA, and at the end point, a colour change from wine to Blue was observed.

Ammonium Ion Ammonium was determined in accordance with the American Public Health Association (APHA 417).

1000mg/L Ammonium ion stock solution was prepared by dissolving 2.965g of NH_4Cl salt in 500ml of distilled water in 1000ml capacity volumetric flask. After the dissolution, a volume was made to mark with distilled water. A working standard solution was prepared from the 1000mg/L standard stock solution, 0.50, 1.00, 1.50, 2.00 and 2.50mg/L into 100ml capacity volumetric flasks. Also a reagent blank was prepared. 20.0ml of each standard solution was placed in 50ml volumetric flask. 4.0ml tri-sodium phosphate solution was added. 10ml of phenate reagent 1 was added and shaken gently. 2.5ml of 3.5% alkaline bleach was added and shaken gently. The volume was made to mark. Colour development was allowed for about 25minutes. Same was carried out for the reagent blank. The absorbance of the standard and reagent blank on DR 2000 was read at 635nm. Then the calibration graph of absorbance vs. concentration in mg/l was plotted.

Statistical Analysis

The analysis procedure applied for this study is multivariate statistical analysis. Multivariate statistical analysis is a quantitative and independent approach applied to groundwater studies in order to group groundwater samples into hydrogeochemical facies, solve water quality problems and determine groundwater spatial associations (CLOUTIER *et al.*, 2008), (GÜLER & THYNE, 2004). The parameters were first checked for normality using the Shapiro-wilk test and quantile plots, the latter revealed that the data were positively skewed. The parameters were log-transformed to normalize before standardization to their z-scores using the formula below (Figure. 3.1), then multivariate statistical analyses was applied using Stata 13 software (STATACORP, 2013).

$$z = \frac{x - \bar{x}}{s}$$

Where z, x, $\bar{x}$, and s respectively represent the z-score, value, mean and standard deviation of the parameter. Data standardization is a requirement in multivariate analysis. The results of multivariate statistical analysis are more unbiased and have a higher degree of accuracy when the parameters used in the analyses are of the same units and equally weighted. Data standardization is a process of achieving both objectives. The use of the raw data in multivariate statistical analysis, especially cluster analysis and factor analysis, where dissimilarity and similarity measures are determined tend to favor the parameters (variables) with the highest variances (CLOUTIER *et al.*, 2008), (YIDANA, 2008). Data standardization makes the dataset uniform so that the determination of similarity/dissimilarity measures and factors will be fairly distributed among all the variables used in the analyses.

Hierarchical cluster analysis (HCA) was then applied to the standardized dataset to classify the data into spatial associations. Squared Euclidean distance measures were chosen to measure similarity/dissimilarity among variables and the Ward's linkage method was chosen to link initial clusters resulting from the initial clustering steps. The combined use of squared Euclidean distance as a similarity/dissimilarity measure and the Ward's method as a linkage algorithm has been observed to produce very reliable clusters (GÜLER *et al.*, 2002; CLOUTIER *et al.*, 2008, CLOUTIER *et al.*, 2006).

Principal component analysis (PCA) and Varimax rotation was also applied to the standardized dataset to determine the major sources of variation in the hydrochemistry within the study area. Components loadings greater than 0.3 are typically regarded as excellent and less than 0.3 very poor. Then, the (KAISER,1960) Criterion (The Kaiser Criterion suggests to retain those components with eigenvalues greater than or equal to 1) was applied to eliminate components which do not represent unique sources of variation in the hydrochemistry. The rationale behind the (KAISER,1960) criterion is that a factor which represents a unique process in the hydrochemistry should be able to account for the variance of at least one variable in the dataset. In reality, it is possible to obtain as many components as there are variables but a lot of the components will be very unnecessary. The resulting components loadings were in turn used to calculate components scores for the different parameters and sample locations. Piper and Stiff diagrams are plotted using the Enviroinsite 9.2.0.44 software (HydroAnalysis, 2015) to establish a tie with the results of the multivariate statistical analyses.

RESULT AND DISCUSSION

Interpretation

Hydrogen Potential (pH)

The groundwater quality data for the study area is presented in Table 2. The hydrogen-ion concentration (pH) of the groundwater in the study area ranges from 4.00 – 4.78. The ground water in most parts of the Niger Delta Region has been found to be generally Acidic (UDOM, *et al.*, 1999); this acidity in the groundwater has been attributed partly to gas flaring in the area. (WHO, 2006) and (NIS, 2007) stipulate the ground water with pH in the range of 6.5 – 8.5 is good for domestic use. All of the samples analysed fell below the stipulated limit of 6.5 thus indicating corrosiveness

Electrical Conductivity (EC)

Electrical conductivity (EC) of the groundwater samples ranged from 12 μS/cm to 219μS/cm, with a mean of 74.2 μS/cm. Electrical Conductivity is a measure of salinity, which greatly affects the taste and hence user's acceptance of the water for drinking. Table 2 shows that 100% of groundwater samples taken from boreholes were within the maximum permissible limits of 1000μS/cm for (NIS, 2007); However, all of the samples taken (BH-1 – BH-10) had conductivity values lesser than the WHO permissible limits with BH-2 and BH-6 having the highest conductivity value. No sample collected had conductivity value above the NIS Standard for drinking water of 1000 µS/cm.

Temperature

Groundwater temperature values in the study area ranged from 28.0-31.6°C, with an average value of 29.49°C. This suggest that the groundwater temperature is generally ambient and good for consumers who prefer cool or warm water for specific reasons; since high temperature negatively impact water quality by enhancing the growth of micro-organisms why may increase taste, odour, colour and corrosion problems (UNICEF,2008).

Therefore, it is important that groundwater temperature is not too high in order to not to have microbial proliferation. Temperature affects biological, chemical and physical activities in the water. Besides, increase in temperature of water decreases solubility of gases such as O_2, CO_2, N_2 and CH_4 (YILMAZ & KOC, 2014).

Total Dissolved Solids (TDS)

This is a quantitative measure of the sum of organic and inorganic solutes in water. The samples collected had TDS concentrations ranging of from 6 – 109mg/l and a mean concentration of 36.6. This implies that groundwater in the area is quite fresh and good enough both for drinking and irrigational purposes, as this would not affect the osmotic pressure of soil solution. (FREEZE & CHERRY, 1979) and (SHAHIDULLAH *et al*, 2000). TDS in all the locations is below the (WHO, 2006) and (NIS, 2007), stipulated value of 500mg/l. Low TDS is said to be a characteristic of hills and upload areas that represent areas of recharge according to (OLABANIYI *et al*,2007), thus it is an apt description of the study area topographically. However, the classification of TDS by (NADAGOUDA, *et al.,* 2012) implies that all the samples are permissible for drinking as seen from table 4.

Table 4: Pearson Correlation Matrix For Parameters Analysed

Correlation Matrix

	pH	TDS	EC	Cl	HCO_3	PO_4	SO_4
pH	1						
TDS	-0.1762	1					
EC	-0.1716	**0.9999**	1				
Cl	-0.2754	0.1908	0.194	1			
HCO_3	**0.9939**	-0.1387	-0.1342	-0.2545	1		
PO_4	-0.5986	0.1799	0.1806	0.7806	-0.5846	1	
SO_4	0.074	0.2934	0.3003	0.7829	0.0753	0.6525	1
NO_3	-0.3446	0.4588	0.4575	0.7953	-0.3429	0.5957	0.6633
NH_4	-0.4827	0.4494	0.4476	**0.8111**	-0.4688	**0.8318**	0.7009
Ca	-0.5052	0.5081	0.5073	0.7593	-0.4798	**0.8928**	0.6917
Mg	-0.2451	0.2557	0.2563	**0.9163**	-0.2235	**0.8543**	**0.8231**
Na	-0.4739	0.3317	0.3282	0.7639	-0.4743	**0.8371**	0.5955
K	-0.6392	0.3117	0.3086	0.6753	-0.6546	**0.8447**	0.5275
Ar	-0.3315	0.01	0.0155	0.0114	-0.3996	0.2064	0.0483

Correlation Matrix

Pearson's correlation matrix (Table 4) shows the relationship between the parameters. Only correlation coefficients above 0.8 were chosen since these indicates very high positive correlation. Correlations such as those indicated in the table suggests that the relationship between the parameters are very strong and that such relationships depend heavily on each other. For example, an increase in pH (increase towards basicity) would result in an increase in bicarbonate concentration and a decrease in pH will result in a decrease in bicarbonate concentration. Ammonium correlates highly with phosphate implying that their source may be the same and they increase and decrease together.

The results of PCA show that five components account for the variation in the hydrochemistry within the study area. Component 1 is dominated by TDS, nitrate, phosphate and ammonium, and accounts for 41.1% of the variation. Component 2 is dependent on EC, chloride and sulphate, and responsible for 16.97% of the variation. Component 3 is accountable for some 15.88% of the variation and dominated by calcium, magnesium and bicarbonate. Component 4 is dominated by pH only but still responsible for some 14.92% of the hydrochemical variation. Component 5 has only 7.79% of the variation but holds sodium and potassium accountable for that variation.

Carbonates and pH loads heavily on factor 2. Sulphate and Magnesium loads heavily on component 1 which accounts for the highest percentage of variation while Potassium has the least loading on component 1

The Piper plot shows that the all the samples belong in the Ca^{2+}-Mg^{2+}-Cl^{-}- SO_4^{2-} hydrochemical facies. Chloride ion is the dominant parameter in the anion while Calcium is the dominant cation in the categories.

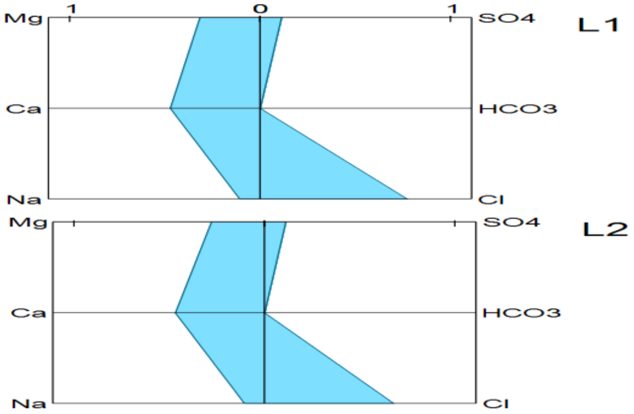

Figure 2: Stiff Plots of sample locations

Table 5: PRINCIPAL COMPONENT WITH VARIMAX ROTATION APPLIED (PCA)

Components	Variance	Difference	Proportion	Cumulative
Comp1	5.75418	3.37867	0.411	0.411
Comp2	2.37551	0.151762	0.1697	0.5807
Comp3	2.22375	0.134391	0.1588	0.7395
Comp4	2.08936	0.998821	0.1492	0.8888
Comp5	1.09054	.	0.0779	0.9667

DISCUSSION

The presence of chloride and calcium ion as the dominant parameter and the fact that it doesn't correlate with any other parameter in the correlation matrix suggest that it has an external source. This source is from surface saline water close to those locations with high chloride concentrations since the presence of high chloride ion concentration is independent of the pH. The correlation matrix support this idea since chloride and pH have a weak relationship. And so in the Agbor axis areas close to water bodies with saline waters are dominated by groundwater with very high but safe levels of chloride ion concentration.

Calcium chloride is a type of calcium salt used for many purposes, including deciding sidewalks and acting as a stabilizer in foods. Calcium chloride solutions are sometimes used in medicine to treat hypocalcemia (when the body has too little calcium); it may alleviate symptoms of depression from a magnesium sulfate overdose or it maybe used in open heart surgery to stimulate heart contractions. Although it is generally considered safe for humans to handle, some dangers exist if too much enters the body.

Gastrointestinal Distress Calcium chloride can cause a burning pain in the stomach, nausea and vomiting if ingested according to the International Programme on Chemical Safety (IPCS)

To avoid ingestion IPCS recommends you do not eat, drink or smoke while working with calcium chloride.

Skin Reactions

Prolonged skin exposure to calcium chloride may cause dry and irritating skin, according to the IPCS. To treat skin reaction, wash with plenty of soap and water, see a physician if the irritation doesn't go away, gets worse or is bothersome. To avoid skin irritation from calcium chloride exposure the IPCS recommends using gloves and long pants and long sleeves when working with calcium chloride

Lungs damage

If inhaled regularly, calcium chloride can create lesions in the mucus membrane that line the nose, throat and lungs according to the IPCS. To avoid damage from inhalation, you should wear a mask when working with calcium chloride. If you begin to cough or have a sore throat while working with calcium chloride, the IPCS recommends moving into fresh air or a well ventilated area and resting until your symptoms subsides. If symptoms, persist, see your Doctor

CONCLUSION

The groundwater within the study area is mostly acidic with high chloride concentrations. Contamination by anthropogenic sources is mainly from leaky septic tanks.The presence of chloride is from the proximity of areas that lie southward towards the Atlantic Ocean and the fact that water doesn't mix excessively at greater depths but the chloride levels are still within accepted standards for domestic use. Domestic wastes from septic tanks and improper waste disposal are the main sources of ammonium in the groundwater of the study area and this reduces the groundwater quality in the area markedly.

HCA and PCA are very reliable statistical methods for water analysis in general. The graphical methods are essential in providing a visual guide to access dominant chemical constituents.

REFERENCES

[1]. Abdullah Kandy Rootle, 1972.Hazards of Heavy Metal Contamination in Groundwater.International Journal of Technology Enhancements and Emerging Engineering Research, vol 3.

[2]. Adejuwon, O. A., 2012. Rainfall Seasonality in the Niger Delta Belt, Nigeria. Journal of Geography and Regional Planning, 5(2), pp. 51-60.

[3]. Akpokodje, E. G., Etu-Efeotor, J. O. & Mbeledogu, I. U., 1996. A study of environmental effects of deep subsurface injection of drilling waste on water

resources of the Niger Delta. Port Harcourt, CORDEC, University of Port Harcourt, Choba, Port Harcourt, Nigeria.

[4]. Alabaster, J.S. and Lloyd, R. 1984. Water quality criteria for freshwater fish. 2nd edition. Food and Agriculture Organization of the United Nations. 361 pp.

[5]. Alimesat Meteorology, 2013. Weather and Climate In South - South Nigeria. [Online]Available at: http://www.alimesatmetorology.com/climate/africa/nigeria/Delta.html.

[6]. Allen, J. R. L., 1965. Late Quaternary Niger Delta, and adjacent areas-sedimentary environments and lithofacies. AAPG Bulletin, Volume 49, pp. 547-600.

[7]. Alther, G. R., 1979. A simplified statistical sequence applied to routine water quality analysis: a case history. Groundwater, Volume 17, pp. 556-564.

[8]. Bouchard et al ; 2011. The Antimicrobial Effects of wed coffee Extracts and their Chelating Properties.

[9]. Climate-Data, 2015. Climate and temperature graph. [Online] Available at: http://en.climate-data.org/location/513/ [Accessed 25 November 2015].NIS, 2007. Standard for Drinking Water Quality, Lagos: Standard Organisation of Nigeria

[10]. Nwajide, C.S., 2013. Geology of Nigeria's Sedimentary Basins. Lagos: CSS Bookshops Ltd.

[11]. Reyment, R. A., 1965. The Cretaceous Ammonidea of Southern Nigeria and the Cameroons. Geological Survey of Nigeria Bulletin, Volume 25, p. 112.

[12]. Salgado-Bustamante et al; 2010. Environmental pollution and its Disastrous effect. A Review.

[13]. Stiff, H. A. J., 1951. The interpretation of chemical water analysis by means of patterns. Journal of Petroleum Technology, 3(10), pp. 15-17.

[14]. Stumm, W. and Morgan, J.J. 1970. Aquatic chemistry. An introduction emphasizing chemical equilibria in natural waters. John Wiley & Sons, New York. 583 pp.

[15]. Todd, D. k. & Mays, L. W., 2005. Groundwater Hydrology. In: 3rd ed. s.l.:John Wiley & Sons, pp. 359-366, 329-340.

[16]. USEPA (U.S. Environmental Protection Agency). 1979. Water-related environmental fate of 129

[17]. priority pollutants. Vol. I. Introduction and Technical Background, Metals and lnorganics,