Physico Chemical Study of Hydrochemical Parameters of Groundwater in Okehi Local Govrnment, North Central Nigeria.

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ABSTRACT: Major elemental composition of ground water in some parts of Okehi Local Government area in North central Nigeria were investigated. Twenty two water samples were collected from open and hand dug wells for hydrochemical analysis. In situ measurements such as conductivity, well depths and water column were also carried out. The hydochemical analysis results indicates mean anionic dominance of the anions in the order of Co_3^{2-} (124.41mg/L)>Cl^- (65.86mg/L)> PO_4^{2-} (17.93mg/L)>SO_4^{2-} (14.41mg/L)> NO_3^- (8.80mg/L)> F^- (0.11mg/L), whereas, the mean cationic dominance are in order of Ca^{2+} (37.68mg/L)> Na^+ (25.23mg/L) > K^+ (10.65mg/L) > Mg^{2+} (14.13mg/L) > Fe^{3+} (0.45mg/L). The ground water in the area is highly conductive. It is within the range of (104 – 805) μs/cm except the water sample collected from the central part of the study area having conductivity 62μs/cm. The areal distribution of the hydrochemical parameters from the contour plot did not form a definite pattern on the basis of ionic classification. However, the depth of the well influences the concentration of some hydrochemical parameters notably Cl^-, NO_3^-, F^-, SO_4^{2-}, Ca^{2+}, Mg2+, K^+ e.t.c. The regression analysis between conductivity and TDS indicate strong correlation with a correlation coefficient of 0.6119 whilst the conductivity and chloride regression analysis results indicate a weak correlation coefficient of 0.1156.
Key words: Conductivity, hydrochemical, in-situ measurement, anionic, cationic.

I. INTRODUCTION

Groundwater is an important source of water supply in many parts of the word. It is the water found beneath the crust and are always in continuous motion under the influence of some factors and forces. They find their way to the subsoil through percolation when the rainfalls, while some takes their channel from the crest of mountains and rocks. Among the forces causing water movement in the soil are the forces of gravity and capillary attraction. The underground circulation depends on how porous the soil is. Other factors influencing water flow are the topography of the ground layer and the fluctuation in the water table zones. In Nigeria, the groundwater accounts for about 63% of the nation drinking water supply (Hanson 2004)

In recent years this vital resource is endangered by multitude of chemical contaminants such as unregulated disposal of industrial wastes mainly from solid-waste disposal sites and storage tanks. The contamination occurs as a result of dissolved gases and ions embedded in the subsoil flowing water. The contaminant level varies from one place to the other due to the variation in some natural and artificial processes. Although, safety measure reduce the risk of ground water contamination, once such a contamination takes place, the clean-up operation is a difficult undertaking. This is primarily due to the highly heterogeneous nature of the subsurface environment and the complex interaction of the contaminants with the groundwater and the porous media.

The study of the physical process that govern the transport of the contaminant has its basis in the work of petroleum Engineers, where multiphase flow and transport was examined and first numerical simulation was carried out in the content of the oil recovery. The ability to predict the transport underground contaminants is one of the most challenging problems facing the hydro geologists. The overarching scientific issue is how we take scientific knowledge about the behavior of chemical and fluid obtained in the laboratory and use that knowledge to predict accurately contaminant movement through miles of soils and ground water over many years. As a result there is need to study the chemical parameters present in the underground water flow from one region to the other. This will be of hydrological importance in

understanding the net distribution and variation of physical and hydrochemical parameters.

Groundwater contaminants

Groundwater contaminants occur when unsaturated substance dissolves in groundwater and moves through the fracture of soil profiles to the saturated zone (Adekunle,2009). Various sources or the potential contamination include; sources designed to discharge substances e.g septic tanks, cesspoll and injection wells; sources designed to treat, store or dispose substances e.g landfills, open clumps, surface and subsurface storage tanks, radioactive waste disposal sites; sources designed to retain substance during transport e.g pipelines. Sources discharging substance in such a way that leaching of waste product is inevitable e.g irrigation, pesticide/fertilizer applications, farm animal waste, urban runoff, percolation of atmospheric pollutants and naturally occurring sources created and enhanced by human activities e.g seawater, intrusion, saltwater up-coming and ground water surface interaction. In short, contamination is caused mainly from artificial and natural sources.

Natural Source

One of the natural sources of underground water contaminant is nitrogen. It occurs chiefly as a free element in the air making up about 78% by volume of the atmosphere. It gets dissolved with the underground water through the action of some bacteria living in the root nodules of leguminous plant by the process called nitrogen fixation. In the combined formed, nitrogen occurs abundantly in the earth crust as trioxonitrate (V) of Sodium, calcium as well as ammonium salt. Excessive rainfall or irrigation tend to leach nitrogen below the root zones and ultimately to the groundwater. Moreover some microbial activities also convert atmospheric nitrogen to nitrate through the process of nitrogen fixation. Furthermore, during the process of decaying, bacterial or buried plants and animal under the ground surface leading to the release of some toxic waste like methane and sulphuric gases. These wastes are soluble in water and may later exist as a carbonates or nitrates ions after the required element have been taken by the plants. The remaining parts may be easily washed down through the soil profile by leaching as a result a result of heavy rainfall and then deposited in the groundwater table to form ground water contaminants.

Consequently, different type of rocks present beneath the earth crust contains different composition due to their mode of formation. For example, limestone contains minerals called gypsum which is one of the major composition of cement. When this dissolves in water, it render the water unfit exist in the groundwater as contaminants. Moreover, many solid minerals in the earth crust exist as ores or as combination of nuclides – when any of these nuclides undergo radioactive decay, they produce ionizing radiation which has a side effect on living organisms (Adefemi&Awokunmi, 2010). When these elements or nuclides are then hydrolyze in water, they are transported down to the ground water table as a contaminants and then deposited permanently. Finally, pathogens which exist as soil fauna (virus, bacterial) which occur in sewage sludge, animal waste, when these pathogens are carried in suspension with water through soil, they are then deposited in the groundwater table to form ground water contaminants.

Artificial or manmade contaminant source.

Water pollution is a big problem in the present day world. It threatens aquatic life and changes water bodies into unsightly, foul-smelling scenes. It also affects health because of the harmful substances that accumulate in aquatic animals fed o by man. The main cause of water pollution is the indiscriminate dumping of solid and liquid wastes into water bodies. The common pollutants are as follows;
i. Refuse and sewage
ii. Industrial and Agricultural wastes
iii. Crude oil spills e.t.c.

Statement of the problem

In the recent past, people of the local Government digging wells and bore-holes have not been taken into consideration the level and nature of the contaminant movement in the subsoil while sighting the location of the wells and bore-holes and this has resulted in people drinking water containing high level of Anionic and Cationic contaminants impacting negatively on the health of several people unknowingly.

Purpose of the study

The ability to predict the transport of underground contaminants is one of the most challenging problem facing the hydro geologist (Chukwu, 2008). The overarching scientific issue is how we take scientific knowledge about the behavior of chemical and fluid obtained in the laboratory and use the knowledge to predict accurately contaminant movement through miles of soil and ground water. As a result, there is need to study chemical parameters present in the

underground water flow from one location to the other. This will be of hydrological importance in understanding the net distribution and variation of physical and hydro chemical parameters within the local government and consequently help in sighting the location of the hand-dug wells and bore-holes to have a safe drinking water.

Methodology

Chemical analysis of groundwater, trace elements and isotope are important for characterizing water conducting features. In this study, groundwater survey were carried out in Okehi Local Government to assess the extent and concentration of hydro chemical parameters namely; Total dissolved solid (TDS), Total Suspended Solid (TSS), Chloride (Cl^-), Fluoride (F^-), Bicarbonate (HCO_3^-) , Carbonate (CO_3^{2-}), Sulphate (SO_4^{2-}), Phosphate (PO_3^{4+}), Sodium (Na^+), Potassium (K^+), Magnesium (Mg^{2+}), and Iron (Fe^{3+}).

Physical parameters such as colour, pH value, Turbidity, Electrical conductivity, well depth, and water column for both raining and dry season were also measured.

Reconnaissance survey

This involves taken the inventory of open and hand dug wells within the study area. The depth and water column were measured during rainy and dry season, samples were collected from the wells.

sampling

Twenty-two water samples were collected from open and hand dug wells spread within the locality of the area of study. The cleanliness of the container used for the collection of the samples were highly maintained by firstly rinsed with soap and detergent and finally with distilled water. The samples were preserved at the point of collection with tetraoxosulphate VI acid and trioxonitrate V acid to prevent the ions present in them from coagulation to the walls of the containers. The samples were also taken to the laboratory on the day of collectionfor analysis in order to identify and evaluate the concentration of hydrochemical parameters present in them.

Measurements

Two categories of measurement were carried out, namely; in-situ and laboratory measurement or analytical techniques. The in-situ are basically physical measurement which includes well depth, water column and electrical conductivity of the water samples. Depths and water column were measured by tying a heavy stone suspended at zero end of the measuring tape and dipped into the well. The electrical conductivity was measured using conductivity digital metre.

Analytical techniques

This involves laboratory measurement for the concentration of the following hydrochemical parameters; Total dissolved solid (TDS), Chloride (Cl^-), Fluoride (F^-), Bicarbonate (HCO_3^-) , Carbonate (CO_3^{2-}), Sulphate (SO_4^{2-}), Phosphate (PO_3^{4+}), Sodium (Na^+), Potassium (K^+), Magnesium (Mg^{2+}), and Iron (Fe^{3+}). Other laboratory measurements carried out are colour, pH value, and Turbidity.

Colour

The colour of the water samples was determined by visual comparison of its colour with the colour of known concentration of coloured solutions.

Turbidity

Turbidity of the samples were determined using a turbid meter HACH

Total Dissolved Solid and Total Suspended Solid

Total Dissolved Solid of samples was determined by centrifugal method.
- Mix sample well and fill a 50ml centrifuge tube to the mark and centrifuge the sample for 5 minutes
- Decant the supernatant liquid and pour in a pre-weighed platinum crucible
- Dry the liquid in an oven at 105^oC for 1 hour
- Allow the crucible to cool and weigh. Repeat heating and cooling of crucible (for 15 minutes) until constant weight is attained
- Calculation

$$TDS = \frac{W2-W1}{50} \times 100 \text{ mg/l.}$$

Where W_1 weight of crucible, W_2 = constant weight of crucible with dried water.

Total Suspended Solid
- Wash the residue in the centrifuge with a little distilled water into a pre- weigh crucible,
- Dry the crucible with the residue in oven at 105^oC for 1 hour
- Allow the crucible to cool and weigh. Repeat the drying, cooling and weighing (for 15 minutes) until constant weight is obtained.

Calculation;

$$TSS = \frac{W2-W1}{50} \times 100 \text{ mg/l.}$$

Where W_1 weight of crucible, W_2 = weight of crucible dried residue

Total Hardness
Total hardness was determined by titrimetric.

Table 1: Determination of anions concentration

Alkalinity	OH^-	CO^{3-}	HCO^{3-}
P = 0	0	0	T
P<T/2	0	2P	T-2P
P = T/2	0	2P	0
P>T/2	2P-T	2(T-P)	0
P=T	T	0	0

Table 2: Determination of cations concentration

Cation	Stock solution	Fuel of AAS	Wavelength (nm)
Ca^+	Dissolve 2.417g $CaCO_3$ in 1L distilled water. 1mL= 1.0mg	Nitrous oxide-acetylene	422.7
Mg^{2+}	Dissolve 10.136g $MgSO_47H_2O$ in 1L distilled water 1mL= 1.0mg Mg	Air - acetylene	285.2
Fe^{3+}	Dissolve 1.404g $Fe(NH_4)2(SO_4.6H_2O$ in conc.H_2SO_4 and dilute to 1L with distilled water 1mL=1mgFe	Air -acetelene	248.3

Corrosivity ratio
From the results, the corrosivity ratio were calculated using Ryzner expression:

$$\text{Corrosivity ratio} = \frac{0.028\,Cl^- + 0.021\,SO_4^{2-}}{0.02\,(HCO_3^- + CO_3^{2-})}$$

NAMES OF THE AREAS WHERE THE SAMPLES WERE COLLECTED

1 Iku-ehi 6 Eika-Adagu   11 Ahogede   16 Ohueta21 Apipa
2 Oboroke   7 Abobo   12 Ebako   17 Ohuepe22 Apamba
3 Obangede   8 Aguro13 Idarere   18 Ikaturu
4 Okaito   9 Eika-Ehi14 Itakata   19 Ukako
5 FCE   10 Eika-Eba15 Obeiba   20 EbakoUvete

II. ANALYSIS AND DISCUSSION OF RESULTS

The study area is a semi- urban area located within longitude 6^o81^1E and 6^o88^1E and latitude 7^o42^1N and 7^o49^1N north central Nigeria. There is presence of rocks surrounding the metropolis. The main source of water is open and dug wells and little boreholes.

Hydrological setting
The area consists of the relatively sand body, which underlain by the crystalline basement. The sandy deposit in some part of the area is found cemented well by the organic colloidal matter and hydrous iron oxide in the near surface layer at some places.

The major source of water are hand dug and open wells with abundant supply of water during the rainy season and with little or no water (< 1.0m column) during the dry season especially at Otite side of the study area. Natural shortage of water have occur due to weather conditions and geologic setting (e.g prolong drought and crystalline bedrock aquifers with low yields)

III. DISCUSSION OF RESULTS

The mean ionic dominance of both cations and anions are depicted in the table below

Table3 : Mean values of cations

Cations	Mean value (mg/L)
Ca^{2+}	37.68
Na^+	25.23
K^+	10.65
Mg^{2+}	4.13
Fe^{3+}	0.45

Table4 : Mean value of anions

Anions	Mean value (mg/L)
CO_3^{2-}	124.41
Cl^-	65.86
PO_4^{2-}	17.93
SO_4^{2-}	14.41
NO_3^-	8.80
F^-	0.11

The above tables shows that the mean anionic dominance are in order of $CO_3^{2-}>Cl^->PO_4^{2-}> SO_4^{2-}>NO_3^->F^-$, whereas, the mean cationic dominance are in order $Ca^{2+}>Na^+>K^+>Mg^{2+}>Fe^{3+}$. This shows that the area under investigation is highly conductive (104 - 805µs/cm) with the exception of the water sample collected from the central part of the study area having 62µs/cm.

IV. CONCLUSION

The areal distribution of the hydrological parameters from the plots did not form a definite pattern on the basis of ionic classification. However, the depth of the well influences the concentration of hydrochemical parameters. For example from the graph, it is observed that as the well depth increases so also increased the concentration of sodium ion. The same observation is indicated for Ca^{2+}, SO_4^{2-}, and Mg^{2+}. Also from the plot the concentration of chloride increases at the point where there is decrease in the well depth e.gOboroke, Okaito and Eika-Adagu this assumption is also true for HCO_3^-, F^-, and Fe^{3+}.

Table5 :Corrosivity ratio

Sample	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	Corrosivity ratio
1	20	3.4	43	0.934
2	128	30.8	210	1.007
3	83	2.1	65	1.822
4	148	15.8	160	1.399
5	23	3.0	70	0.505
6	126	9.1	152	1.223
7	35	25.7	81	0.938
8	58	13.4	53	1.798
9	64	4.6	47	2.009
10	44	15.9	195	0.402
11	43	5.5	95	0.694
12	46	7.3	155	0.465
13	78	13.4	71	1.736
14	60	14.3	46	2.153
15	80	3.1	195	0.591
16	82	5.8	57	2.121
17	60	79.7	210	0.799
18	60	4.9	444	0.201
19	50	3.3	115	0.693
20	51	47.8	153	0.795
21	20	5.5	75	0.450
22	90	2.7	45	0.889

TDS against Conductivity

y = 0.611x - 10.48

Chloride against Conductivity

y = 4.076x + 103.9
$R^2 = 0.496$
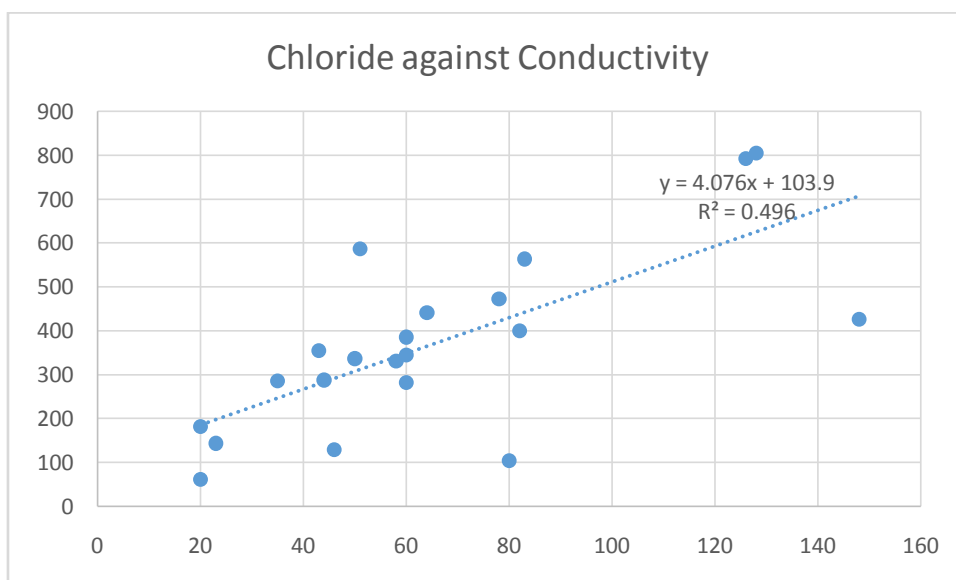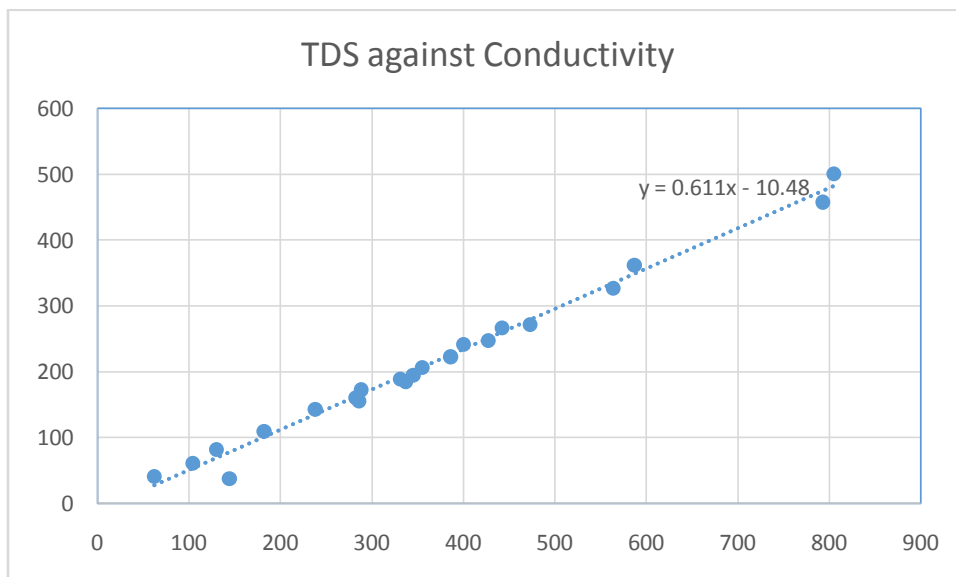
Table 6: concentration values of physico chemical parameters of the analysed samples

	TEST	SAMPLES																					
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
1	Conductivity (s/cm)	182	805	564	427	144	793	286	331	442	288	355	130	473	345	104	400	282	386	337	587	62	238
2	Colour (Pt/Co)	25	146	13	21	23	9	17	12	1	21	0	45	55	25	51	40	37	88	16	15	2	9
3	Turbidity (FTU	2	20	3	5	5	3	3	0	1	8	0	1	1	1	8	4	1	14	0	2	0	0

	)																						
4	TSS (mg/L)	3	3	0	7	4	0	0	0	5	6	3	0	4	6	4	7	0	4	0	6	0	0
5	TDS (mg/L)	110	501	327	248	38	458	156	189	267	173	207	82	272	195	61	242	161	223	185	362	41	143
6	Total Hardness (mg/L CaCO3)	82	174	84	118	108	161	102	112	84	218	110	60	142	114		84	85	80	86	76	116	86
7	Total alkalinity (mg/L CaCO3)	43	210	65	160	70	152	81	53	47	195	95	155	71	46	46	57	210	444	115	153	75	45
8	Chloride (mg/L)	20	128	83	148	23	126	35	58	64	44	43	46	78	60	80	82	60	60	50	51	20	21
9	Flouride (mg/L)	0.18	0.24	0.11	0.12	0.08	0.22	0.25	0.06	0.05	0.00	0.13	0.15	0.05	0.03	0.01	0.00	0.14	0.26	0.20	0.23	0.00	0.15
10	Nitrate (mg/L)	7.9	8.6	9.5	8.7	6.9	14.1	8.2	8.1	7.7	7.6	6.5	9.2	6.4	15.2	7.8	9.3	6.9	13.5	7.1	6.6	8.6	8.1
11	Hydroxide (mg/CaCO3)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
12	Bicarbonate (mg/CaCO3)	43	210	65	160	70	152	81	53	47	195	95	155	71	46	195	57	210	444	115	153	755	82
13	Carbonate (CaCO3)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.00	0.00	0.00
14	Sulphate (mg/L)	3.4	30.8	2.1	15.8	3.0	9.1	25.7	13.4	4.6	15.9	5.5	7.3	13.4	14.3	3.1	5.8	79.7	4.9	3.3	47.8	5.5	5.6
15	Sodium (mg/	34	40	16	40	20	36	24	28	16	54	32	16	22	24	18	15	16	16	14	30	26	18

	L)																						
16	Potassium (mg/L)	8.0	137	3.0	5.0	1.5	8.0	1.3	3.4	2.1	15.5	3.8	2.3	6.5	3.8	2.9	2.5	2.5	5	5.5	6.5	5.3	2.9
17	Calcium (mg/L)	31	68	32	25	37	62	36	32	30	79	38	22	50	37	31	32	29	30	31	28	40	29
18	Magnesium (mg/L)	1.2	1.1	1.7	16	4.6	2.0	2.9	9.2	2.8	5.2	4.0	1.1	5.5	6.3	6.4	1.7	3.1	1.1	2.8	1.2	4.6	4.0
19	Iron (mg/L)	0.39	0.48	0.52	0.56	0.44	0.35	0.45	0.26	0.56	0.55	0.58	0.41	0.48	0.32	0.45	0.41	0.44	0.51	0.49	0.44	0.36	0.44

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