

Hydrogeochemical signatures and estimates of underground water quality in Okpoko and neighborhoods, south-east Nigeria

Abstract

This study is aimed at assessing the hydro-geochemical signature of groundwater in Okpoko and surroundings in Anambra, Southeast Nigeria. Fifteen groundwater samples were collected and analyzed by physicochemical, heavy metals and hydrocarbon content. Heavy metals in groundwater were analyzed using an atomic absorption spectrometer. Groundwater analyzes showed that the average pH (6.05), Fe (0.68 mg/L) and Ni (0.028 mg/L) values are exceeded by the WHO and NSDWQ guidelines. Total petroleum hydrocarbons (TPH) in groundwater were relatively low and recorded only in BH1 (0.04 mg/L) and BH2 (0.002 mg/L) and below the detection limit for all other selected wells. Piper diagrams showed two hydrochemical facies: 3mg-HCO and Ca-HCO₃-rich water, while the rigid regimens were confirmed by four separate water types (Ca²⁺, mg²⁺, 3HCO; CA²⁺, 3HCO; CA²⁺, Na⁺⁺⁺; K Cl⁻, HCO₃; CA²⁺, Cl⁻ class). Gibbs diagrams showed that chemical weathering of rocks and sediments, the main factors affecting the quality of groundwater. Different ionic ratios: mg/Ca (0.56), HCO₃/Cl (3.31), (Na+K)/Cl (1.45), Na/K (1.61), Ca/Na (7.0)/Cl (0.67) and CEV (-0.45) suggests groundwater sources are of internal origin. The direction of the groundwater flow indicates that the areas are drained along the Niger River in the western part of the study area.

Keywords: groundwater quality, water, hydro geochemistry, facies, heavy metals, drinking

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Introduction

Water is an essential component of all living things you need to survive, and it consists of about two-thirds of the body weight of a person (blood, 2006). Groundwater is very important for life on earth, as it is a good source of freshwater resources. As of 2012, more than two billion people around the world cannot access safe drinking water¹

The consequences of using unsafe, polluted water are enormous. According to WHO,¹ drinking contaminated water is one of the main causes of certain diseases, like diarrhea diseases; these diseases are one of the second leading cause of child mortality, which resulted in the death of about 760000 children aged <5 years annually. For this reason, WHO has identified a lack of access to safe drinking water as the most important factor that adversely affects the overall health and welfare of the population in developing countries.

In general, providing safe drinking water can limit or eliminate preventable deaths and improve the quality of life for low-income households around the world.² The quality of water, otherwise known as drinking, can be defined as the chemical, physical and biological properties of water, as far as safe consumption is concerned. It also includes the process of assessing their physical, chemical and biological properties with respect to natural qualities and effects on human health.^{3,4}

Johnson et al.,⁵ reported that water quality is highly dependent on the geology of indigenous peoples, ecosystems, and human activities. Drinking water can be dependent on the intended use of water. For example, great concern is for the water needed for direct human use, compared to water used for industrial and other environmental

purposes.⁶ People all over the world have used groundwater as a source of drinking water, and now even more than 50 percent of the world's population depends on groundwater to survive.⁷ Even in sub-Saharan Africa, groundwater proved to be the most reliable source of drinking water.⁸ Yet groundwater's are one of the biggest challenges facing policymakers in order to support it.

Natural filtration through soil and sediments makes groundwater contaminated with organic impurities. But as a result of some anthropogenic activities, such as rapid urbanization, industrialization, exploitation of natural resources, pollution, heavy agricultural activities, the quality of soil and groundwater is significantly reduced. Thus, assessment of soil quality and groundwater resources and appropriate hydrochemical studies need to implement suitable strategies designed to ensure that water resources are suitable to meet human needs.

Brief geology and hydrogeology of the district

The field of study is located in Onitsha Northern local government of the region from Anambra and the limited geographical longitude N 00° 06' 06" 06' 09" 00" N and latitude E 00 45' 06" 06' 49' 30" E. Communities located within the study area include the Woliwo and Awada mock-ups in the eastern part of the district.

The city in which the site is located is densely populated. Several filling fuels and service stations are cited in very close proximity. The main station in the area is located along the Onitsha-Owerri Expressway 20m from the main road, about 30m from the holding capacity of the high voltage cable of Nigeria (PHCN), about 50 m from the dwelling houses, about 200m from the new engine parts

of the Market Dealers, about 540 m from the hospital. Lwngas and Maternity School of Health and Technology, about 300 m from Sako Oil and Gas LLC petrol station on the left side of the road and about 400 m from the lake side of the oil filling station on the right hand side of the road. Generally, the exploration area has a very good road in the network and connect roads. Two large rivers are responsible for the wing area, which includes the Niger River and its main tributary of the river Ulasi. However, there are local streams and ponds in the entire region area.⁹

The anambrasic basin, which includes a study area located in the southwest Extreme Benue Trough, formed after the Santonian tectonic hollow, dates back to 84 Mya.¹⁰ This is a chalky sedimentary domain, partially confined between the South Benue Trench below and the Delta River Niger above. It originated after the subsidence of the platform in the southern part of the Benue trough, simultaneously with lateral translocation of theepocentres during the thermotectonic Santonian event, folded and the Abacalics of the region was also elevated.¹¹

It is believed that the basins were formed as a direct effect of stresses generated by the movement along the zones of fracture. It borders on the west with the Precambrian basement complex of the cliffs of Western Nigeria and the east of the Abakalikantiklinorium. In the southern part of the border is on Onich, which is the northern limit of the Niger Delta Basin. The northern boundary of the Anambra basin is unclear. The basin is connected to the NW-SE trendy Bida basin. Prior to the Santonian period, its Western rift valley was tectonically stable Anambra platform. The Santonian longitudinal event was followed by magmatism, folding and fractures, which led to the formation of Abakaliki Anticlinorium. To the west and to the south the anticlinorium was depocentre, creating an Anambra and basins, Afikpo, respectively.¹² The subsidence in these basins continued even after the compression of the Santonian.¹³ It is believed that isostatic response at the beginning of the Cretaceous crust thinning and post drift of the thermal relaxation of the lithosphere was due to an accelerated subsidence that continued until the Eocene.

Predominantly aquicludes and aquiferous Nkporo group facies. Mom formations also made itself mainly aquicludes and aquiferous in its lower part, an improvement for fine sandstones at the top.¹² Mama's education contributes to almost all the underground waters, introducing Enugu coal mines. It is a source of rainfall replenishment.^{14,15} The main aquifer forming the Anambra basin is the formation of Ajali. The texture is very favorable allowing for simple and fast replenishment in its vast area of economic water yields at the top of the Slates.¹²

Methods of research

Sampling of groundwater

A sample of groundwater in the study area was conducted during the rainy season (March, 2017). 15(fifteen) underground waters were samples from wells, distributed randomly in Okpoko and surroundings. As near as possible to the wells, water samples were collected to prevent ion loss or water contamination. Water samples were collected in washed and pre-cleaned plastic bottles. Before sampling, water was allowed to flow for about three minutes to prevent ion samples that settled in the pipes.

The sampling containers were washed with water to try several times before the sampling began and immediately clogged to prevent

the introduction of oxygen. All groundwater samples were carefully labeled and stored in ice before transport to the laboratory for analysis. Parameters that were analyzed in the field in the field include: pH, temperature and using electrical conductivity of drinking-held meters.

Groundwater analysis

Physical, chemical, hydrocarbons and heavy metals were installed from each sample of groundwater in the Zetta allies of the Digital energy laboratory, Elemenwo, and Port Harcourt, Nigeria. PH samples were determined electronically using Mettler Toledo seven easy pH meter.

The electrical conductivity (EC) was determined using a conductivity meter. The temperature was determined using Mercury in a glass thermometer

Turbidity was determined with the HACH2100AN Turbidimeter. All dissolved solids (TDS) were determined as being distributed. Alkalinity and total hardness (TH) were determined by the titrimetric method. Chloride was determined by titration.

Sulphates were determined using a gravimetric method, while nitrates were determined using the Brucine method. Cations were analyzed using a flame photometer. The total volume of organic carbon is determined by Walley-black titrimetric method. Soxhlet mining gravimetric method was used to determine hydrocarbon oil for example all petroleum hydrocarbons (UNG). Concentrations of heavy metals were determined by acid digestion, using nitric acid and further analyzed with the PerkinElmer Analyst 200 flame atomic absorption spectrometer.

Results and discussion of groundwater analysis

The results of physico-chemical, heavy metals and hydrocarbons in groundwater samples from the study area are presented in Table 1, while the results of a one-dimensional statistical analysis are presented in Table 2 and compared to both¹ and Nigeria's drinking water quality standard.¹⁶

The pH of groundwater varies from 5.3 to 7.1 with an average and standard deviation (SD) of 6.05±0.6 (Table 1). This means that the groundwater in the area is mostly acidic in composition. Only BH11 is located 1km to the southwest of filling large gasoline and the service station shows a slightly basic composition.

Hardness varies from 5 to 108 mg/L with average and SD 48.22±35.52 mg/l. High values, standard deviation and dispersion (1261.82 mg/L) show a wide degree of variability in the hardness of groundwater in this region.

The water hardness is high in BH1 (gas station) and the lowest in BH12.

Turbidity ranges from 0.7 NTU to BH1 to 11 NTU at BH15 with an average and SD of 4.69±3.38 NTU.

The temperature ranges from 24.11 in BH4 29.300C to BH1 with an average and SD of 27.01±1.58 0C. Electrical conductivity and TDS are relatively low and range from 3.20 to 139.32 mg/L and 8.65 to 180 mg/L with average and SD 47.32±45.20 mg/L and 78.49±58.71 mg/L, respectively (Table 2).

Total petroleum hydrocarbons (TPH) in groundwater were relatively low and recorded only in BH1 (0.04 mg/L) and BH2 (0.002 mg/L) and below the detection limit for all other selected wells (Table 1).

Cations and anions were comparatively very low in groundwater samples in the study area. For calcium cations, it ranges from 23 in BH1 to 64 mg/L in BH8 with an average and SD of 37.14±13.39 mg/L with magnesium ranging from 2.20 to 23.70 mg/L with an average and SD of 11.08±7.53 mg/L (Table 2).

Table 2 Results of the creation of a one-dimensional statistical analysis of groundwater quality, compared to regulatory constraints

Options	Units	Min	Max	Average	SD	Dispersion	WHO(2011)	NSDWQ (2007)
Physical properties								
pH		5.3	7.1	6.05	0.6	0,36	6.5-8.5	6.5-8.5
Hardness	mg/L	4	108	48.22	35.52	1261.82	500	150
TDS	mg/L	8.65	180	78,49	58.71	3446.7	1200	500
Turbidity	NTU	0,7	11	4.69	3.38	11.46	5	5
EC	µs/cm	3.2	139.3	47,32	45.2	2042.92	1250	1000
Pace	OC	24.11	29.3	27.01	1.58	2.5	Environment	Environment
ALK	mg/L	8.4	23	13.28	3.96	15,67	400	NA
TPH	mg/L	< 0,001	0,04	0.02	0,03	0	NA	NA
Chemical properties								
CL ⁻	mg/L	10	67.32	24.64	15.38	236.48	250	250
TAKK42 ⁻	mg/L	5	14	8.8	2.41	5.83	500	100
NO ₃ ⁻	mg/L	0,8	35	8.47	8.49	72	50	50
CO ₃ ⁻	mg/L	12	45	26.61	9.86	97.16	NA	NA
HCO ₃ ⁻	mg/L	3.2	240	102.5	93.48	8739.14	NA	NA
CA	mg/L	23	64	37.14	13.39	179.3	75	70
Mr	mg/L	2.2	23,7	11.08	7.53	56.64	50	30
Na	mg/L	2.43	23.43	10.44	6,73	45.29	200	200
K	mg/L	6.8	24	13.08	5,62	31.58	55	200
Heavy metals								
Fe	mg/L	< 0,001	3.7	0,68	1.17	1.38	0,3	0,3
Zn	mg/L	0,04	3.12	1.152	0.967	0,936	5	3
Ni	mg/L	0.001	0,056	0,028	0,024	0.001	0.02	NA
MN	mg/L	0.001	0.31	0,08	0,095	0.009	0.2	0.2
Pb	mg/L	0.001	0,007	0.003	0.003	-	0.01	0.01
Cu	mg/L	< 0,001	< 0,001	< 0,001	0	-	1	1
CD	mg/L	< 0,001	< 0,001	< 0,001	0	-	0.003	0.003
Hg	mg/L	< 0,001	< 0,001	< 0,001	0	-	NA	NA

Sodium and potassium, ranged from 2.43 23.43 mg/L and 6.80 to 24.0 mg/L with average and SD values of 10.44±6.73 and 13.08±5.62 mg/L, respectively. For anions, bicarbonate and carbonate has the highest average concentrations, from 3.20 to 240 mg/L and 12 to 45 mg/L with average and SD 102.48±93.48 and 26.61±9.86 mg/L, respectively, whereas nitrate had a low average level concentrations ranging from 0.80 to 35 mg/L with an average and SD 8.47±8.49 mg/L of chlorides and sulfates has an average and SD values of 24.64±15.38 mg/L and 8.80±2.41 mg/L, respectively.

For heavy metals, zinc and iron recorded the highest concentration, ranging from 0.04 to 3.12 mg/L and <0.001 to 3.70 mg/L, with an average and SD of 1.15±0.97 and 0.68 to 1.17 mg/L, respectively (Table 2). Nickel and manganese vary from 0.001 to 0.056 mg/L and 0.001 to 0.31 mg/L with average and SD values of 0.028±0.024 and 0.08 0.095 of the lead composition mg/l ranged from 0.001 to 0.007 and have a mean and standard deviation of 0.03±0.003 mg/l copper, Cadmium and mercury were compositions too small to be detected using measuring equipment.

Classification of groundwater and hydro geochemical signatures

Piper diagram

Piper (1953) presented a trilinear scheme for assessing the geochemical evolution of water and the relationship between rock type and water composition.

The Piper's analysis of the trilinear plot for groundwater in the area shows that Mg, Ca and HCO_3^- are the dominant cations and anions, hence groundwater samples are classified as Mg- HCO_3^- and Ca- HCO_3^- hydrochemical facies).

Rigid scheme

The rigid scheme (1951) classifies the qualities of groundwater on the basis of similarity in form. Water of the same quality has a distinctive shape. The diagram is the sections of the cation anions to the right side and to the left. This method of classification is in addition to the Pipertrilinear diagram. Four different forms were separated from the hard sections for groundwater sources. Groundwater from BH1, BH2, BH3, BH10, BH14 and BH15 displayed identical forms, with Ca^{2+} and Mg^{2+} being the dominant cations, and bicarbonate is currently the dominant anion. Class II of groundwater includes BH4, BH6, BH7 and BH8, displaying all similar forms, with Ca^{2+} being the dominant cation, while bicarbonate is the predominant anion. Class III water includes BH5, BH9, BH11 and BH13 and Ca^{2+} and $\text{Na}^{+}+\text{K}^{+}$ as the dominant cations and Cl^- and bicarbonate as the dominant anions. Only BH12 belongs to the category IV class, having Ca^{2+} as the dominant cation and Cl^- as the dominant anion. The distribution of various facies hydro chemical can be clearly visualized on the map view.

Durov chart

The main ions of groundwater samples were plotted on the Durov diagram because it helps in interpreting evolutionary trends and reveals the hydro chemical processes taking place in any groundwater system. On the diagram, Durov showed three geochemical processes that could affect the Genesis of the water in the area. The plot was shaped and colored using Total mineralization concentration. Most groundwater samples (8 samples) on the diagram in field 3, Na and HCO_3^- are dominant. They are usually the result of ion exchange of Ca- HCO_3^- rich waters. Two of the samples of subterranean sites in field 5, which is the field is not the dominant anion or cation and indicates water exposure by simple decay or mixing. The remaining 5 samples depict in field 6, which are both 4 and Na dominant. This type of water is not found often and indicates a likely mixing or affects the rarity of disintegration.

Gibbs diagram

The Gibbs site is used to interpret the effect of hydro geochemical processes, such as precipitation, rock interaction water and evaporation on the geochemistry of groundwater (Boatengal, 2016). With the goal of a discerning source of water pollution in the area, Gibbs ratio the plot (GR) is a useful tool for finding the interaction between rock and water. The concentration of dissolved ions in groundwater samples is usually regulated by litho logy, the nature of geochemical reactions and the solubility of rock interactions. The functional sources of dissolved ions are widely estimated by constructing the samples,

according to the variation in the ratio $\text{Na}^{+}/(\text{Na}^{+}+\text{Ca}^{2+})$ and $\text{Cl}^{-}/(\text{Cl}^{-}+\text{HCO}_3^{-})$ as a function of TDS (Gibbs, 1970).

$$\text{GR-I (anion)} = \text{Cl}^{-} / \text{Cl}^{-}+\text{HCO}_3^{-} (1)$$

$$\text{GR-II (for cation)} = \text{Na}^{+}+\text{K}^{+}/\text{Na}^{+}+\text{K}^{+}+\text{Ca}^{2+} (2)$$

Where all the ions are mg-eq/l.

Gibbs coefficients for all conspiracy samples versus TDS (ppm) in, to know whether groundwater chemistry is due to rock dominance, domination of evaporation, or dominance of precipitation. From the pot of the Gibbs coefficient plot, it can be seen that most of the examples are rock dominated (shown around the line dash line) and the remaining samples suggested to be precipitation dominated. This scenario assumes that it increases the salinity control field, increasing the Na and Cl ions due to the increase in TDS and agricultural fertilizers.

Groundwater quality control mechanism

The chemical data of groundwater samples were plotted by Gibbs,¹⁷ which is widely used to evaluate functional sources of dissolved chemical constituents, such as precipitation dominance, rock dominance, and evaporation dominance.¹⁷ The distribution of groundwater samples suggests that the chemical weathering of rock formation of minerals together with precipitation from the surface is an in fl uencing of the quality of groundwater. Hence the interaction of rock water and precipitation are responsible for ions in underground sources.

Ionic coefficients

Ionic coefficients are usually used to determine the intrusion of sea water in coastal areas. In this study, the following ionic bonds were identified to deduce the salinity and origin of ions in the groundwater of the study area. These include: mg/Ca, $\text{HCO}_3^-/\text{Cl}^-$, $(\text{Na}+\text{K})/\text{Cl}^-$, Na/K, Ca/Na/Cl4 and cation exchange values (EKB) (Table 3). The ionic coefficients were calculated (in mg-eq/L) and the results compared to sea water values and early Cretaceous brine. Calcium is dominant in fresh water, while magnesium is dominant in sea water. Hence the ratio mg/Ca acts as an indicator for the delineation of fresh water by the salt interface.

The results of the mg/Ca ratio in this study range from 0.08 to 1.09, with an average and SD 0.56 ± 0.39 (Table 2). These results show a strong deviation from the mean sea water (3.30) obtained, while the results are similar to those of early Cretaceous brine (0.501) obtained from a study in Israel by Bentor.¹⁸

The average chemical ratio of groundwater ions in this area deviates from the sea water ratio, however, there are some places where the ionic coefficient in the groundwater closely approximates those of seawater.

The critical ratio $(\text{Na}+\text{K})/\text{Cl}^-$ range from 0.55 to 4.04, with an average and SD 1.45 ± 1.03 (Table 3). In addition to BH1, BH2, BH9 and BH15, which indicators are similar to seawater and indicate possible freshwater marine mixing, all other wells have ionic coefficients that deviate from mean sea water. CEV seawater varies from 1.2 to 1.3, where the low salt of inland waters give values close to zero, positive or negative.¹⁹ CEV values for underground exploration areas are generally below 0.5, ranging from -3.04 to 0.45, indicating that the origin of groundwater is internal.

Table 3 Ionic ratio versus sea value

Options	Mg/Ca	Na/K	Ca/Na	/Cl (Na+K)	HCO ₃ /Cl	TAK4/Cl	CEV
BH1	1.09	0,63	8.73	0.91	9.19	0,89	0,09
BH2	0.88	0.88	8.69	0.74	6.98	0.44	0.26
BH3	0.90	2.07	5.40	1.00	7.02	0.78	0.00
BH4	0,11	0,85	5.94	4.04	2.21	0,89	-3.04
BH5	0,69	1,66	1.85	2.62	1.85	0,72	-1.62
BH6	0.25	0,36	18.26	1.46	2.28	0,55	-0.46
BH7	0,08	0,23	21.30	0,55	0,76	0.39	0,45
BH8	0,14	1.81	4.60	1.10	0,70	0.51	-0.1
BH9	0.28	1,66	2.22	0,80	0,14	0.30	0,20
BH10	0.91	1.00	8.25	0,61	5.54	0,63	0.39
BH11	0.19	1.13	2.49	1.51	0,45	0.67	-0.51
BH12	0,55	1.20	2.12	0,55	0,03	0,14	0,45
BH13	0,23	4.18	1.62	2.76	0.56	1,66	-1.76
BH14	1.09	5.84	1,78	2.35	6.30	0.66	-1.35
BH15	0,96	0,69	11,69	0,77	5.70	0,85	0,23
Options	Mg/Ca	Na/K	Ca/Na	/Cl (Na+K)	HCO ₃ /Cl	TAK4/Cl	CEV
Min	0,08	0,23	1.62	0,55	0,03	0,14	-3.04
Max	1.09	5.84	21.3	4.04	9.19	1,66	0,45
Average	0.56	1.61	7.00	1.45	3.31	0.67	-0.45
SD	0.39	1.51	6.09	1.03	3.11	0,35	1.03
Sea water*	3.300	46.970	0,044	0.871	0,004	0,105	-
E.Cret.**	0.501	105.060	0,105	0.882	0,007	0.009	-

*Average based on the values of the data for sea water.22

**Based on data for early Cretaceous brines in Israel.18

Variations of HCO₃/Cl, Na+K, and the coefficients of mg/Ca with TDS show similar trends and undergo similar interpretations, whereas the /Cl (Na+K) region showed different trends compared to TDS. The ionic coefficient of HCO₃/Cl versus TDS, while the ionic coefficient of Na+K compared to TDS. The ionic coefficient mg/Ca vs. TDS during ionic coefficient /Cl (Na+K) versus TDS.

Conclusion

The classification of groundwater was achieved using Piper, Durov, rigid and Gibbs diagrams. Piper diagram shows two types of dominant water; MG-HCO₃ and Ca-HCO₃ hydrochemical facies. The rigid diagram shows four separate figures representing different sources for groundwater in the area.

The groundwater class I includes BH1, BH2, BH3, BH10, BH14 and BH15, which are Ca²⁺, mg²⁺ and 3 rich in HCO. Class II includes BH4, BH6, BH7 and BH8, which are Ca²⁺ and HCO₃ rich. Class III includes BH5, BH9, BH11 and BH13, which are Ca²⁺, Na⁺+K, Cl- and HCO₃-rich. Class IV include BH12, which are Ca²⁺ and Cl-rich. Durov diagrams show three geochemical processes that can affect the Genesis of water, which includes; (i) ion exchange, (ii) simple decay

or mixing, and (iii) probably mixing or rarely decaying influences.

Gibbs shows that chemical weathering of rocks and sediments are the main aspects of the impact on the quality of groundwater. Different ionic ratios; Mg/Ca, HCO₃/Cl, (Na+K)/Cl, Na/K, Ca/Na, therefore 4/Cl and CEV offer underground sources of internal origin.

Confirmation

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Conflict of interest

Author declares there is no conflict of interest.

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