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HYDROCHEMISTRY AND ENVIRONMENTAL STATUS OF RIVER OWAN WATER, EDO STATE NIGERIA.

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ABSTRACT: *Hydrochemistry of River Owan water and groundwater in its vicinity were examined to decipher their quality status and evaluate the impact of man on the coastal area of the river. Twelve River Owan water and three groundwater samples were subjected to hydrochemical and bacteriological investigations using standard methods. Temperature, pH and electrical conductivity were measured insitu employing pH Testr Meter. The waters were alkaline (average pH of 9.27) signifying a slight trend of alkaline chemical reaction within the system. Electrical resistivity (EC) was virtually less than 1000µS/cm in all water samples indicating fresh water. The dominance of the major ions was as* $Na^{+} > Ca^{2+} > Mg^{2+} > K^{+}$ *and* $HCO_3^{-} > Cl^{-} > SO_4^{2-} > NO_3^{-}$. *The average values of major ions (mg/L) in the order of dominance were 23.15, 11.56, 9.25, 9.07 and 79.63, 48.92, 29.18, 5.49 respectively. Total hardness of the water revealed that 12 out of 15 water samples were under soft water category* $(0 \leq TH \leq 75 mg/L)$. *All water samples tested positive to bacterial infection* $(1.60*10^{2} \leq$ *e-coli* $\leq 8.10*10^{3}$ *Cfu/ml). Anthropogenic activities dominated ionic sources in River Owan while that of the groundwater was mainly geogenic. Much of the natural character of the coastal environment of River Owan has been modified by human activities. Hygiene education of the public must be encouraged in order to ameliorate the unhygienic status of River Owan.*

KEYWORDS: pollution, alkaline, major ions, geogenic, waste dumps.

INTRODUCTION

Water is a key ingredient in food production, sanitation, rural livelihoods as well as ensuring continuity and functioning of ecosystem. It dictates the pace of settlement, agricultural and industrial development of any society and even in recent time, establishment of any human settlement was usually centered on available sources of water supply. In modern time too, issues of water have taken prominences in global matters. In the Millennium Summit of the United Nations in 2000, target was set to reduce in half the proportion of people unable to reach or afford safe drinking water by 2015 (United Nations 2000a). Despite this laudable goal and concerted efforts of the United Nations in collaboration with individual Nations, universal coverage for water and sanitation continue to be inadequate.

Globally, water is abundant especially in the oceans. However, the amount of potable fresh water available is a tiny fraction of the total amount of water in the world. As per WHO (2006) estimates, only 0.007% of all water on earth is readily available for human

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consumption. The fresh water resources are vulnerable to human abuse and not evenly distributed in both time and space. Fresh water resources around the world have been overused, polluted, fought over and squandered with little regard for human health and ecological consequences (Lavado *et al.,* 2004). The finite nature of renewable fresh water makes it a critical natural resource to examine in the context of population growth.
Falconer (2003), described water as one of the world's most precious resource. He highlighted that the challenges of urbanization include how to ensure adequate water supply and a suitable water environment for future generation worldwide. Settlement of Owan community close to River Owan might have been consequent upon the uses of the river's water for domestic and agricultural activities. Freshwater ecosystems are critical elements of earth's dynamic processes and essential to human economies and health.

An increasing population of settlement close to River Owan resulted into increasing anthropogenic activities and continually growing demand on the use of the river's water without taken cognizance of adverse health implications. Open refuse dumps were observed in close proximity to the river (Figure 1). The failure to provide safe drinking water and adequate sanitation services to all people in the world is perhaps the greatest development failure of the twentieth century (Gleick, 1998, 2000). The most egregious consequence of this failure is the high rate of sickness and mortality among young children from preventable water related diseases. The lack of safe drinking water and adequate sanitation measures led to a number of water borne diseases such as cholera, dysentery, salmonellosis and typhoid (Nwidu *et al.,* 2008).

Earth environment is a system that requires careful management. This management issues is not restricted to global/continental measures and in some instances could not be handled alone locally. However, it is an issue that must be tackled effectively to warrant a decrease in the total population at risk from water related diseases. This research becomes necessary because the community that settled close to River Owan has little awareness about the dangers inherent in contaminated water. Research on hydrochemistry and quality status of Owan River water was embarked upon in an attempt to decipher the quality status of the water and direct attention to issues of effective management of the environment and the protection of the water qualities therein.

Study area
The study area is located within Longitudes 6°45′ and 6°45.3′ and Latitudes 5°45′ and 5°47.5′ E. and is situated within Owan West Local Government Area. River Owan rises from the Northwest of Otuo and flows South West to Eme and Uhonmora before turning South West to join River Ose in Ondo State (Figure 2). The Local Government Area has tropical Climate Characterized by two distinct seasons, namely, the Wet and Dry seasons. The Wet season occurs between April and October with a break in August and average rainfall which ranged from 1800mm – 2500mm while the dry season last from November to April. The harmattan season is experienced between December and January. The various periods highlighted may vary slightly arising from recent change in climate.

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Geology of the study area.

Geology of the area revealed sedimentary rocks comprising mainly of sandstone, clay, clayey sand and shale of Quarternary age. The area belongs to the gently dipping sedimentsry rocks of the Benin Flank Section of the Eastern Nigeria Dahomey Embayment that lies unconformably on the Basement Complex rocks (Onuoha, 1999). The sedimentary rocks strike generally in the NE – SW direction and dip in the SW direction, suggesting that the rocks were affected by the Pan-African Orogeny.

Figure1. Typical example of waste dump close to River Owan channel

METHODS

Twelve River Owan water samples and three groundwater samples within its vicinity was collected in preconditioned polyethylene bottles for hydrochemical investigations. Sampling of groundwater within the vicinity of River Owan became necessary to foster comparison of quality status with River Owan water. All the samples were analyzed for major ions ($Ca^{2+,}$ Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-} , SO_4^{2-} , Cl^{-} and NO_3^{-}) using the standard methods (APHA, 1998). Temperature (°C), Electrical conductivity (ECµS/cm) and hydrogen ion concentration (pH) were measured insitu using Portable pH-Testr meter. Bicarbonate (HCO_3^{-}) was determined by titration against standard HCl, Cl^{-} was estimated by titration against standard solution of $AgNO_3$ while SO_4^{2-} was determined gravimetrically. Ca^{2+} and Mg^{2+} were analyzed by compleximetric titration against standard EDTA solution while the analysis of Na^{+} and K^{+} was by flame photometry. NO_3^{-} was determined colorimetrically using spectrophotometric technique (APHA, 1998). For *E. coli* count, multiple fermentation tubes containing MacConkey broth were inoculated with 1 ml of sample and incubated at 44^{o} C for 48 hr. The *E. coli* count was evaluated using standard methods (APHA, 1998 and Hulton, 1983). Total hardness (TH) was estimated using:

$$TH\ (mg/L) = 2{:}497\ Ca^{2+} + 4{:}115Mg^{2+}\ (UNESCO,\ 2007)$$

Obtained chemical results were subjected to evaluation employing Microsoft Office Excel 2007.

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RESULTS

Results of physical/bacteriologica and chemical parameters are presented in Tables 1 and 2 respectively. The pH of Owan River water varied within range of 8.6 – 11.3 while that of the groundwater was within narrow range (8.3 – 8.9). EC ranged from 45 - 533µS/cm in River Owan water while in the groundwater it ranged between 422 and 1,110 µS/cm. As for the TDS (mg/L), the values in the river water and the groundwater ranged from 33.75 - 399.75 and 316.5 – 832.5 respectively. Total hardness (TH (mg/L)) in all the water samples varied between 6.46 and 474.44 (Table 1).

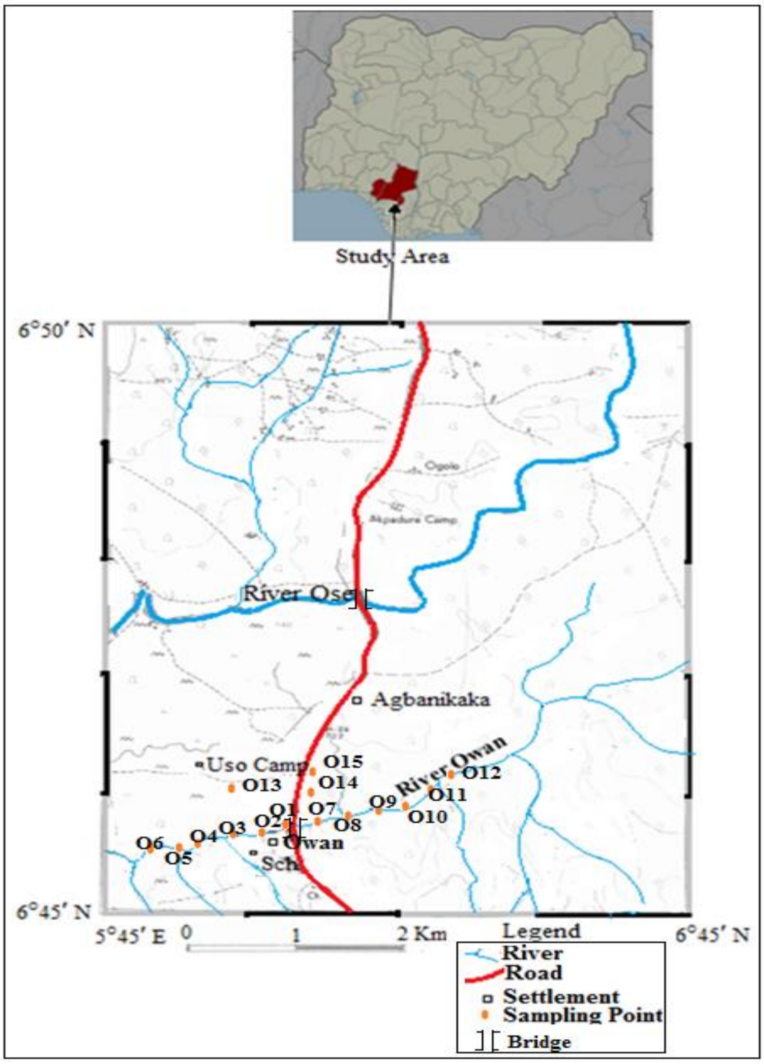

Figure 2. Location of Study

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Table 1. Physical/bacteriological and Revelle index parameters of Water from the Study Area

Code	**Temp.**	**pH**	**EC (µS/cm)**	**TDS (mg/l)**	**TH (mg/L)**	Revelle Index	E-Coli (cfu/ml)
O1	27.6	11.3	69	51.75	12.08	0.51	$1.60*10^{2}$
O2	27.8	10.6	45	33.75	6.61	0.35	$3.20*10^{2}$
O3	26.9	10.2	45	33.75	6.46	0.98	$2.28*10^{2}$
O4	27.2	9.5	48	36	6.61	0.59	$4.50*10^{2}$
O5	27.1	9.2	58	43.5	7.08	0.48	$4.17*10^{2}$
O6	27.8	9	47	35.25	6.48	0.47	$4.20*10^{2}$
O7	28.3	8.6	533	399.75	120.05	0.39	$8.30*10^{2}$
O8	27.4	9.2	64	48	17.54	0.34	$7.80*10^{2}$
O9	27.1	9.1	46	34.5	6.57	0.42	$5.70*10^{3}$
O10	27.3	8.9	67	50.25	9.78	0.59	$6.70*10^{3}$
O11	27.4	8.8	76	57	10.63	0.59	$7.10*10^{3}$
O12	27.4	8.8	45	33.75	7.19	0.59	$6.40*10^{3}$
O13	28	8.6	422	316.5	63.63	3.40	$8.10*10^{3}$
O14	29.3	8.3	586	439.5	258.28	0.54	$2.20*10^{3}$
O15	28.8	8.9	1,110	832.5	474.44	0.92	$4.10*10^{3}$
Min	26.90	8.30	45.00	33.75	6.46	0.34	$1.60*10^{2}$
Max	29.30	11.30	1110.00	832.50	474.44	3.40	$8.10*10^{3}$
Mean	27.69	9.27	217.40	163.05	67.56	0.74	$2.93*10^{3}$
Stdev	0.67	0.82	312.13	234.09	131.69	0.76	$3.04*10^{3}$
WHO (2006)	-	6.5 – 8.5	1000	600 - 1000	200 - 500	-	0.00

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The concentrations of Ca^{2+} in the River Owan water ranged from 0.94 to 30.32 mg/L while in the groundwater it was between 5.75 – 71.06mg/L. Other major cations (Mg^{2+}, Na^{+} and K^{+}) follow similar trends with concentrations of Mg^{2+}, Na^{+} and K^{+} ranging from11.82 – 71.23mg/L, 38.35 – 199.21mg/L and 4.82 – 27.65mg/L in groundwater while in the River Owan's water, the values ranged from 0.95 - 10.62mg/L, 2.42 – 28.11mg/L and 2.20 – 35.53mg/L respectively. As for the major anions, HCO_3^- SO_4^{2-}, Cl^- and NO_3^- had the following respective concentrations ranges in groundwater; 36 – 134.2mg/L, 26.08 – 103.88mg/L, 72 – 122.4mg/L and 7.66 – 11.19mg/L while in River Owan's water the concentrations in mg/L ranged from 36.60 – 256.20m, 0.86 – 44.61, 21.6 – 100.8 and 0.47 – 7.08 respectively (Table 2).

Table 2. Result of Chemical Parameters of Water Samples from the Study Area

Code	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	HCO3 (mg/L)	SO_4 (mg/L)	Cl (mg/L)	NO_3 (mg/L)
O1	2.23	1.56	4.23	8.82	85.4	0.86	43.2	0.47
O2	1.01	0.98	2.45	2.34	61	7.76	21.6	4.06
O3	1.00	0.95	2.42	2.2	36.6	9.05	36	6.43
O4	1.01	0.98	2.63	3.01	61	21.34	36	2.18
O5	1.10	1.04	2.81	4.23	60.4	25.65	28.8	6.76
O6	0.94	0.99	2.6	2.34	61	28.23	28.8	4.14
O7	30.32	10.62	28.11	35.53	256.2	44.61	100.8	2.75
O8	2.45	2.74	5.42	23.24	61	29.96	21	4.47
O9	1.01	0.97	2.78	2.56	85.4	33.19	36	3.32
O10	1.53	1.43	3.64	4.33	48.8	25.86	28.8	4.31
O11	1.62	1.58	4.11	3.34	48.8	7.33	28.8	7.08
O12	1.11	1.06	2.83	2.23	48.8	18.32	28.8	6.76
O13	5.75	11.82	45.62	4.82	36	26.08	122.4	7.66
O14	51.23	31.25	38.35	27.65	134.2	55.63	72	11.19
O15	71.06	71.23	199.21	9.45	109.8	103.88	100.8	10.76
Min	0.94	0.95	2.42	2.20	36.00	0.86	21.00	0.47
Max	71.06	71.23	199.21	35.53	256.20	103.88	122.40	11.19
Mean	11.56	9.28	23.15	9.07	79.63	29.18	48.92	5.49
Stdev	21.79	18.96	50.79	10.71	55.74	25.20	33.16	3.00
WHO 2006	75	50	20	-	<100	250	250	50

Graphical plots in forms of Gibbs diagram and variation plots are presented in Figures 3 and 4 respectively. In addition, the waters classifications are represented by the Piper trilinear diagram (Figure 5) and the Schoeller diagram (Figure 6)

DISCUSSION

The range of pH in the waters of the study area with pH>7 signifies a slight trend of alkaline chemical reaction within the system. Both the river water and groundwater are alkaline waters with values exceeding approved WHO (2006) standard for drinking water in 14 samples (>93%). Drinking alkaline water helps people with acidosis, detoxicate some harmful heavy metals, assist in weight loss and can reduce harmful cholesterol level

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significantly (Abraham and Jorge, 2011, Ong, 2004, Rylander and Ragnar, 2004 and Wynn *et al.*, 2008). However, alkaline water can cause nutritional imbalance if consumed in excess.

The EC of the river water is generally low than 80µS/cm except in location 07 with EC value of 533µS/cm arisen from local anthropogenic activity. The groundwater has higher EC values ranging between 422 and 1,110µS/cm. Electrical conductivity may be attributed to leaching processes along the flow direction, high rates of evaporation and anthropogenic activities prevailing in the area (Adil *et al.*, 2012). Electrical conductivity shows the total soluble salt content in water. The high EC values of groundwater arose from longer residence time allowing rock-water interactions to take place. The deepest well (015) with depth of about 37m has the highest EC values (1,110µS/cm) while the shallow well (depth of 3.6m) has the least value of 422µS/cm. EC in all water samples are less than 1000µS/cm except in location 015. Hence the waters in the study area are fresh (Freeze and Cherry, 1979).

The determination of total dissolved solids is a measure of all salts in solution or elements dissolved in water. This can include inorganic anions (negative charged ions) like Carbonates, Chlorides, Sulfates and Nitrates. The inorganic cations (positively charged ions) include Sodium, Potassium, Calcium and Magnesium. Water with high TDS produces scales on cooking vessels and boilers (Vanitha and Shunmugavelu, 2012). TDS values are generally low. The TDS values are less than 500mg/L except location O15 with 832.5mg/L. The TDS values are within approved standard (WHO, 2006) as none of the values exceeded the maximum permissible level of 1000mg/L. It is clear that there is a gradual increase in water salinity of the river from upstream to downstream and this coincides with its flow direction.

The presence of cations (Ca^{2+}, Mg^{2+}) and anions (CO_3^{2-}, HCO_3^-, SO_4^{2-} and Cl^-) in water are responsible for the hardness of water. Water hardness has no known adverse effects; however, some research work indicated its role in heart disease (Schroeder, 1960). Hard water is unsuitable for domestic use. In River Owan water, the total hardness varied between 6.46 to 120.5mg/L while that for the groundwater was from 63.63 - 474.44mg/L. Hardness classification (Sawyer and McCarty, 1967) revealed that in River Owan water, 11 samples were under soft water category ($0 \leq TH \leq 75mg/L$) while one sample fell into the moderately hard class ($75 \leq TH \leq 150mg/L$) indicating suitability for domestic uses. As for the groundwater samples one sample fell under soft water class, another one in the hard water category ($150 \leq TH \leq 300mg/L$) while the remaining one sample fell into the very hard class (TH>300mg/L). The health implications of long term consumption of extremely hard water has been suggested to result into an increased incidence of urolithiasis, anecephaly, pre-natal mortality, some types of cancer and cardiovascular disorders (Agrawal and Jagetai 1997; Durvey *et al.*, 1991).

It's observed that Ca^{2+} concentrations were high in the groundwater (5.75 – 71.06mg/L) compared to River Owan's water (0.94 – 30.32mg/L). The permissible limit for Ca^{2+} for drinking water is specified as 75 mg/l (WHO 2006) and all water samples from the study area had concentrations within the approved permissible limit. The dominance of the major ions were $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$. Rock-water interactions in the groundwater had enough time to take place compared to the River water which resulted into higher values of ions. The concentrations of dissolved ions in groundwater samples are

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generally governed by lithology, nature of geochemical reactions and solubility of interacting rocks. The functional sources of dissolved ions can be broadly assessed by plotting the samples according to the variation in the ratio of Na/ (Na+Ca) and Cl/ (Cl+HCO_3) as a function of TDS (Gibbs, 1970). Gibbs diagram clearly demonstrates the dominance of non-geogenic activity being responsible for the chemistry of Owan River water as most of the samples fell away from the three major natural factors viz., precipitation dominance, rock dominance and evaporation-crystallization dominance indicating that the chemistry of water is decided predominantly by anthropogenic activities (Figure 3). Most of the groundwater samples fell into the rock-water dominance indicating geogenic source of ions in the groundwater of the study area i.e. chemical weathering of rock-forming minerals along with dissolution of the rock forming minerals.

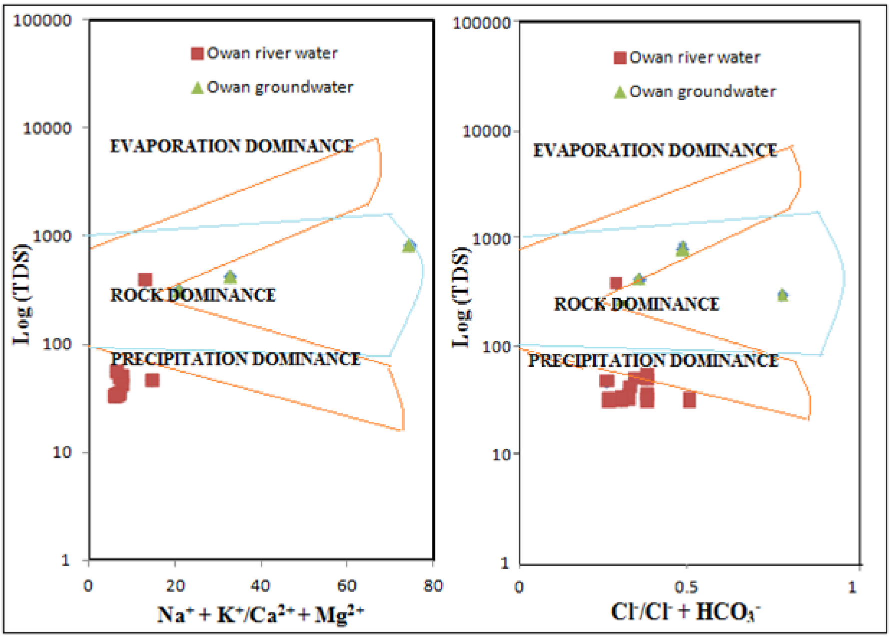

Figure 3. Mechanisms governing groundwater/River Owan chemistry (after Gibbs, 1970)

To further assess ionic sources in the waters of the study area, correlation and trend line analysis were employed. The major hydrochemical ions contributor to the waters of the study area will definitely be from Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, and SO_4^{2-}. Cross plots and trend analysis of few cations and anions as well as TDS were made as presented in Figure 4. Strong correlation coefficients of 0.9 (Ca^{2+} vs. SO_4^{2-}), 0.7 (Cl^- vs. $Na^+ + K^+$) and 0.91 (Mg^{2+} vs SO_4^{2-}) revealed that the nature and origin of these ions would have come from the same source, especially from rock-water interaction (Figure 4). It was observed from the trend diagrams that HCO_3^- did not show much linearity with regards to TDS (r = 0.52) whereas SO_4^{2-} vs. TDS (r = 0.90) as well as Cl^- vs. TDS (r = 0.82) showed improved linearity suggesting that in addition to hydrochemical changes, anthropogenic activities were also responsible for the variation in the chemical evolution of the River Owan water and that of the groundwater in the study area. Furthermore, NO_3^- in water may result from point sources pollutants such as sewage disposal systems and livestock facilities, non-point sources such as fertilized cropland, parks, golf courses, lawns, and gardens or naturally occurring sources of nitrogen.

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In this research, NO_3^- vs. Cl^- has low correlation (r = 0.39) indicating that the NO_3^- might have originated from different source or that anthropogenic contributions to the chemical concentrations of Cl^- in the waters of the study area was minimal. There is high correlation between NO_3^- and TDS (r = 0.78). NO_3^-, unlike many ions is not derived from rocks; rather it is often associated with anthropogenic activities mostly faecal pollution (Adeyemi *et al*,. 2003). Therefore, both rock-water and anthropogenic activities contributed to ions in the waters of the study area. This submission is supported by the fact that all water samples tested positive to bacterial infection with e-coli that ranged from $1.60*10^2$ – $8.10*10^3$ cfu/ml (Table 2). The bacterial contamination of water was mainly due to the unhygienic conditions of the people living within the vicinity of river Owan. Open dump of refuse and washing of house hold utensils to the flowing river were observed during the sampling exercise of this research (Figure 1). These ugly trends can be reversed if necessary sanitary conditions are maintained.

Water classification

The Piper trilinear diagram (Piper, 1944), shows the relative abundance of the major ions of water analyses (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and HCO_3^-) and produces a single point for each sample. This plotting technique allows numerous water analyses to be plotted on a single diagram and hence provides the user with a quick and concise means of visually comparing chemical similarities and differences among groups of water analyses as well as mixing trends between different waters. The general distribution of River Owan water and the groundwater of the study area are shown on a Piper diagram (Figure 5). The diagram revealed the analogies, dissimilarities and different types of waters in the study area. On the basis of this diagram, it is clear that in all waters, alkali elements (Na^+ + K^+) were more than alkali earth elements (Ca^{2+} + Mg^{2+}) and strong acids (Cl^- + SO_4^-) higher than the weak acids (HCO_3^-). The abundance of the alkali elements is attributed to dissolution of feldspar rich minerals in the aquifer matrix. Generally, water chemistry is related to the different rocks and their interaction with water as well as impact of human activities which tend to alter the groundwater quality.

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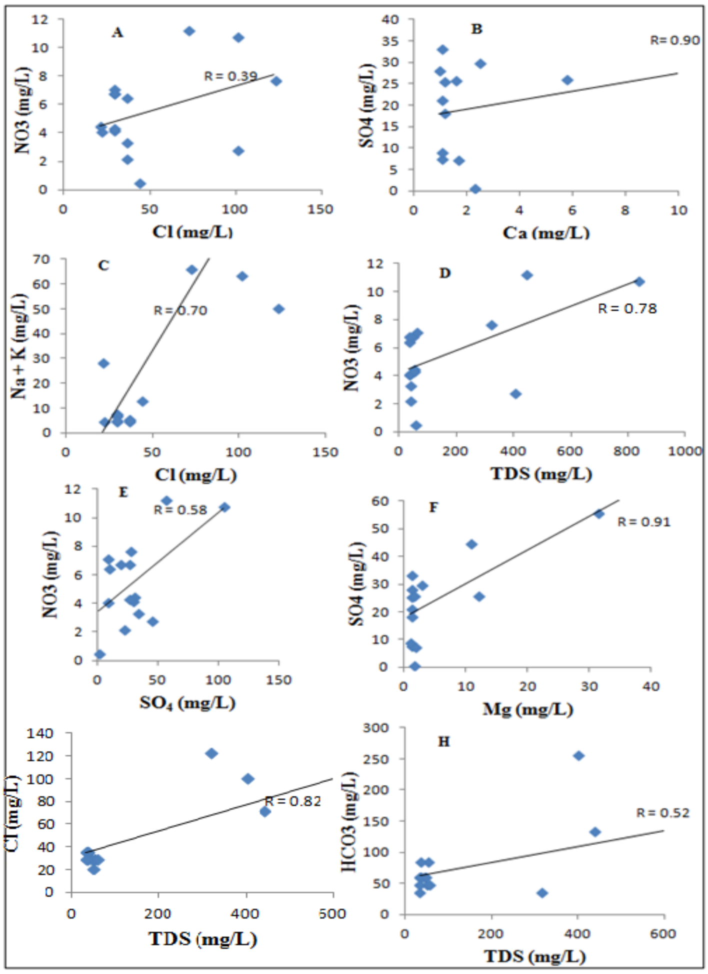

Figure 4. Variation diagrams of some ions in water samples of the Study Area

Furthermore the waters were classified into hydrochemical facies representing water types based on the subdivisions of the Piper trilinear diagram in manner suggested by Ravikumar et al., (2010). Using the aforementioned water classification scheme, the waters of the study area are classified into four water types namely Na-Cl (66.67%), mixed Ca-Mg-Cl (13.33%), mixed Ca-Na-HCO_3 (13.33%) and Ca-HCO_3 (6.67%). The Piper diagram discriminate the groundwater from the River Owan water with majority of the groundwater in the mixed Ca-Mg-Cl water type.

Logarithmic diagrams of major ion analyses in meq/l employing Schoeller diagram (Figure 6) illustrate different water types on the same diagram. Similar waters exhibit similar fingerprints. The difference between ionic composition lines of waters on the Schoeller diagram (Schoeller, 1967) indicated the major water types originating during water–rock interaction as well as impact of anthropogenic activities. The Schoeller diagram revealed Na-Cl water type as dominant while Ca-HCO_3 water type is in the minority.

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Environmental status evaluation

Water pollution could be from wastewater discharge from refuse dumps and faeces sewer water of household waste. Different degrees of contamination are possible over the course of a river arising from localized anthropogenic activities. Thus, evacuation of wastewater containing organic material can lead to ameliorating the degree of cleanliness in an environment.

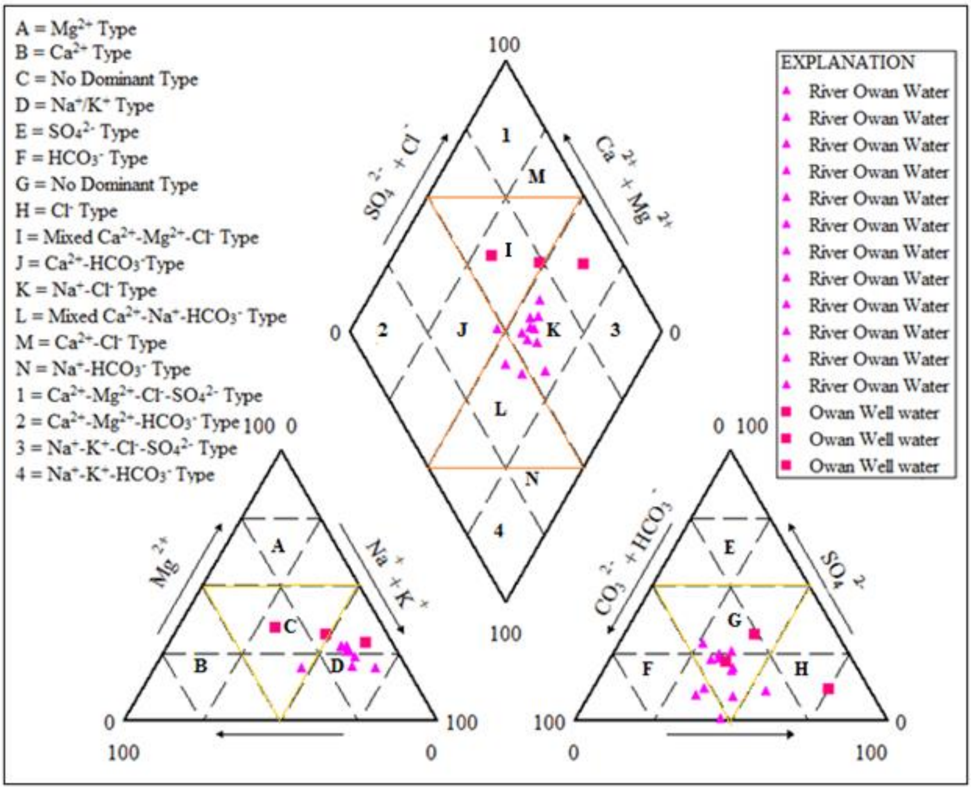

Figure 5. Piper diagram of River Owan water and Owan groundwater

The degree of contamination of the water samples in this study were determined using Revelle index of contamination. The calculation of the Revelle Index (Gounari *et al.,* 2014, Revelle, 1946) was based on the ionic ratio of chloride to carbonate and bicarbonate (Cl / (CO_3+HCO_3)).

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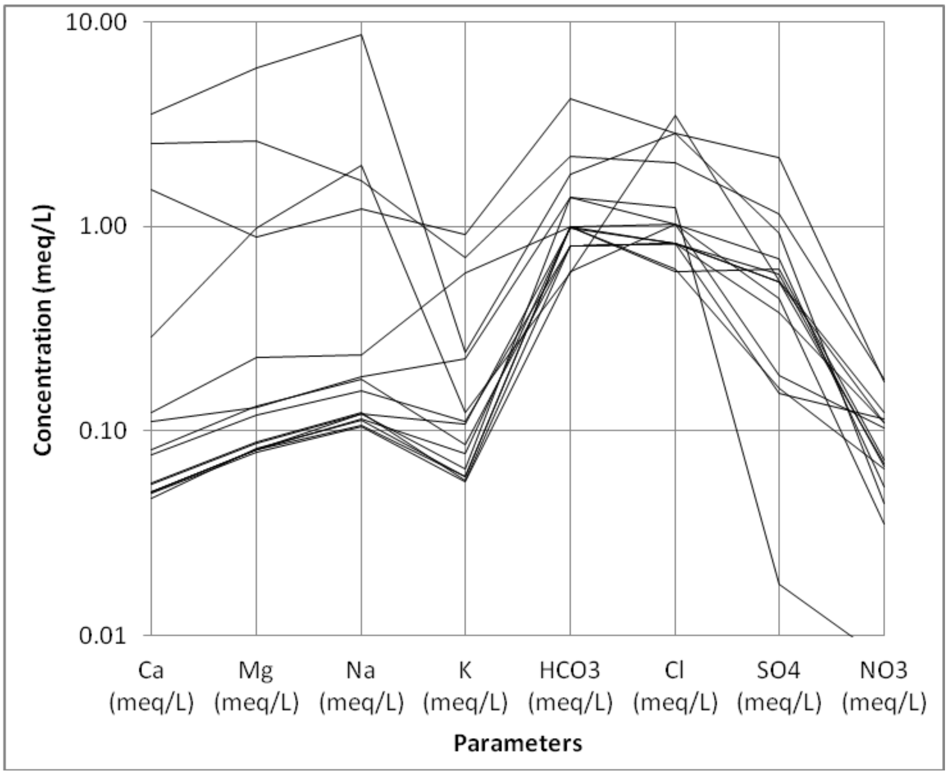

Figure 6. Schoeller diagram of water from the Study Area

Revelle index <1 indicates good water quality. The average values of Revelle Indices in River Owan water and the groundwater within the Owan community are 0.53 (range = 0.34 – 0.98, Standard deviation = 0.17) and 1.62 (range = 0.54 – 3.4, Standard deviation = 1.55) respectively (Table 1). All the values calculated from the River Owan water samples are less than 1 while 2 out of 3 samples from the groundwater also have their values less than 1. The groundwater sample with Revelle index>1 (3.4) must have resulted from localized anthropogenic contamination. Hence, it is concluded that water from the Owan River and the groundwater are good for domestic consumptions based on chemical evaluation.

CONCLUSIONS

This study has thrown light on the hydrochemistry, quality and water facies of River Owan water and the groundwater in its vicinity. Physical and chemical parameters of all the waters fell within the WHO (2006) guidelines for drinking water except pH that exceeded the approved standard value. In addition, all water samples tested positive to e-coli evaluation and depict that the waters, though chemically potable but need to be treated before consumption. The dominance of the major ions is as $Na^{+} > Ca^{2+} > Mg^{2+} > K^{+}$ and $HCO_3^{-} > Cl^{-} > SO_4^{2-} > NO_3^{-}$.

Total hardness of the water revealed that majority of the water samples (12 out of 15) were under soft water category ($0 \leq TH \leq 75 mg/L$). The chemistry of water in the study area was decided predominantly by anthropogenic activities while four water types (Na-Cl (66.67%),

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mixed Ca-Mg-Cl (13.33%), mixed Ca-Na-HCO_3 (13.33%) and Ca-HCO_3 (6.67%)) characterized the study area. River Owan water and the groundwater in its vicinity were infected by bacterial pollutants but chemically suitable for domestic uses. Settlement of people along the coast of River Owan was due to the living resources exploited for food.

Measures such as reducing nutrient discharge, the use of interception fields, collecting/evacuation wastes before reaching the River environment and preventing the use of destructive fishing equipments must be encouraged in order to ameliorate the unhygienic status of River Owan.

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