



Evaluation of Physicochemical Characteristics and Carbonate Equilibria System of the New Calabar River, Choba, Rivers State, Nigeria

OJOBO, KC; *ADOWEI, P

Department of Pure & Industrial Chemistry, University of Port Harcourt, PMB 5323, Choba, Port Harcourt, Nigeria
*Corresponding Author Email: pereware.adowei@uniport.edu.ng

ABSTRACT: Carbonate equilibrium helps to critically determine the degree or level of pollution and its possible source. In this study the physicochemical properties and carbonate equilibria system of the New Calabar River, Choba, Rivers State, Nigeria was evaluated using standard techniques by analyzing the pH, total dissolved solid, bicarbonate ion, sulphate ion, chloride ion, total alkalinity and total hardness of five samples collected from strategic points along the River. Data obtained show that the pH ranged 5.93-6.33, while TDS values varied from 4770mg/l to 5280mg/l. The total alkalinity of the sample 1, sample 2, sample 3, sample 4 and sample 5 analyzed and their results are 70mg/l, 68 mg/l, 66 mg/l, 73 mg/l and 60.5 mg/l respectively. The total hardness of sample 1, sample 2, sample 3, sample 4 and sample 5 collected from the New Calabar River and the results are 913mg/l, 904 mg/l, 942 mg/l, 933 mg/l and 939 mg/l. The sulphate ion concentration for sample 1, sample 2, sample 3, sample 4 and sample 5 are 519.20mg/l, 510.5mg/l, 552mg/l, 543mg/l and 549.00mg/l, while the Chloride concentration varied from 3390.5 mg/l to 4,802 mg/l mg/l. Result indicated that all physiochemical parameters apart from total alkalinity was not within the WHO guidelines or standard and the river shows presence of weak acid deposits but very high concentration of chloride ion which indicates higher degree of organic pollution and also acidic in nature. Thus, the river poses a health risk to the rural communities who rely primarily on them as the only source of domestic water supply.

DOI: <https://dx.doi.org/10.4314/jasem.v25i10.12>

Copyright: Copyright © 2021 Ojobo and Adowei. This is an open access article distributed under the Creative Commons Attribution License (CCL), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Dates: Received: 22 August 2021; Revised: 17 September 2021; Accepted: 06 October 2021

Keywords: New Calabar River, Carbonate Equilibria, Physicochemical parameters

Surface water includes water in streams, rivers, lakes, oceans. Coastal pollution has been increasingly recognized as a significant and expanding environmental problem in many developing nations. In Nigeria, the marine environment is subjected to contamination by persistent organic pollutants (POPs) and metals largely due to the discharge of untreated domestic and industrial waste waters, agricultural waste water, boat traffic, oil transportation, oil pipeline leakages/spillages and atmospheric fallouts (Odukuma and Okpokwasili, 1997; Otokunefor and Obiukwu, 2005; Rim-Rukeh *et al.*, 2006; Abu and Egenonu, 2008; Nduka *et al.*, 2008; Udotong *et al.*, 2008). Aquatic animals are exposed to chemicals in both the dissolved (ambient water) and dietary (sediment or prey) phases. Carbonate equilibria is a fundamental concept within the geosciences. An understanding of carbonate equilibria is necessary for geologic studies of weathering, surface and ground water chemistry, and global climate. Adejuwon and Adelakun (2012) examined the physicochemical and bacteriological analysis of surface water in Ewekoro Local Government Area of Ogun State, Nigeria - a case study of Lala, Yobo and Agodo Rivers and Water

samples were collected from the rivers in October and December 2008 and the result indicated that total alkalinity, total hardness, calcium, nitrate and calcium carbonate were above maximum permissible limits. The rest of the parameters measured fall within these limits. The implication of the results is that the rivers pose a health risk to the rural communities who rely primarily on them as the only source of domestic water supply but favorable to aquatic organism. Gupta *et al.* (2013) carried out analytical research study to determine the physico-chemical properties of Yamuna River water from nine different sampling sites in Agra City. River water samples were collected from nine locations (viz Runkata, Naire Ghat, Kailash Mandir, Pohiya Ghat, Balkeshwar, Rambagh, Etmad-ud-daula, Hathi Ghat and Tajganj) of Agra City, during the months of March and April, 2011 and River water samples were taken to the laboratory and analyzed. The analysis was done for the parameters like Turbidity, pH, Total Dissolved Solids, Electrical Conductivity, Total Hardness, Total Alkalinity, Chloride, Calcium and Magnesium. pH shows that Yamuna River water is alkaline in nature. Turbidity and Total Dissolved Solids was found above the WHO

*Corresponding Author Email: pereware.adowei@uniport.edu.ng

permissible limits. Although, in this study the total dissolved solids was not in co-relation with other carbonate equilibrium parameters of surface water. All other physio-chemical parameter established shows that carbonate equilibrium existed between the carbonate systems in the Yamuna River. Saravanakumar and Ranjith (2011) evaluated ten different points of water samples in India. The parameters studied were pH, total alkalinity, total hardness, turbidity, chloride, sulphate, fluoride, total dissolved solids and conductivity. From overall analysis, it was observed that there was a slight fluctuation in the physicochemical parameters among the water samples studied. Comparison of the physicochemical parameters of the water sample with WHO and ICMR limits showed that the water is highly contaminated and account for health hazards for human use. In the study the total hardness was found in the sample water ranges from 220-310mg/l, which shows that water is safe for drinking purpose. Hardness has no known adverse effects on health. However, maximum permissible level prescribed by WHO for drinking water is 500 mg/l as set. According to some classifications, water having hardness up to 75mg/l is classified as soft, 76-150 mg/l is moderately soft, 151-300 mg/l as hard (Dufor aand Becker, 1964) and more than 300 mg/l as very hard. On this basis, the results show that all the samples were moderately soft except sample B4 (Ravisankar and Poogothai, 2008). Total alkalinity of water in terms of CaCO_3 varied from 270-320mg/l. The values of total alkalinity were comparatively moderate. The water for domestic use having alkalinity less than 100mg/l is safe. From the study the results shows that the samples were a co-relation between the alkalinity and the hardness. Thus, the carbonate equilibrium of the system was established. One of the earliest water analysis research study specifically on carbonate equilibrium of fresh water was investigated by Andrew and Raymond (1984) in analyzing the carbonate equilibrium of fresh water, a strategy for determining the hydrogen ion content of fresh waters was proposed that involves total dissolved inorganic carbon (DIC or σCO_2) and CO_2 partial pressure (P_{CO_2}) measurements rather than pH electrode measurements. This recommendation derives from discrepancies between pH and carbon dioxide equilibria measurements made on several soft water lakes at the experimental Lakes Area, northwestern Ontario. The pH calculated from DIC, P_{CO_2} , and the first dissociation constant of carbonic acid (K_1) data was consistently higher than that directly measured with a pH electrode. Similarly, calculation of P_{CO_2} of surface waters from pH, DIC, and K_1 data gave values up to twice that of atmospheric saturation despite repeated equilibrations with atmospheric P_{CO_2} . Laboratory experiments

demonstrated that the high dissolved organic carbon content of these waters appears to alter the electrode response yielding pH values lower than the true values. Furthermore, the uptake of protons by weak organic acid anions appear to be the cause of the measured difference between total (Gran) and carbonate (DIC- dissolved CO_2) alkalinity. Therefore bicarbonate ion concentration must be calculated from the difference between the total dissolved inorganic carbon content and uncharged dissolved CO_2 content. These procedures should provide more accurate and consistent results in the pH trend in surface waters and hence yield a solid baseline against which the effects of acid precipitation can be assessed. Amosa (2016) employed kinetic model to determine the carbonate equilibrium of an aqueous medium (hard water). The New Calabar River is one of the most stressed Rivers in the Niger delta of Nigeria, which takes its rise from Elele-Alimini where is closer to industries such as drilling company and other production industry and it is joined by a smaller tributary river at Aluu, which takes its rise at Isiokpo. The New Calabar River is an important river in Rivers state and its region due to locations across communities and as a source of major natural water it provides these communities with domestic drinking water, sufficient foods by providing fishes and a means of agricultural activities. The water across the season exhibited variation in the increase and decrease in the physicochemical parameters such as pH, alkalinity and hardness and this could be attributed to the industrial activities going on in and around the river and level of discharge of domestic waste into the river which are prevalent along the upstream of the river. Thus, the carbonate equilibrium state of the river can be affected by absorbing CO_2 , which is a notable greenhouse gas emitted by the industrial activities in these areas and other human activities such as burning of fossils fuel. Thereby, affects the water quality and the lives of the aquatic organisms therein.

The importance of water quality monitoring of the New Calabar River cannot therefore be over emphasized. The New Calabar River is an important river in Rivers state and its region due to locations across communities and as a source of major natural water. Due to high population density, location and increased industrial activities in areas along the stretch of the river, water and sanitation infrastructure in these areas are now overstretched. As a result, the new Calabar River has become a receptacle for all genera of wastes as industries along the stretch of the river now discharge their effluents directly into the River. Although series of work have been carried out in different reaches of the river, but this study therefore focuses on strategic points located at the New Calabar

River identified as fishing spot, Olukwu spot, sand digging spot, python spot and River bank spot and this will complement the existing knowledge on the physico-chemical parameters of the River.

Hence, the objective of this study is to evaluate the physicochemical characteristic and the carbonate Equilibria system of the New Calabar River, Choba, Rivers State, Nigeria

MATERIALS AND METHODS

Description of the Study Area: The New Calabar River (Figure 1) and its tributaries are all located in Rivers State. It is a low lying deltaic river which rises at approximately latitude $5^{\circ}10'N$ and longitudes $6^{\circ}50'E$ near Elele-Alimini and flows Southward for roughly 150km before its discharge into the Atlantic Ocean at about latitudes $4^{\circ}20'N$ and longitudes $7^{\circ}00'E$ (Francis and Elenwo, 2012). It occupies a low relief region, ranging from 0-50m above sea level at the low zone,

to 50-100 above sea level at its source. The soil of the river basin consists of clays, silt and sand, with high organic matter. The river is unidirectional in the upper reach and tidal in the lower reach. Its upstream reach is fresh water with tropical lowland, dense rainforest through secondary forest/farmland vegetation. The downstream reach is however brackish and consist of Mangrove swamp forest. The Choba section of the New Calabar River is within ObioAkpof Local Government Area alongside the Port Harcourt Local Government Area which forms the Port Harcourt Urban Area in Rivers State, Eastern Niger Delta, Nigeria. Rivers State is located in the South-South geopolitical zone of Nigeria and the eastern sector of the oil-rich Niger Delta region of the country. Port Harcourt doubles as the Capital City of Rivers State, and also the largest city in the State. The Port Harcourt urban area has a total population figure of 1,382,592 (NPC, 2006).

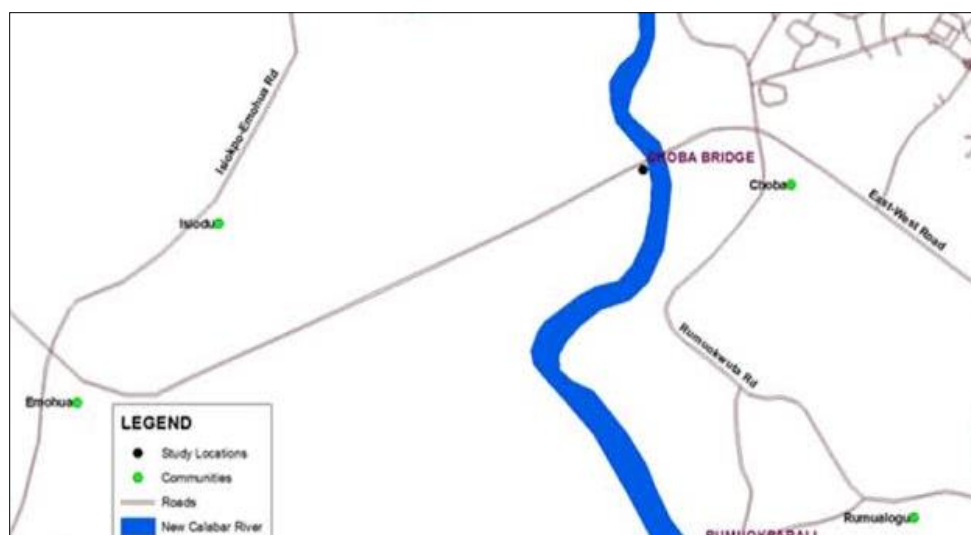


Fig 1: Map of study area

Sample Collection and Preparation: Five (5) samples were aseptically collected and analyzed between on 28th- 30th April 2021, using 500 ml sterilized amber bottles at early morning when activities at the source sites were at their peak. Each sample was collected from five different location of the new Calabar River at Choba and these locations include; Fishing spot (Plate 1), Olukwu spot (Plate 2), Sand digging spot (Plate 3), Python spot (Plate 4), and River Bank spot (Plate 5), (i.e. at the river bank). These samples were identified as Sample 1, Sample 2, Sample 3, Sample 4 and Sample 5 respectively. Standard sampling and analytical methods were employed to investigate each water sample to assess the physicochemical characteristics of the water samples.



Plate 1: Fishing Spot, New Calabar River

OJOBO, KC; ADOWEI, P



Plate 2: The Olukwu spot, New Calabar River (Sample 2).



Plate 3: Sand digging site, New Calabar River (Sample 3).



Plate 4: The python spot of the New Calabar River (Sample 4).



Plate 5: The River bank spot, New Calabar River (Sample 5).

Determination of pH: The pH of the water samples was determined using the Hanna microprocessor pH meter. It was standardized with a buffer solution of pH range between 4-9.

Determination of Alkalinity: 50mL of the sample was pipetted into a clean 250mL conical flask. Two drops of methyl red indicator were then added and the solution titrated against a standard 0.01M NaOH solution to a pink end-point. (American society for testing and Materials, 1982). The total alkalinity was calculated as

$$\text{Total alkalinity (T) as mg/L CaCO}_3 = \frac{V_2 \times 1000}{\text{mL of sample}}$$

Where V= Volume of acid used.

Each samples analyzed was compared with the WHO standard for total hardness and total alkalinity of water for human health and consumption using the table below:

Table 3.0: WHO standard for total hardness and total alkalinity of water.

Total hardness	500mg/l
Total alkalinity	500mg/l

Determination of total Hardness: 25mL of the samples was placed in different clean 250mL conical flask. To this were added 3mL of ammonium chloride in concentrated ammonia buffer (NH₄Cl/conc.NH₃) and 2 drops of Eriochrome Black T indicator. This was titrated against 0.01M EDTA solution until there was a color change from violet to blue. And the hardness was calculate thus:

$$\text{Hardness in mg/l CaCO}_3 = [V \times M \times 100,000] / \text{ml of the sample used}$$

Where M= Molarity of EDTA used
V= Volume of EDTA used.

Determination of the major anions: The bicarbonates, chloride and sulphate ions were analyzed by titrimetric method while nitrate analysis was carried out by spectrophotometer method. The quality control measure of Batley and Gardner were adhered to during the sampling and analysis (American society for testing and Materials, 1982).

Statistical Analysis: Statistical tools include the use of histogram to present and interpret the data with the aid of Microsoft excel.

RESULTS AND DISCUSSION

This study assessed carbonate equilibrium in New Calabar River, Rivers State. The values of various physicochemical parameters for measurement of carbonate equilibrium are presented from figure 4.1 to figure 4.7 in histograms representing the values of each samples and their standard according to WHO. Figure 4.1 represent the results analyzed for the pH of each sample and their values. The pH of each samples analyzed are Sample 1, (6.32); Sample 2, (6.27); Sample 3, (5.97); Sample 4, (6.33) and Sample 5, (5.93). pH is an important parameter which determines the suitability of water for various purposes. In the present study pH ranged 5.93-6.33. The SON and WHO set a pH guideline value of between 6.5 and 8.5 as generally considered satisfactory for drinking water.

The pH of New Calabar River water of our study area was generally below the guideline value. pH is generally considered to have no direct impact on humans. However, long-term intake of acidic water can invariably lead to mineral deficiencies (Fairweather-Tait and Hurrell, 1996). Figure 4.2 represent the analytical result presented in histogram of the TDS of the samples analyzed. TDS indicates the general nature of salinity of water. Water with high TDS produces scales on cooking vessels and boilers. The TDS values varied from 4770mg/l to 5280mg/l. The TDS values were found very much higher than the limits prescribed by WHO (i.e. 500mg/l). Figure 4.3 represent the analytical result presented in histogram of the total alkalinity of the sample 1, sample 2, sample 3, sample 4 and sample 5 analyzed and their results are 70mg/l, 68 mg/l, 66 mg/l, 73 mg/l and 60.5 mg/l respectively. Alkalinity increases as the amount of dissolved carbonates and bicarbonates increase. Alkalinity level varied from 60.5 mg/l to 73 mg/l in the New Calabar River.

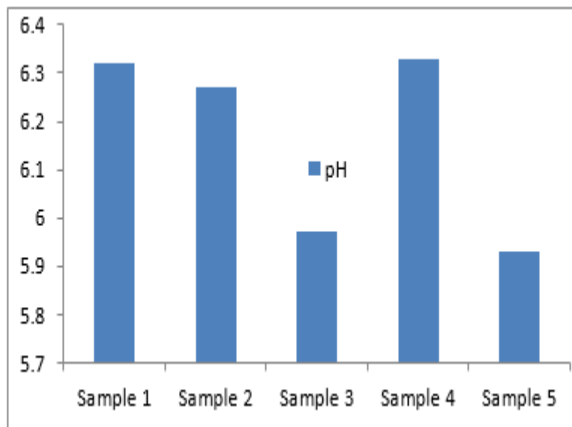


Fig 2: A bar chart showing the pH value of each sample

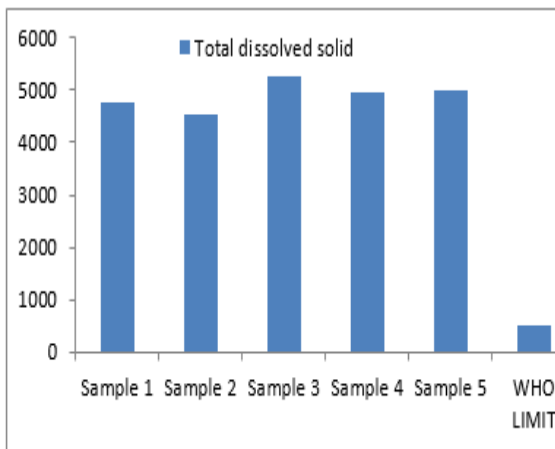


Fig 3: A bar chart showing the amount of total dissolved solid of each sample

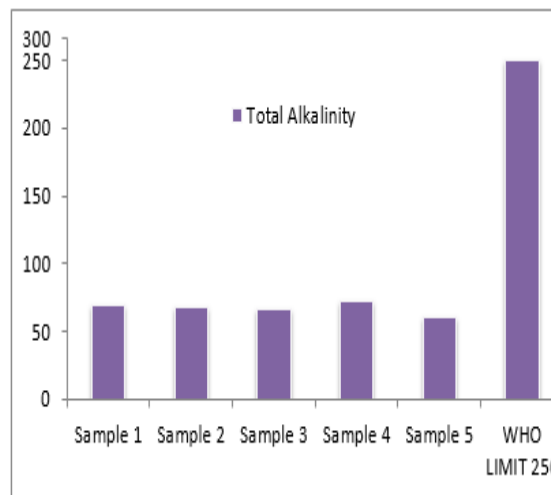


Fig 4: A bar chart showing the concentration of alkalinity in each sample

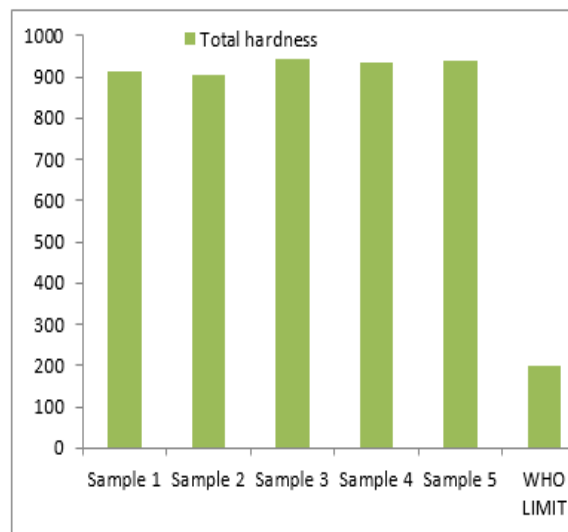


Fig 5: Total hardness of each sample

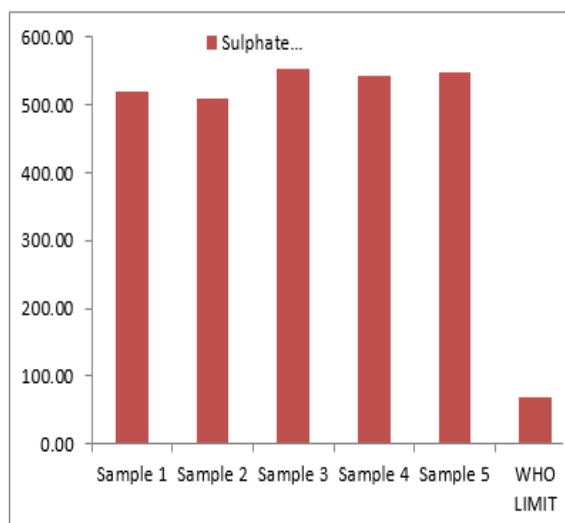


Fig 6: The concentration of sulphate ion found in each sample

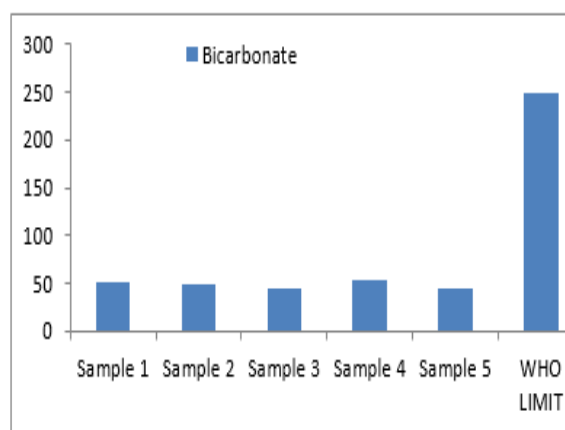


Fig 7: The concentration of bicarbonate in the samples.

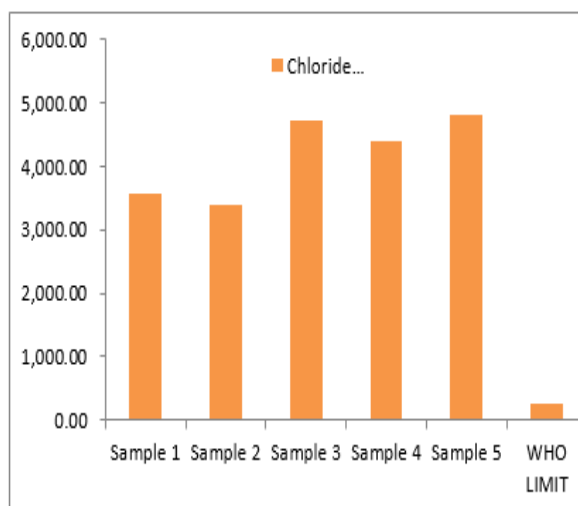


Fig 8: The concentration of chloride ion in the samples

Total Alkalinity value for all the investigated samples were found to be within the limit prescribed by WHO. The histogram in figure 4.4 represent the results of the total hardness of sample 1, sample 2, sample 3, sample 4 and sample 5 collected from the New Calabar River and the results are 913mg/l, 904 mg/l, 942 mg/l, 933 mg/l and 939 mg/l. Total Hardness values ranged from 904 mg/l to 942 mg/l and found above the permissible limit of WHO. According to the WHO standard the New Calabar River is considered very hard. Hardness, whether it is caused predominantly by calcium, manganese or both is usually reported as the equivalent of the total concentration of calcium carbonate (CaCO_3). The total hardness consists of carbonate or temporal hardness and non-carbonate or permanent hardness. Waters become hard primarily due to excessive presence of bicarbonate, chloride and dissolved sulphate in water primarily. The sulphate ion concentration from figure 4.5 for sample 1, sample 2, sample 3, sample 4 and sample 5 are 519.20mg/l, 510.5mg/l, 552mg/l, 543mg/l and 549.00mg/l, while for the bicarbonate ion which is presented as histogram in figure 4.6 for sample 1, sample 2, sample 3, sample 4 and sample 5 are 52mg/l, 48, 45.5 mg/l, 54 mg/l and 44mg/l with a concentration of chloride ion from the results in figure 4.7 are 3570.50 mg/l, 3390.5 mg/l, 4,730mg/l, 4409mg/l and 4,802 mg/l respectively. Chloride concentration in water indicates presence of organic waste particularly of animal origin. Chloride concentration varied from 3390.5 mg/l to 4,802 mg/l mg/l. All the samples were found very much above the permissible limit prescribed by WHO. Chlorides are present in all natural water and are major anions in water and sewage. Sources of chloride include sedimentary rocks, particularly the evaporated salt seeps, oil feed drainage, domestic and industrial contaminants and to some degree, air-borne matter resulting from ocean spray. Apart from some of these sources, precipitation contributed to increase of chloride in these rivers. According to Adejuwon and Adelokun, (2012) most of the chlorine in streams or rivers comes from precipitation. Juang and Johnson (1967) noted that chlorine is deposited in particulate form during the summer and washed away by autumn rains. The salty taste produced by chloride concentration is variable and dependent on the chemical composition of the water, seawater or other saline water (Martins, 1990). High chloride in both surface water and ground water are often due to contamination from ocean water and many brackish supplies (Lennon and Ashley, 1970).

Conclusion: Calcium is usually present in any water system as the carbonate, bicarbonate and sulphate, although in water of high salinity, calcium, chloride or nitrate can also be found. Calcium contributes to the

hardness of water within the bicarbonate, forming temporal carbonate hardness and sulphate, chloride and nitrate forming permanent or non-carbonate hardness. Thus, carbonate equilibrium helps to critically determine the rate or level of pollution and its possible source. In this study it was found that all physicochemical parameters apart from total alkalinity was not within the WHO guidelines or standard and the results indicated that the New Calabar River is polluted and unsafe for human consumption, especially drinking. Also, the river shows presence of weak acid deposits but very high concentration of chloride ion which indicates higher degree of organic pollution and also acidic in nature. Thus, the overall study of the carbonate equilibrium of the New Calabar River is imbalance and when carbonate formation loses equilibrium in natural water, the atmospheric gas carbon dioxide (CO₂) dissolves very easily in water and this might affect the aquatic ecology.

REFERENCES

- Abu, G. O. and Egenonu, C. (2008). The current pollution status of the New Calabar River in the Niger Delta region of southern Nigeria: a survey of antibiograms profile of its bacterial isolates. *Afr. J. Environ. Sci. Tech.* 2, (6): 134-141.
- Adejuwon J. O. and Adelakun M. A. (2012). Physicochemical and bacteriological analysis of surface water in Ewekoro Local Government Area of Ogun State, Nigeria: Case study of Lala, Yobo and Agodo Rivers. *Inter. J. Water Res. Environ. Engineer.* 4(3): 66-72.
- American Society for Testing and Materials (1982). Annual Book of ASTM Standards pp 672
- Amosa, M.K., 2016. Sorption of water alkalinity and hardness from high strength wastewater on bifunctional activated carbon: Process optimization, kinetics and equilibrium studies. *Environ. Technol.*, 37: 2016-203
- Durfor, C.N. and Becker, E. (1964) Public Water Supplies of the 100 Largest Cities in the United States. In: Geological Survey Water-Supply, US Government Printing Office, Washington, Vol. 1812, 364
- Fairweather-Tait, S. and Hurrell, R. (1996) Bioavailability of Minerals and Trace Elements. *Nutrition Res. Rev.* 9, 295-324.
- Francis, A. and Elenwo, U. (2012). Aspects of the biology of trap caught *Chrysichthys nigrodigitatus* (Lacepede: 1803) from the New Calabar River, Nigeria. *Inter. J. Fisheries. Aquacult.* 4(6):9 104.
- Juang, F. and Johnson, N. M. (1967). Cycling of Chlorine through a Forested Watershed in New England. *J. Geophysical Res.* 72: 5641-5647.
- Lennon, F. and Ashley, C (1970). Hydrology for Engineers. Third Edition. McGraw Hill, New York.
- Mark, A. E., Danilo, R., Giorgio, C. and Marco, F. (2002). Mechanism by which 2,2,2-trifluoroethanol/water mixtures stabilize secondary-structure formation in peptides: A molecular dynamics study. *Proceedings of the National Academy of Science.* 99 (19):12179-12184.
- Martins, O. (1990). Manual of Water Quality Assessment and Pollution Control.
- Nduka, JKC; Orisakwe, OE; Ezenweke, LO; Ezenwa, TE; Chendo, MN (2008) Acid rain phenomenon in niger delta region of Nigeria: economic, biodiversity, and public health concern. *The Sci. World J.* 8: 811-818
- National Population Commission (NPC) (2006) Nigeria National Census: Population Distribution by Sex, State, LGAs and Senatorial District: 2006 Census Priority Tables. Vol. 3. Pp140
- Odokuma, L. O. and Okpokwasili, G. C. (1997). Seasonal Influences of the Organic Pollution Monitoring of the New Calabar River, Nigeria. *Environ. Monit. Assessment.* 45, (1): 43-56.
- Otokunefor, T. V. and Obiukwu, C. (2005). Impact of refinery effluent on the physicochemical properties of a water body in the Niger delta. *Appl. Ecol. Environ. Res.* 3 (1), 61-72, 2005.
- Ravisankar N and Poogothai S (2008) A study of ground water quality in Tsunami affected areas of sirkazhi taluk, Nagapattinam district, Tamilnadu, India. *Sci. Tsunami Hazards* .27(1) 47-55.
- Ri-Rukeh, A., Ikhifa, G. O. and Okokoyo, P. A. (2006). Effects of agricultural activities on the water quality of Orogbodo River, Agbor Nigeria. *J. Appl. Sci. Res.* 2(5): 256-259.
- Saavanakumar, K; Ranjith Kumar, R (2011) Analysis f water quality parameters of groundwater near Ambattur industrial area, Tamil Nadu, India. *Indian J. Sci. Tech.* 4 (5) 600-662
- Udotog, I.R., John, O.U.M. and Udotong J.I.R. (2008). Microbiological and Physicochemical Studies of Wetland Soils in Eket, Nigeria. *Proceedings of World Academy of Science Engineering and Technology.* pp34.