



## DETERMINATION OF LEVELS OF PHYSICOCHEMICAL PARAMETERS IN WATER SAMPLES OF NEW CALABAR RIVER, RIVERS STATE, NIGERIA

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### Abstract

Water pollution is a worldwide issue caused by human interference with nature. The physicochemical variables of water samples of the New Calabar River were studied to develop guideline data on the pollution status. Water samples were obtained from several places based on effluent characteristics. The physicochemical characteristics were analysed using standard conventional techniques. The results obtained for some physicochemical parameters were pH ( $6.08 \pm 0.11$ ), BOD ( $9.17 \pm 0.26\text{mg/l}$ ), turbidity ( $25.23 \pm 4.07\text{NTU}$ ), TDS ( $5179 \pm 808.03\text{mg/l}$ ), nitrate ( $5.90 \pm 1.35\text{mg/l}$ ), sulphate ( $73.03 \pm 11.04$ ), chloride ( $1216.67 \pm 175.59\text{mg/l}$ ) and electrical conductivity ( $9690.33 \pm 1112.72\mu\text{s/cm}$ ). Biological oxygen demand, TDS, Total alkalinity, Turbidity, Chloride, and Electrical conductivity were all above the World Health Organization (WHO) and National Environmental Standards and Regulations Enforcement Agency's recommended limits (NESREA). A one-way analysis of variance (ANOVA) was performed at a 95% confidence level which revealed that the value of some parameters differed significantly ( $P < 0.05$ ) from one location to the next. The variation in each parameter observed along the river was caused by pollution from activities that take place along the river's bank and nearby. The river water was found to be unsafe for human consumption. As a result, suitable measures should be put in place to avoid further degradation of the water body.

**Keywords:** Physicochemical parameter, pollution, effluent, concentration, the permissible limit

### Introduction

An environment can be air, water, soil, or sediment. In most cases, there is no discrepancy between the contrasting media as they could drift into each other. Water contaminants, for example, are mostly conveyed into the water through the soil medium, such as surface runoff during the rainy season or radioactive fallout during the dry season. It has the potential to permeate the ecosystem and end up as silt at the bottom of rivers, lakes, and seas (Wonodi & Ekpete, 2021). The standard of drinking water is a major indication of the good health of an organism. There is a need to make certain that the water is clean and pure to prevent health implications that emerge from the utilization of polluted and contaminated water (Okumgba & Ozabor, 2014).

The fast industrialization and the evolution of rural areas had given rise to constant growth and a tenacious increase in the contamination of water bodies. The anthropogenic venture has had a first-hand impact on the atmospheric environment. Nonetheless, some of these pollutants are via natural sources such as the decay of organic matter, synthesis by micro-organisms, volcanic eruptions, and plants. This Human-made engendered pollution results as a direct outcome of man's intervention with the natural environment, such as pollution from commercial and domestic activities, bush-burning, mining, vehicular exhaust, sewage water, Pharmaceuticals, industrial effluents, bunkering activities, etc. (Ekpete, 2019). Pollutants in wastewater released from sewage and industries contribute to oxygen demand and nutrient loading of the water body, stimulating harmful algal blooms and destabilizing the aquatic ecology (Morrison et al., 2001).

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Two types of chemical contaminants have a long-term impact on the aquatic system's natural equilibrium. The first category includes plant nutrients such as nitrate, phosphate, and sulphate, which are not immediately damaging to plants or animals in water but may impart an undesirable odour or flavour. This has the potential to dramatically disrupt the environment. Water pollution caused by the aforementioned category is caused by over-enrichment, which encourages the unrestricted development of aquatic plant biomass. This eventually leads to oxygen deprivation caused by plant deterioration and fish mortality, resulting in bad odours and tastes in the resultant water. The second group consists of chemical species that are environmentally refractory, such as heavy metals, radionuclides, chlorinated hydrocarbons, and polycyclic aromatics, as well as sulphur and nitrogen oxides, which can produce acids in rainfall. This category has the potential to have a direct harmful influence on the ecosystem. The environmentally refractory ones are typically not eradicated from the environment by natural biodegradation, therefore they might have a long-term negative impact on the ecosystem. They tend to bioaccumulate in the bottom sediments of aquatic systems and get concentrated by the biota, and they can reach humans, causing acute and chronic diseases. This study was aimed at evaluating the levels of the physicochemical parameters of water samples collected from the New Calabar River. Water quality indicators such as pH, temperature, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, TDS, BOD<sub>5</sub>, DO, Total alkalinity, Electrical conductivity, Turbidity, and NO<sub>3</sub><sup>-</sup> were measured.

### Materials and Methods

The study area is the New Calabar River, located in the coastal zone of the Niger Delta in Nigeria, between 7°60' east longitude and 5°45' north latitude, directly flowing into the Atlantic Ocean. Riverbank operations such as logging, forestry, and dredging can cause large-scale river pollution. The New Calabar Rivers pass through Aluu in Ikwerre Local Government Area to Bakana in the Degema Local Government Area of Rivers State and are linked to the ocean (Nwineewii & Unochukwu, 2018). The research was carried out due to various human activities in the area. In the upper reaches of the river, they are mainly farmers and fishermen. Their activities have contributed to the pollution of the river. There is a high degree of oil production and exploration activities in the downstream area; in addition, some companies located in the area directly or indirectly discharge their waste into the water body. Three sampling points were identified downstream: Ogbakiri (S1), Minipiti (S2), and Eagle Cement (S3). These locations were chosen based on accessibility, slightly different waste, low tide zone, and economic activities on their territory.

**Table 1: Geographic coordinates of the Sample Locations along the New Calabar River.**

| Sample Location      | Geographic Coordinates     |
|----------------------|----------------------------|
| Ogbakiri Station     | 4°47'47.2" N, 6°54'46.1" E |
| Minipiti Station     | 4°48'37.4" N, 6°55'43.7" E |
| Eagle Cement Station | 4°48'55.9" N, 6°56'38.2" E |

Water sampling bottles were washed with nitric acid and sampling water. The water sample was collected in 1L capacity plastic bottles and 5 ml of concentrated nitric acid was added to prevent further oxidation and degradation of the aqueous solution. The water samples for biochemical oxygen demand and dissolved oxygen were collected separately, put into two sets of 250 ml glass reagent bottles, and packed in dark plastic bags to prevent light from entering. The other parameters were confirmed on the spot. The dissolved oxygen sample was fixed with Winkler reagents I and II. Samples were transported in labelled containers, plastic bags, and glass bottles, kept in an ice chest, and transported to the laboratory, where they were stored in a refrigerator at 4°C until the analysis was completed. Measurement of temperature was done on-site with a thermometer. The thermometer was immersed at a distance of about 5 cm from the water surface for about five minutes, and then the reading was taken. The reading was taken thrice. pH meter was used to measure the pH value of the water sample. It was immersed in the sample, and the reading was recorded. It was done thrice to obtain the average pH value. To determine Dissolved Oxygen (DO), the titration method developed by Winkler was used to measure Dissolved Oxygen in the water sample. 5ml of manganese sulphate, 5ml alkali metal iodide azide, 1ml concentrated sulfuric acid, and 1ml starch indicator was added to the water sample and mixed. Using starch as an indicator, the solution was titrated against standard 0.025M

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sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) until the blue colour becomes colourless, indicating the volume of sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) used, and then Dissolved Oxygen was calculated.

To determine Biochemical Oxygen Demand ( $\text{BOD}_5$ ), the sample was initially incubated in the dark for 5 days, and the Dissolved Oxygen was determined according to the Winkler technique. Two Dissolved Oxygen determinations were performed, one before the incubation and one after the incubation. The Biochemical Oxygen Demand was calculated based on the difference between the two measured DO. The amount of Total Dissolved Solids was obtained using filtration and evaporation techniques. The weighted sample was filtered using Whatman filter paper, and the filtrate was dried in a porcelain plate in an oven at  $110\text{-}120^\circ\text{C}$  for half an hour before cooling in a water bath. The dish was weighed again and the difference in weight was recorded. This represented the amount of TDS present in the sample in  $\text{mg/l}$  by dividing the weight difference by the volume of the water sample and multiplying by  $10^6$  (Eaton, 2005). The total alkalinity of water (usually due to the components of bicarbonate, carbonate, and hydroxide) was determined by titration using the aliquot of the water sample against  $\text{H}_2\text{SO}_4$ , using a mixed indicator of green methyl and Bromo-cresol. The total volume of Tetraoxosulphate (VI) acid used to neutralize bicarbonate, carbonate, and hydroxide was noted and used to calculate the total alkalinity in  $\text{mg/l}$ . To determine Sulphate ( $\text{SO}_4^{2-}$ ) (turbid metric Method), 15 mL of sample was measured and placed into a 50 mL volumetric flask, followed by 5 mL of distilled water. 1ml of gel-like reagent (gum arabic) was added and diluted to make a barium sulphate cloud. The contents were thoroughly shaken and allowed to stand for 30 minutes. A handheld spectrophotometer was used to quantify the optical density (OD) equivalent to the optical density of barium sulphate at 420 nm. Within 4 minutes, readings were recorded at 30-second intervals, and the maximum reading was determined. The calibration curve was generated with anhydrous potassium sulphate ( $\text{K}_2\text{SO}_4$ ) in the concentration range of  $0.01\text{-}1.6 \text{ mg/l SO}_4^{2-}$ . The calibration curve was used to read the sulphate ion concentration corresponding to the observed optical density (absorbance of the test and blank solutions) and the sulphate ion concentration ( $\text{SO}_4^{2-}$ ) in the obtained sample.

To determine Nitrate ( $\text{NO}_3^-$ ), 10 ml of the water sample was transferred to a 25 ml volumetric flask. 2 ml of Brucine reagent (dimethoxy brucine  $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2 \cdot 2\text{H}_2\text{O}$ ) was added to the sample and 10 ml concentrated  $\text{H}_2\text{SO}_4$  was also added. After mixing for around 30 seconds, the contents were allowed to stand for 30 minutes. The flask was air-cooled for 15 minutes to achieve the target temperature, and the absorbance was measured at 470nm using a portable spectrophotometer model. Dissolving 0.8g  $\text{KNO}_3$  in 500 mL distilled water yielded a standard nitrate solution. 0.5ml of chloroform was added to preserve it. An aliquot of the stock solution with a concentration range of  $0.01\text{-}2.0\text{M}$  ( $\text{NO}_3^-$ ) was prepared and utilized to generate a calibration curve. The nitrate content in each sample was calculated by extrapolating the absorbance from the calibration curve. Turbidity was measured with the aid of a turbidimeter. The probe was cleaned with de-ionised water, and inserted in the water sample, and the average reading was obtained from three separate readings. Chemical Oxygen Demand was determined using the titrimetric method (APHA,2005). Anti-bumping granules were introduced into a reflux flask. Twenty millilitres (20ml) of the sample were measured into the refluxing flask and 2ml of 20% m/v mercuric sulphate solution was added and swirled. Ten millilitres (10ml) of 0.021M potassium dichromate were added to the mixture. Using a dispensing pipette, 30ml of concentrated sulphuric acid containing silver sulphate was also added. The contents in the flask were fitted to a condenser and refluxed for 1 hour. After 1 hour, the flask was removed and allowed to cool for approximately 10 minutes. The condenser was washed with distilled water and then the content of the flask was diluted to 100ml. Two drops of Ferroin indicator were added to the content in the flask and the residual dichromate was titrated with standardized ferrous ammonium sulphate. The COD was obtained using equation 1 below

:  $\text{COD mg/l} = (V_b - V_a) \times 8000 \times M/\text{volume of sample}$

Where:

$V_b$  = average number of ml ferrous ammonium sulphate used in titrating the appropriate blank.

Chloride ( $\text{Cl}^-$ ) ion was determined by placing 100ml of water sample in a 250ml beaker. The pH was adjusted to 7-10 by gradually adding 0.4 M  $\text{HNO}_3$ . 1 ml of  $\text{K}_2\text{CrO}_4$  was added as an indicator. The solution was titrated against 0.14M silver nitrate until a pink-yellow endpoint was reached. To determine Electrical conductivity, a 1560 scanning conductivity meter was used. The probe was cleansed with de-ionized water, dipped in the sample, and

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read three times and measurements are taken in  $\mu\text{S}/\text{cm}$ . The raw data were subjected to charts, measures of central tendency, and descriptive statistical analysis like One-way Analysis of Variance (ANOVA).

**Results**

**Table 2: Physical parameters of water samples from a different station in New Calabar River**

| Parameters                                          | Stations    |              |               | Mean±SD         | WHO (2011) | NESREA  |
|-----------------------------------------------------|-------------|--------------|---------------|-----------------|------------|---------|
|                                                     | Ogbakiri    | Minipiti     | Eagle Cement  |                 |            |         |
| Temperature( $^{\circ}\text{C}$ )                   | 28.0±0.17   | 28.5±0.044   | 29.0±0.135    | 28.5±0.5        | 30         | Ambient |
| TDS (mg/l)                                          | 4324±5.568  | 5283±8.0     | 5930±13.89    | 5179±808.03     | 2000       | 500     |
| Turbidity (NTU)                                     | 24.8±0.436  | 21.4±0.180   | 29.5±0.347    | 25.23±4.07      | 15         | 5.0     |
| Electrical Conductivity ( $\mu\text{S}/\text{cm}$ ) | 8645±56.347 | 9566±335.184 | 10860±141.774 | 9690.33±1112.72 | 500        | 1000    |

**Table 3: Chemical parameters of water samples from a different station in New Calabar River**

| Parameters              | Stations    |            |              | Mean±SD        | WHO (2011) | NESREA  |
|-------------------------|-------------|------------|--------------|----------------|------------|---------|
|                         | Ogbakiri    | Minipiti   | Eagle Cement |                |            |         |
| pH                      | 5.98±0.053  | 6.1±0.118  | 6.15±0.127   | 6.077±0.09     | 6.5-8.5    | 6.5-8.5 |
| Total Alkalinity (mg/l) | 59.5±0.072  | 63.8±0.810 | 65.9±0.217   | 63.06±3.26     | 6.5-8.5    | -       |
| Chloride(mg/l)          | 1050±13.229 | 1400±6.00  | 1200±18.520  | 1216.67±175.59 | 200        | 250     |

**Table 4: Gross organic and nutrient parameters of water samples from a different station in the New Calabar River**

| Parameters      | Stations   |            |              | Mean±SD     | WHO (2011) | NESREA |
|-----------------|------------|------------|--------------|-------------|------------|--------|
|                 | Ogbakiri   | Minipiti   | Eagle Cement |             |            |        |
| DO (mg/l)       | 5.98±0.135 | 6.1±0.062  | 6.2±0.044    | 6.093±0.11  | 7.5        | -      |
| BOD (mg/l)      | 8.5±0.046  | 9.0±0.132  | 10.0±0.095   | 9.167±0.76  | 4.0        | -      |
| COD (mg/l)      | 12.7±0.046 | 13.5±0.187 | 15.0±0.106   | 13.73±1.17  | 40         | -      |
| Sulphate (mg/l) | 62.9±0.078 | 71.4±0.135 | 84.8±0.367   | 73.03±11.04 | 400        | 100    |
| Nitrate (mg/l)  | 4.5±0.087  | 6.0±0.089  | 7.2±0.044    | 5.90±1.35   | 10         | 50     |

The result of the physicochemical parameters obtained from Water samples was presented as shown in Tables 1-3. From the result of the physicochemical parameters obtained from the research, Biological Oxygen Demand, TDS, Total Alkalinity, Turbidity, Chloride, and Electrical conductivity were above the World Health Organisation (WHO) and National Environmental Standards and Regulations Enforcement Agency (NESREA) permissible level for drinking water while those of Temperature, pH, Dissolved Oxygen, Sulphate, Nitrate, and Chemical Oxygen Demand were below the standard

**Discussion**

**Table 2: Physical parameters of water samples from a different station in New Calabar River**

From Table 2, the temperature was highest at Eagle Cement station at  $29.0\pm 0.01^{\circ}\text{C}$  and lowest at Ogbakiri station at  $28.0\pm 0.01^{\circ}\text{C}$ . The result of one-way ANOVA showed  $p < 0.05$ , indicating that there was a significant temperature difference recorded in the various location of the river. The mean temperature for the surface water was  $28.5 \pm 0.05^{\circ}\text{C}$ . This correlates with values of  $27.7-29.9^{\circ}\text{C}$  obtained from earlier work carried out by Ogolo et al. (2017) on the New Calabar River, but is higher than the value of  $26.37- 26.77^{\circ}\text{C}$  obtained by Seiyaboh et al. (2016) in a

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research work carried out on Orashi River. The mean temperature falls slightly below the recommended value for drinking water set by World Health Organisation. Temperature affects the metabolic rate of aquatic organisms and causes the water to be warm. High temperature in water reduces dissolved oxygen which can hamper the survival of some aquatic species. At warmer temperatures, some substances become more harmful to aquatic life.

TDS is a measure of both the organic and the inorganic matter that is dissolved in water (Rahmanian et al., 2015). The mean concentration of TDS obtained in the study was  $5179 \pm 808.04$  mg/l. However, the TDS obtained from the locations ranged from  $4324 \pm 0.06$  to  $5930 \pm 0.012$  mg/l. The lowest TDS was recorded at Ogbakiri station, while the highest was at Eagle Cement station. These values were high when compared with the World Health Organisation's permissible limit. The values in the present work were higher than the value of 31.93-39.48 reported by Seiyabo et al. (2013) in their investigation of the physicochemical characteristics of Igbedi Creek. However, the values were low when compared to the value of  $13,250 \pm 187.08$  mg/l obtained by Edori et al. (2019) on work carried out on Silver River. The result of one-way ANOVA revealed  $p < 0.05$ , indicating a significant difference in levels of TDS in all the locations. The quantity of TDS present in any water may be used to describe the degree of contamination. The high TDS found in this research, particularly at the Eagle cement and Minipiti stations, can be linked to the volume of waste created by the several enterprises located nearby. The high concentrations of suspended and dissolved solids may be hazardous to aquatic creatures because they reduce water quality, hinder photosynthetic activities, and eventually result in a rise in bottom silt and a decrease in water depth.

Turbidity is another important parameter in drinking water analysis. It is the haziness of water caused by the presence of particles. The turbidity obtained from the study ranged from  $21.4 \pm 0.3$  NTU to  $29.5 \pm 0.21$  NTU. The lowest turbidity level was recorded at Minipiti station and the highest at Eagle cement station. Results revealed that the turbidity level of all the sampled locations was above the World Health Organisation permissible limit. The mean value was  $25.23 \pm 4.067$  NTU. The result obtained was inconsistent with values of 7.2-88.9 NTU reported by Ogolo et al., (2017) on other stations of the river. The result is, however, lower in comparison to the result of 29.83-35.83 NTU reported for Nun River by Aghoghovwian et al., (2018). The result of one-way ANOVA revealed  $p < 0.05$ , indicating a significant difference in levels of Turbidity in all stations. This result indicated a high rate of anthropogenic activity like fishing, farming, etc, in the area, indicating that more silt/mud flowed into the river. The more turbid the water, the greater the risk of gastrointestinal sickness. Due to lower light penetration, high turbidity limits photosynthetic activity in the environment (Nwineewii and Unochukwu, 2018).

The measured conductivity was highest at Eagle Cement station, with a value of  $10,860 \pm 3.45$   $\mu$ S/cm, and the lowest value of  $8645 \pm 2.78$   $\mu$ S/cm at Ogbakiri station. The result of one-way ANOVA revealed  $p < 0.05$ , indicating a significant difference in levels of conductivity in all stations. The mean value of  $9690.33 \pm 1112.72$   $\mu$ S/cm was below the World Health Organisation permissible limit of 500  $\mu$ S/cm. The value reported in the study was in contrast to values of 58.00  $\mu$ S/cm and 33,489-33,592  $\mu$ S/cm obtained for Taylor creek and Bonny/New Calabar River respectively (Daka et al., 2014; Onajoke et al., 2017). High conductivity could be attributed to strong anthropogenic activities like iron and metal work and oil-related activities in some industries close to the river. It could also result from the underlying geology of the area. Because of the lack of direct health effects, high conductivity is not always a cause for concern. Dissolved ionisable solids, on the other hand, might create aggravating water hardness or alkalinity.

### Chemical parameters of water samples from a different station in New Calabar River

From Table 3, the pH levels of the samples ranged from  $5.98 \pm 0.03$  to  $6.15 \pm 0.01$ . The average pH level was  $6.077 \pm 0.087$ . These pH levels and their mean fell below the World Health Organization's allowable range. The mean pH is consistent with a previous study on the same river conducted by Ogolo et al. (2017), which showed a mean pH of 6.015. The result from the study was slightly lower than the mean pH of 7.46 reported on the same surface water but in different locations by Nwineewii and Unochukwu (2018) and that reported by Aghoghovwia and Ohimain, (2014) on Kolo Creek, was 6.61-7.50. The value for pH is attributed to industrial waste from companies. Most living organisms become inactive or eventually die at a very low pH value (Tom, 2018).

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Alkalinity is the water's capacity to resist changes in pH that would make the water more acidic. The total alkalinity was highest at Eagle cement station, with a value of  $65.9 \pm 0.05 \text{ mg/l}$  and the lowest value of  $59.5 \pm 0.03 \text{ mg/l}$  at Ogbakiri. The mean value of  $63.067 \pm 3.262 \text{ mg/l}$  was below the World Health Organisation permissible limit of  $65\text{--}85 \text{ mg/l}$ . The mean value obtained from the study was consistent with that reported by Ikhuriah and Oronsaye, (2016), in the study of physicochemical characteristics of the Ologbo River in Edo state. In their studies, they reported a value range of  $48.63\text{--}53.28 \text{ mg/l}$ . However, it was contrary to the value of  $6.34\text{--}9.65 \text{ mg/l}$  reported in an earlier study on Woji Creek (Emmanuel & Woke, 2019). The alkalinity of the water poses no immediate health dangers. Water with high alkalinity may have a raised pH, nuisance concerns with chemical precipitates and coatings, soap scum, a salty taste, and elevated levels of certain metals, whereas water with low alkalinity may have an increase in acidity (Tom, 2018).

The levels of chloride ( $\text{Cl}^-$ ) ranged from  $1050 \pm 0.170 \text{ mg/l}$  to  $1400 \pm 0.42 \text{ mg/l}$  with the highest value gotten from Minipiti station and the lowest value at Ogbakiri station. The mean value was  $1216.67 \pm 175.594 \text{ mg/l}$ . The results of a one-way ANOVA conducted revealed  $p < 0.05$  showing that there was a significant difference in the concentration of chloride in all the stations of the New Calabar River and were far above the World Health Organisation standard of  $200 \text{ mg/l}$  indicating that the water from New Calabar River is excessively polluted with chloride. The result from the study was lower than the mean value of  $1557.66 \text{ mg/l}$  reported by Nwineewii and Unochukwu, (2018) in the study carried out on the New Calabar River. Ikhuriah and Oronsaye, (2016) reported higher values ranging from  $26.44\text{--}36.39 \text{ mg/l}$  in the study assessing the physicochemical parameters of surface water from the Ologbo River. This might be due to the nature of the water. Chloride in water is mostly caused by the re-suspension of chloride-contaminated sediment, industrial effluents, and sewage. One significant impact of chloride in water is an increase in electrical conductivity and metal corrosion (Marcus, 2011).

### Gross organic and nutrient parameters of water samples from a different station in the New Calabar River

From Table 4, the concentration of dissolved oxygen in  $\text{mg/l}$  varied from  $5.98 \pm 0.02 \text{ mg/l}$  to  $6.20 \pm 0.01 \text{ mg/l}$ . However, the dissolved oxygen (DO) from all the locations was within World Health Organisation's permissible limit for drinking water. The mean level of DO was  $6.093 \pm 0.11 \text{ mg/l}$  and was consistent with values of  $5.80 \pm 0.5 \text{ mg/l}$  obtained from previous research by Nwineewii and Unochukwu (2018) and higher than the  $4.01 \text{ mg/l}$  reported by Kpee, (2012) on the same river. A high dissolved oxygen (DO) content in the water is beneficial since it improves the flavour of the water. High DO levels, on the other hand, hasten rusting in water pipes. When dissolved oxygen levels in a waterfall are below  $5.0 \text{ mg/l}$ , aquatic life suffers. Large fish deaths can occur when oxygen levels fall below  $1\text{--}2 \text{ mg/l}$  (MPCA, 2009).

The biochemical oxygen demand obtained was in the order Eagle cement > Minipiti Station > Ogbakiri Station. The BOD levels of the various stations were more than the limit recommended for drinking water by the World Health Organisation. The result of a one-way ANOVA conducted revealed  $p < 0.05$ , indicating that there was a significant difference in levels of BOD in the three stations sampled. The BOD from this study had a mean value of  $9.167 \pm 0.764 \text{ mg/l}$  and was higher than the value obtained from an earlier study by Edori and Nna (2018) on the New Calabar River. In their study, values obtained were in the range of  $4.28\text{--}6.11 \text{ mg/l}$ . The result was also higher than the values of  $1.50\text{--}3.35 \text{ mg/l}$  reported by Aghoghovwian and Ohimain, (2014) in their studies on Kolo Creek. High BOD in this research indicates that the water includes a lot of organic matter, implying pollution from the discharge of residential waste, and industrial run-off in the area. Low BOD levels, on the other hand, indicate that less oxygen is being taken from the water, implying that the water is typically purer. Excessive BOD levels are hazardous to ecosystems because fish and other aquatic life may perish in oxygen-depleted water. As a result, it is responsible for its odour and flavour (MPCA, 2009).

The chemical oxygen demand ranged from  $12.7 \pm 0.046 \text{ mg/l}$  to  $15.0 \pm 0.106 \text{ mg/l}$ . The result of a one-way revealed that  $p < 0.05$ , indicating a significant difference in the levels of chemical oxygen demand in all sampled stations revealing that Eagle Cement station had the highest chemical oxygen demand value while Ogbakiri Station was the least. Further analysis showed that the values from the stations and the corresponding mean were below the World Health Organisation permissible limit of  $40 \text{ mg/l}$ . The mean value of  $13.73 \pm 1.17 \text{ mg/l}$  was consistent with a value range of  $11.96\text{--}14.78 \text{ mg/l}$  reported by Emmanuel and Woke, (2019) in the assessment of the

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physicochemical parameters of Woji Creek and below the value of 24.845mg/l reported by Nna and Don-Lawson, (2018) in surface water of Woji Creek.

Sulphate ions ( $\text{SO}_4^{2-}$ ) occur naturally in most water. The mean concentration obtained for sulphate was  $73.033 \pm 11.041 \text{ mg/l}$ . The result of one-way ANOVA revealed  $p < 0.05$ , indicating a significant difference in levels of TDS in all the stations with Eagle Cement station having the highest value and Ogbakiri the lowest. The level of sulphate obtained in the study was low compared with the World Health Organisation limit of 400mg/l set for drinking water. However, the result was higher than the value of  $0.94 \pm 0.77 \text{ mg/l}$  reported by Ikhuoriah and Oronsaye, (2016) and 22.48mg/l reported by Nwineewii and Unochukwu, (2018). The negative impacts of sulphate on freshwater systems include pH reduction, and increased mobility of toxic metallic ions and nutrients (Zak et al., 2021).

The nitrate ( $\text{NO}_3^-$ ) concentrations obtained varied from 4.50.02mg/l to 7.20.043mg/l. The mean concentration was  $5.9 \pm 1.353 \text{ mg/l}$ , which was below the World Health Organization's allowed limit of 10mg/l. However, these values were at variance with that obtained from other stations of the same river by Edori and Nna, (2018) which were 0.32-0.56mg/l and 11.10-14.33mg/l in Tombia and Gbaratoru axis of Nun River in Bayelsa by Aghoghovwian et al., (2018). The presence of degraded organic waste and water run-off from agriculture and leaky septic tanks might explain the elevated nitrate levels in all areas. Excess nitrates, when associated with phosphorus, can drive eutrophication, resulting in substantial increases in algal growth. This has an impact on dissolved oxygen, temperature, and other indicators (De Jong et al., 2007).

### Conclusion

The study revealed a correlation between increased commercial and industrial activities within the metropolis and the elevation of key parameters such as Biological oxygen demand, TDS, Total alkalinity, Turbidity, Chloride, and Electrical conductivity water samples. This was clearly shown in Eagle Cement being the most polluted due to its proximity to urban settlements and industrial layout. The waste of factories, urban run-off, artisanal refineries, city sewage, and agricultural activities are affecting the physicochemical characteristics of the New Calabar River. The Continuous pollution of water bodies can lead to a high risk of water poisoning, which may ultimately affect the biota, distorting the food web and ultimately causing the death of plants and animals. Hence, waterbodies should be protected against undue anthropogenic influence. The following recommendations were fashioned out based on the results of this study: Industries must comply with waste disposal rules set by relevant institutions such as FMENV and NESREA. Farmers in the areas should be educated against the indiscriminate use of chemical fertilizers, because they are the main sources of pollutants that affect water quality parameters such as nitrate, phosphate, total alkalinity, etc. Local fishermen should be enlightened on the dangerous effect the use of chemicals and dynamites in fishing has on aquatic life. Finally, the government must put in place measures that guide against the upsurge of illegal refineries in the area.

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