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# Water quality index and correlation study for the assessment of water quality and its parameters in Etim Ekpo, Nigeria

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**Abstract** Water bodies can be polluted by the addition of nutrients such as nitrates, phosphates, sulphates and chlorides through urbanization, agricultural, industrial and domestic activities. This study was aimed at determining the pollution status of EtimEkpo River, AkwaIbom State, Nigeria, during wet and dry seasons. Physicochemical parameters of water including, temperature, pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), and conductivity, were measured using USEPA protocol. Other parameters were determined using UV-Visible spectrophotometric techniques. They were nitrates ($NO_3^-$), sulphates ($SO_4^{2-}$), phosphates ($PO_4^{3-}$), carbonates ($CO_3^{2-}$) and chlorides ($Cl^-$). Mean temperature were of 27.87°C and 27.98°C for wet and dry seasons respectively. The pH of the river water samples during the wet season ranged from 6.90 to 7.83 while the pH during the dry season ranged from 6.63 to 7.73.Mean values of dissolved oxygen ranged from 12.41mgIl – 15.32 mg/l for wet season and 12.94mg/l – 13.98mg/l for the dry season. Mean BOD were 4.75mg/l and 4.15mg/l respectively for wet and dry season. The conductivity levels ranged from 13.09µScm$^{-1}$to 19.04µScm$^{-1}$ in the wet season and 12.12µScm$^{-1}$ to 13.90µScm$^{-1}$ in the dry season. Concentrations of $PO_4^{3-}$, $SO_4^{2-}$, $NO_3^-$, $CO_3^{2-}$ and $Cl^-$ in the samples were within safe limits. The Pearson's correlation coefficient revealed weak correlations amongst the parameters measured, indicating different sources of their input to the water body. Over-all the study revealed a low pollution status of the river under study. The results from the present study serve as a base-line for future researches. Continuous monitoring of the river is encouraged, as anthropogenic activities in the area increases.

**Keywords** Water pollution, pollution indicators, correlation studies, Etim Ekporiver

## 1. Introduction

The interaction of man with the natural environment and the quest for man to attain a higher standard of living often result in the degradation of the environment of which water is an integral part [1,2]. Surface water bodies such as lakes, streams and rivers are veritable natural resources which provide man comfort, means of livelihood and contribute towards the balance of natural cycles. Surface water bodies are in a state of continuous pollution due to industrialization and urbanization. Apart from heavy metal pollution, water bodies are also being polluted by the addition of nutrients such as nitrates, phosphates, sulphates and chlorides through urbanization, agricultural, industrial and domestic activities. These lead to eutrophication which refers to accumulation of organic matter, nutrients, and growth enhancers resulting in undesirable changes in aquatic ecosystem.

The physical condition of a body of water strongly influences the chemical and biological processes that occur in water. Temperature, transparency and turbulence are the three main physical factors affecting aquatic lives [3]. Extremely low water temperature causes slow biological activities while high water temperature is fatal to water organisms. The transparency of water helps in determining the growth of algae while turbulence is an important physical factor in mixing process and transport of nutrients and waste products in water. The upper layer of water which is exposed to light may have heavy algal growth, hence the photosynthetic activity of the algae makes the water to contain higher levels of dissolved oxygen. On the other hand the bottom layer of water becomes anaerobic due to bacterial action on biodegradable organic matter.

The addition of nutrients such as nitrate $NO_3^-$, phosphate, $PO_4^{3-}$, sulphate, $SO_4^{2-}$, and chloride, $Cl^-$ invariably contribute to water pollution. Introduced into the environment as a consequence of urbanization, industrialization and agricultural practices, the nutrients find their way to the water environment via municipal discharges and run-off during rainfall [4]. The presence of excessive nutrients in water bodies lead to eutrophication. The nutrient enrichment of surface waters in turn can profoundly affect the chemical and biological characteristics of bodies of water [3].

The combination of physical and chemical factors in aquatic environment results in productivity. Productivity is the ability of a water body to produce living matter. The presence of chemical species such as $CO_2$, nitrogen as nitrates, phosphorus as orthophosphates and trace elements such as nickel, iron and chromium can enhance high productivity of water bodies. High productivity of aquatic ecosystem supports aquatic live, however, excessive productivity results in the consumption of dissolved oxygen, odour and eventually water pollution.

In recent times, AkwaIbom State Nigeria, has been on the spotlight of increased urbanization, agricultural, social and commercial activities. These activities are known to increase both the heavy metal and nutrient concentrations of water bodies. One area are that is rapidly developing is EtimEkpo, which houses the EtimEkpo river, The river is the main source of water for several communities in the area, for domestic, agricultural and recreational activities. Although some studies have been carried out on the effects of pollution on Nigerian aquatic environments [5-8]. No research has however been carried out to ascertain the level of pollution of EtimEkpo river.

Most researches in recent times investigated the pollution status of major metropolitan settlements and industrial areas especially oil exploration areas. However, it is obvious that the natural environment is integrated sequel to the fact that the pollution of any given area has far reaching effects on distant environments. This research will therefore provide information which will serve as a database on the state of EtimEkpo River. The research will also present information on the physicochemical parameters as well as nutrients present in the water of EtimEkpo River. The general information obtained will enable administrators to control the pollution sources of the area.

## 2. Methodology

### 2.1. Study area

The study area (EtimEkpo river) is located in EtimEkpo, south west AkwaIbom State, Nigera. It is a semi-urban area with public facilities such as government housing estates, hospitals, administrative buildings, schools, markets and residential houses. It serves as an important commercial route between AkwaIbom and other south eastern states of the country. The people of the area are predominantly farmers, petty traders and fishermen [9]. A number of people are engaged in wine tapping, sand excavation and craft making. The area lies in the tropical rain forest belt and has two distinct seasons: wet and dry. Several species of fishes are found in the river and many indigenes make their living from fishing. The river is the main source of water for several communities in the area.

### 2.2. Samples and sampling

Sampling to obtain reasonable amounts of water which are representative of the larger whole [10, 11] was carried out during wet season (April – July, 2014) and dry season (October 2014 – January, 2015).

Five sampling points were chosen. The Sampling points were different villages through which the river passes. The villages include Uruk Ata Ikot Isemin, Etok Uruk Eshiet, Etim Ekpo Bridge Head, Uruk Ata Ikot Ekpor and Nkwot Ikot Ebo.

At each sampling station, water samples were collected and made into composite samples at the site. 2.5 liter polyethylene bottles previously sterilized and rinsed thoroughly with the river water were used for sample collection [12]. The sampling bottles were filled such that air was not trapped inside the bottles. Water samples meant for the determination of dissolved oxygen (DO) were collected in 250 ml brown polyethylene bottles and fixed on the spot with $MnCl_2$ and alkaline potassium iodide (K1) to avoid decomposition of oxygen and were analysed within 24 hours of sampling. Two sets of samples were obtained at each sampling station.

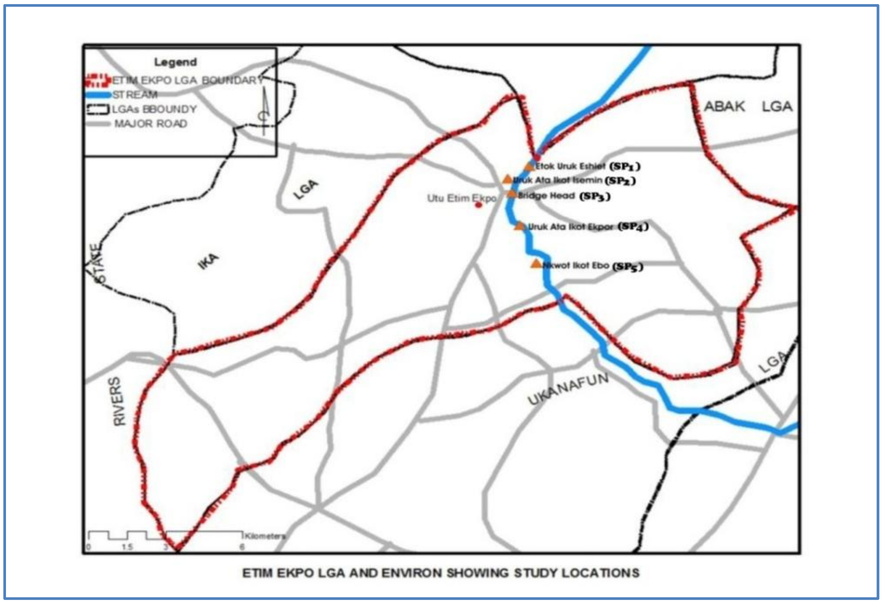


*Figure 1: EtimEkpo and environ showing study location*

**2.2.1. *Water preservation and treatment***

Once taken from its natural environment, the physicochemical parameters of water such as oxidation state of trace metals, colour, DO, and pH may change. To avoid the occurrence of any of these changes water samples meant for metal determination were acidified with concentrated $HNO_3$ to pH≤2 and stored at 4°C in the dark. The samples earmarked for DO and BOD determination were treated with $MnCl_2$ and KI at sampling sites and preserved in the laboratory at 4°C until analysed.

**2.3. *Determination of the physicochemical parameters of the water samples***

The physiochemical parameters of the water samples determined in this study include; temperature, pH, DO, BOD, conductivity and total dissolved solids, TDS. These parameters were determined as described below.

**2.3.1. Determination of Temperature of the Water samples**

The temperature of the water samples were measured *in situ* using mercury-in glass Celcius thermometer (0-100 °C). The measurements were obtained by dipping the thermometer vertically into the samples. The thermometer was allowed to stand until the temperature reading was steady [13] and then the reading was recorded.

**2.3.2. Determination of pH of the water samples**

The pH of the water samples were determined with the use of an electronic pH meter (UNICAM model 3320 JENWAY). Before the determination of the pH, the instrument was standardized with buffer solutions of pH 4.0 and 9.2 respectively to ensure proper instrument response. All necessary precautions such as thorough rinsing of the electrode with deionized water before the immersion into the samples and stabilization of the needles were taken. The pH was then reported as the value displayed on the meter scale when the needle became steady.

**2.3.3. Determination of Dissolved Oxygen (DO)**

Dissolved oxygen was determined by Winkler's method [13]. $MnCl_2$ ($2cm^3$) was added to 200 $cm^3$ of each water sample. This was followed by the addition of 2 $cm^3$ of alkaline–iodide acid reagent (solution containing KOH, K1and $KN_3$) using separate dropping pipettes. The bottles were stoppered with care to exclude air bubbles and mixed by inverting the bottles a number of times until a clear water solution was obtained and the precipitate was allowed to settle. Concentrated HCl (2 $cm^3$) was then added to the bottle, stoppered and shaken to dissolve the already formed brown precipitate. Each solution (100 $cm^3$) was then titrated against a standard 0.0125 M $Na_2S_2O_3$ using starch indicator (2 drops). Titration was continued until the colour changed from blue to colourless.

Equation of the reaction;

$$Mn^{2+} + 2OH^- \longrightarrow Mn(OH)_{2(s)}$$

$$2Mn(OH)_2 + O_2 \longrightarrow 2MnO_{2(s)} + 2H_2O(1)$$

$$MnO_{2(s)} + 2I^- + 4H^+ \longrightarrow Mn^{2+}_{(aq)} + I_{2\,(s)} + 2H_2O\ (1)$$

Dissolved oxygen was then calculated using the formula;

$$DO\ (mg/l) = \frac{16{,}000 \text{ x M x V}}{V2/V1(V1-V2)}$$

Where;

M = molarity of the thiosulphate solution

V = volume of thiosulphate solution used for titration

V1 = volume of bottles with stopper in place

V2 = volume of aliquot taken for titration

**2.3.4. Determination of biochemical oxygen demand (BOD) of water samples**

The method for determination of BOD was similar to that for DO, except that for BOD test the water samples were kept in an incubator in the dark preset at 20$^o$C for 5 days. After incubation, The DO determination was repeated. The difference between $DO_1$ and $DO_2$ gave BOD ie BOD = $DO_1$- $DO_2$

Where $DO_2$ = concentration of dissolved oxygen at day five.

**2.3.5. Determination of total solids**

The determination of total solids was performed as described [13]. The water sample (100 $cm^3$) was measured into a clean dish that was previously oven-dried at 105 $^o$C and designated as $W_1$. The dish was evaporated to dryness on a steam bath. The outside of the dish was wiped and the dry residue was further dried in an oven for 1 h at 105 $^o$C. The process was repeated until the weight of the dish and the residue was constant ($W_2$)

Weight of residue = $W_1 - W_2$

$$\text{Total solids (mg/l)} = \frac{(W1 - W2) \times 1000}{100}$$

**2.4. Determination of Nutrients in Water**

**2.4.1. Determination of chloride**

Mohr's method which employs silver nitrate ($AgNO_3$) as titrant and potassium chromate ($K_2C_rO_4$) as the end point indicator was used. The chloride ions present in the sample precipitated as white silver chloride [13].

Each water sample (50$cm^3$) was put in a clean conical flask. $K_2CrO_4$ indicator (2 drops) were added and titrated with 0.02 M $AgNO_3$ until the colour changed from yellow to brick red indicating the presence of chromate. The concentration of the $Cl^-$ present was calculated using the relationship:

$$\text{Concentration of } Cl^- \text{ (mg/l)} = \frac{\text{Volume of } AgNO_3 \times 1000 \times 35.5}{50 \text{ cm}^3 \text{ of sample used}}$$

**2.4.2. Determination of carbonates**

Carbonate, $CO_3^{2-}$ was determined by titration with standard acid to pH about 8.3 [13]. The end point was detected using phenolphthalein indicator.

Each sample (50 $cm^3$) was put in a clean conical flask. One drop of 0.05 M sodium thiosulphate solution was added to remove free residual chloride that might be present. Then phenolphthalein indicator (2 drops) were added to the solution and then titrated with 0.02 M standard HCl until the solution became colourless.

The concentration of $CO_3^{2-}$ was calculated using the relationship

$$\text{Conc. of } CO_3^{2-} = \frac{10{,}000 \times V \times M \text{ (mg/l)}}{50 \text{ cm}^3 \text{ of sample used}}$$

Where V = Volume of acid used, M = Molarity of acid

**2.4.3. Determination of sulphate**

Each sample solution (10 $cm^3$) was measured into 250 ml conical flask. 5 $cm^3$ and diluted to 100 $cm^3$ with water. The conditioning reagent solution (5 $cm^3$) which is a mixture of NaCl (75 g) dissolved in 96 % propan-2-ol (300 $cm^3$)) and glycerol (50 $cm^3$) was added and thoroughly mixed. This mixture was stirred with a magnetic stirrer at a constant speed and $BaCl_2$ crystals (0.5g) was added and the stirring continued for one minute. The absorbance of this solution was measured spectrophotometrically at 420nm.

A standard sulphate solution was prepared by dissolving 0.148g of anhydrous sodium sulphate $Na_2SO_4$ in distilled water and diluting to 1 litre

The concentration of the sulphate was determined by extrapolation from the calibration curve.

**2.4.4. Determination of nitrates**

Each sample (10 ml) was transferred into different 25 ml standard flasks. Brucine reagent (2 ml) was added, then 10 ml of conc. $H_2SO_4$ was also added rapidly. It was mixed for about 30 seconds and allowed to stand for 5 minutes. The flasks were set in cold water for 5 minutes and then made up to volume with deionized water. The absorbance was read at 470 nm with Unicam 8626 UV/VIS spectrometer.

**2.4.5. Determination of phosphates**

Each sample (25 ml) was measured into 50 ml volumetric flask. 19 ml of vanadiummolybdate reagent was added and diluted to volume with deionized water. A reagent blank was prepared by making up 20 ml of reagent to volume in a 50 ml volumetric flask. The solutions were mixed and allowed to stand for about 10 minutes for colour development the absorbance was read at 470 nm with UNICAM spectrometer.

The results of analysis of the physicochemical parameters, trace metals and nutrients in water, sediment and *Pelmatolapiamariae* sampled in two seasons from five sampling sites of EtimEkpo River are presented in this chapter. Tables 1 and 2 present the levels of physicochemical parameters of water samples during the wet and dry seasons respectively.

## 3. Results and Discussion

### 3.1. Physicochemical characteristics of water

The physicochemical parameters measured for EtimEkporiver for the wet and dry season are shown in Tables 1 and 2. The observations for the various parameters are as follows:

#### 3.1.1. Temperature

The temperature of the water samples during the wet season ranged from 27.35 $^oC$ - 28.50 $^oC$ while the temperature of the water samples during the dry season ranged from 27.76$^oC$ to 28.15$^oC$ (Tables 1 and 2), with means of 27.87 $^oC$ and 27.98 $^oC$ for wet and dry seasons respectively, the values of the temperatures recorded during the two seasons fell within the FEPA and WHO recommended limits of 29.40 $^oC$ to 30.30 $^oC$. Factors such as weather condition, time of sampling, river gradient and rate of flow of the river affect the temperature of river water [14]. The temperature of particular water usually affects the solubility of substances in the water body. Many substances become soluble in water as the temperature of the water increases. On the other hand decreasing water temperature can significantly reduce the rate of metabolism of aquatic animals. This is because temperature controls to some extent the chemical reactions in water and the metabolic processes in some fishes [15]. Aquatic species alter their behavior as temperature changes and they also respond to fluctuating levels of sediments, dissolved oxygen and minerals [13]. Surface water temperature affects aquatic environment. On the other hand, aquatic organisms only adapt to certain temperature range.

**Table 1**: Levels of physicochemical characteristics and nutrients (mg/l) in water samples from EtjmEkpo River in the wet season

| Parameters | | SS1 | SS2 | SS3 | SS4 | SS5 |
|---|---|---|---|---|---|---|
| Temp °C | Mean | 27.53 | 28.50 | 27.35 | 28.03 | 27.75 |
| | SD | 0.360 | 0.431 | 0.930 | 0.452 | 0.260 |
| pH | Mean | 6.90 | 7.45 | 7.83 | 7.10 | 7.20 |
| | SD | 1.610 | 0.312 | 0.260 | 0.421 | 0.450 |
| DO (mg/l) | Mean | 12.41 | 13.06 | 15.32 | 14.07 | 14.30 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | SD | 1.302 | 0.491 | 1.031 | 1.840 | 1.931 |
| BOD (mg/l) | Mean | 4.97 | 4.41 | 4.11 | 5.10 | 5.12 |
| | SD | 0.232 | 0.351 | 0.140 | 1.471 | 0.991 |
| Cond (µScm$^{-}$ | Mean | 19.04 | 16.09 | 16.95 | 13.09 | 15.51 |
| | SD | 5.681 | 3.270 | 1.691 | 4.310 | 3.041 |
| TDS (mg/l) | Mean | 109.87 | 107.71 | 120.92 | 102.75 | 95.00 |
| | SD | 41.751 | 31.972 | 17.990 | 24.932 | 37.041 |
| **Nutrients** | | | | | | |
| $NO_3^-$ (mg/l) | Mean | 0.02 | 0.02 | 0.02 | 0.01 | 0.02 |
| | SD | 0.010 | 0.000 | 0.010 | 0.000 | 0.000 |
| $PO_4^{-3}$ (mg/l) | Mean | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| | SD | 0.001 | 0.001 | 0.010 | 0.011 | 0.000 |
| $SO_4^{-2}$ (mg/l) | Mean | 0.42 | 0.31 | 0.31 | 0.38 | 0.32 |
| | SD | 0.222 | 0.091 | 0.123 | 0.120 | 0.009 |
| $CO_3^{-2}$ (mg/l) | Mean | 0.24 | 0.30 | 0.26 | 0.32 | 0.22 |
| | SD | 0.003 | 0.002 | 0.001 | 0.002 | 0.001 |
| $Cl^-$ (mg/l) | Mean | 38.98 | 30.36 | 32.91 | 29.88 | 31.23 |
| | SD | 11.321 | 5.611 | 4.615 | 4.863 | 3.631 |

Where, SS1 = EtokUrukEshiet Sampling Station
SS2 = Uruk Ata IkotIsemin Sampling Station
SS3 = EtimEkpo Bridge Head Sampling Station
SS4 == Uruk Ata IkotEkpor Sampling Station
SS5 = NkwotIkotEbo Sampling Station

**Table 2**: Levels of physicochemical characteristics and nutrients (in mg/l) in water samples in the dry season

| **Parameters** | | **SS1** | **SS2** | **SS3** | **SS4** | **SS5** |
|---|---|---|---|---|---|---|
| Temp (°C) | Mean | 28.15 | 27.97 | 27.76 | 28.10 | 27.92 |
| | SD | 0.762 | 1.091 | 0.362 | 0.412 | 0.341 |
| pH | Mean | 6.65 | 6.96 | 7.73 | 6.77 | 7.05 |
| | SD | 0.210 | 0.172 | 0.221 | 0.230 | 0.092 |
| DO (mg/l) | Mean | 13.68 | 13.06 | 13.97 | 12.94 | 13.98 |
| | SD | 0.220 | 3.122 | 2.171 | 0.561 | 0.301 |
| BOD (mg/l) | Mean | 4.35 | 3.42 | 4.18 | 4.75 | 4.06 |
| | SD | 0.650 | 0.152 | 0.072 | 0.481 | 0.131 |
| Cond (µScm$^{-1}$) | Mean | 12.49 | 13.25 | 12.12 | 13.90 | 12.17 |
| | SD | 0.882 | 1.042 | 1.761 | 1.242 | 1.371 |
| TDS (mg/l) | Mean | 99.63 | 131.94 | 121.79 | 109.98 | 120.53 |
| | SD | 4.611 | 2.371 | 3.082 | 1.441 | 11.241 |
| Nutrients | | | | | | |
| $NO_3^-$ (mg/l) | Mean | 0.03 | 0.02 | 0.02 | 0.02 | 0.03 |
| | SD | 0.010 | 0.000 | 0.000 | 0.000 | 0.010 |
| $PO_4^{-3}$ (mg/l) | Mean | 0.02 | 0.02 | 0.02 | 0.01 | 0.02 |
| | SD | 0.001 | 0.000 | 0.000 | 0.001 | 0.001 |
| $SO_4^{-2}$ (mg/l) | Mean | 0.35 | 0.35 | 0.39 | 0.41 | 0.40 |
| | SD | 0.010 | 0.050 | 0.050 | 0.070 | 0.050 |
| $CO_3^{-2}$ (mg/l) | Mean | 0.33 | 0.36 | 0.40 | 0.35 | 0.28 |
| | SD | 0.001 | 0.002 | 0.003 | 0.001 | 0.003 |
| $Cl^-$ (mg/l) | Mean | 29.69 | 28.85 | 28.22 | 27.13 | 28.47 |
| | SD | 1.180 | 1.890 | 0.720 | 0.850 | 3.300 |

### 3.1.2. pH

The pH of the river water samples during the wet season ranged from 6.90 to 7.83 while the pH during the dry season ranged from 6.63 to 7.73. This indicated that the water was near neutral in both seasons. These values were within the range of 6.50 to 8.50 for fishing water as recommended by WHO (2008). There was no significant difference ($P<0.05$) between the pH values in both seasons The values were also close to values reported by [16], for the river Niger at Onitsha bank. pH has an impact on the solubility and bioavailability of metals in natural waters. The lower the pH values, the higher the metal bioavailability [17]. pH along with other physicochemical factors such as temperature, transparency and nutrients as major factors affecting the productivity of fresh water bodies [5]. pH is the negative logarithm of hydrogen ion concentration and usually determines the acidity or alkalinity of a water system. Aquatic organisms are affected by pH because their metabolic activities depend on pH [5]. Decreasing pH increases corrosiveness of water and enhances the mobilization of metal salts from soil. Metallic compounds may also be mobilized from minerals and this may eventually reach water bodies [18].

### 3.1.3. Dissolved oxygen

The mean values of dissolved oxygen recorded in this study ranged from 12.41 mg/l - 15.32 mg/l for wet season and 12.94 mg/l -13.98 mg/l for the dry season. The highest value of 15.32 mg/l was recorded at $SS_3$ in the wet season while the lowest value recorded was 12.41 mg/l also in the wet season at $SS_1$. There was no significant difference ($P<0.05$) between the DO values in both seasons. Oxygen is available to aquatic organisms for their metabolic activities as dissolved oxygen in water Dissolved oxygen (DO) is therefore the key parameter in determining the extent and kinds of life of a water body as the deficiency of oxygen is fatal to many aquatic animals such as fish [19]. Temperature has a significant influence on dissolved oxygen. This is because DO decreases with increasing temperature. In a water course, when oxygen is consumed by respiring organisms faster than it is being replenished, an oxygen deficit which may lead to extinction of life forms results [14] Compared with results obtained by [20] on the studies of Miniweja fresh water stream in eastern Niger Delta, the DO values of this study were higher. This indicated a lower pollution status of the river under study. This is because most pollution enhancing facilities especially industries are non-existent in the area under study.

### 3.1.4. Biochemical Oxygen Demand

The range of BOD for wet season was 4.11-5.12 mg/l while the range for dry season was 3.42-4.75 mg/l. Their corresponding means were 4.75 mg/l and 4.15 mg/l respectively. Biochemical oxygen demand, BOD, measures a short-term oxygen demand exerted by a pollutant. BOD is a reasonable realistic measure of water quality with regards to oxygen. It gives information on the presence of biologically active microorganisms in water. A good knowledge of parameters such as DO and $BOD_5$ guide decision makers, especially in countries with rivers affected by severe organic pollution in the establishment of control strategies to decrease the potentials for oxygen depletion. The values for BOD recorded in this study were high compared to values reported by[20]. The permissible level for BOD is 10.00mg/l [21].

### 3.1.5. Electrical Conductivity

The conductivity levels of EtimEkpo River ranged from 13.09 $\mu Scm^{-1}$to 19.04 $\mu Scm^{-1}$ in the wet season and 12.12 $\mu Scm^{-1}$ to 13.90 $\mu Scm^{-1}$ in the dry season. The EC values of the river under study for both seasons are lower than the WHO (2008) limit of 250 $\mu Scm^{-1}$ for drinking water. The highest conductivity value of 19.04 $\mu scm^{-1}$ for the wet season was recorded at EtokUrukEshiet (SS1) while the highest value of 13.90 $\mu Scm^{-1}$ was recorded at Uruk Ata IkotEkpor (SS4) for the dry season (Tables 1 and 2). Electrical conductivity is the capacity of water to conduct electricity and varies both with the number and types of ions the solution contains [22, 23]. The number and types of ions of a river system is closely linked with the geology and water movement within a catchment [24]. The relatively low conductivity values could be attributed to the non-existence of industrial activities of the area. The EC values were however greater than the values reported by [25] for both the pre-monsoon and post monsoon seasons of India and lower than values reported by [16].

### 3.1.6. Total Dissolved Solids

The range of TDS in this study was 95.0 mg/l- 120.92mg/l in the wet season and the range for dry season was 99.63 mg/l-131.91 mg/l. The mean for both wet and dry season were 107.27mg/l and 116.83 mg/l respectively. Total dissolved solids provide information on the general water quality as it affects the aesthetic value of water. It also has effect on the turbidity of the water [24]. The density of water depends also on the total dissolved solids that occur in natural water. This is because natural water contains complex mixture of cations and anions. TDS also influences water use such as for drinking, irrigation, industrial use and recreational use. Cations and anions such as bicarbonate, sulphate, phosphate, nitrate, magnesium, calcium, sodium, trace metals and organic ions contribute to the total dissolved solids in water [24]. During the dry season, the water level is reduced thus leading to the concentration of dissolved solids. Studies by [26] and [27] reported high TDS values in Asa River and Rivers Ona and Alaro in Ibadan. TDS could cause a reduced development and survival of salmonid eggs and larva and clogging on fish gills [28].

### 3.2. Nutrients in water

Rain water run-off and discharge of sewage into rivers are two common ways that nutrients enter and pollute the aquatic environment [5]. The nutrients in water analysed for in this research work were $PO_4^{3-}$, $SO_4^{2-}$, $NO_3^-$, $CO_3^{2-}$ and $Cl^-$. The results on nutrients in water are also presented in Tables 1 and2. The $NO_3^-$ levels in EtimEkpo River ranged from 0.02 mg/l to 0.01 mg/l in the wet season and 0.03 mg/l to 0.02 mg/l in the dry season. The values were within the range reported by [16] for the River Niger at Onitsha bank. It was however lower than the levels reported by [29] for five river systems in Delta State, Nigeria. The WHO permissible limit of nitrates in water is 50mg/l [29, 30]. The water samples from EtimEkpo River therefore had safer level of nitrates.

The $PO_4^{3-}$ levels in EtimEkpo River was 0.02mg/l in all sampling stations in the wet season and ranged between 0.02mg/l – 0.01mg/lin the dry season. Phosphorus as $PO_4^{3-}$ is not very soluble in water but is readily adsorbed to clay particles and reacts to form nearly insoluble precipitates with Fe, Al and Ca. The levels of $PO_4^{3-}$ in EtimEkpo River were within the range reported by [29], but lower than the values reported by [16] and [31]. The levels of $PO_4^{3-}$ in the river were below the WHO permissible limit of 1.0mg/l [16, 30]. Thus it would not contribute towards the eutrophication of the river.

The $SO_4^{2-}$ levels in EtimEkpo River ranged from0.42 mg/l - 0.31mg/l in the wet season and from 0.41mg/l – 0.35 mg/l in the dry season. The WHO permissible limit of $SO_4^{2-}$ in water is 250mg/l [16]. The values were also below those reported by [31] and within the range reported by [29].

River water readily dissolves $CO_2$ from the atmosphere and converts it to $HCO_3^-$. The $CO_3^{2-}$ levels in EtimEkpo River ranged from 0.32mg/l – 0.22mg/l in the wet season. The range in the dry season was 0.40mg/l – 0.28mg/l. These values were consistent with the range reported by [16].

Chlorides enter the waterways through anthropogenic means such as sewage and also from agricultural fertilizers. The WHO permissible limit of $Cl^-$ in water is 200mg/l [29]. In EtimEkpo River the levels of the $Cl^-$ ranged from 38.98mg/l – 29.88mg/l in the wet season and from 29.69mg/l – 27.13mg/l in the dry season.

### 3.2.1. Correlation between physicochemical parameters and nutrient in water from EtimEkpo River

The result of the correlation analysis between the physicochemical parameters and nutrients in water samples from EtimEkpo River during the wet and dry seasons are presented in Tables 3 and 4. During the wet season the following physicochemical pair showed a negative correlation at $P<0.05$. This was pH and BOD ($r = -0.895$). The negative sign implied an inverse relation between the pair signifying that as the BOD increased, the pH increased. During the dry season, the following physicochemical pairs showed negative correlation at $P < 0.01$. These include Temperature and pH($r = -0.964$), DO and Conductivity ($r = -0.975$), and $PO_4^{3-}$and $SO_4^{2-}$ ($r = -0.996$). The negative correlations showed that as the temperature increases the pH decreased. The decrease in pH could be attributed to the decomposition of organic matter which results in the increased acidity of the water, with a corresponding decrease in the pH of the water. On the other hand it showed that the sources of the input of the parameters are different. The sources of nutrient inputs into the river include agricultural runoff, municipal discharges.

**Table 3:** Pearson's correlation matrix for physicochemical parameters and nutrients in water from EtimEkpo river in wet season

| | **Temp** | **pH** | **DO** | **BOD** | **Cond** | **TDS** | **$NO_3^-$** | **$SO_4^{2-}$** | **$CO_3^{2-}$** | **$Cl^-$** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Temp** | 1 | | | | | | | | | |
| **pH** | -0.102 | 1 | | | | | | | | |
| **DO** | -0.389 | 0.708 | 1 | | | | | | | |
| **BOD** | 0.065 | -0.895* | -0.362 | 1 | | | | | | |
| **Cond** | -0.473 | -0.021 | -0.398 | -0.294 | 1 | | | | | |
| **TDS** | -0.404 | 0.614 | 0.219 | -0.829 | 0.485 | 1 | | | | |
| **$NO_3^-$** | -.245 | 0.306 | -0.118 | -0.439 | 0.786 | 0.264 | 1 | | | |
| **$SO_4^{2-}$** | 0.826 | 0.184 | -0.450 | -0.384 | 0.021 | 0.044 | 0.229 | 1 | | |
| **$CO_3^{2-}$** | 0.640 | 0.104 | -0.037 | -0.152 | -0.606 | 0.117 | -0.701 | 0.452 | 1 | |
| $Cl^-$ | -0.597 | -0.384 | -0.487 | 0.075 | 0.872 | 0.346 | 0.421 | -0.289 | -0.534 | 1 |

*. Correlation is significant at the 0.05 level (2-tailed).

**Table 4:** Pearson's correlation matrix for physicochemical parameters and nutrients in water from EtimEkpo River in dry season

| | **Temp** | **pH** | **DO** | **BOD** | **Cond** | **TDS** | **$NO_3^-$** | **$PO_4^{3-}$** | **$SO_4^{2-}$** | **$CO_3^{2-}$** | **$Cl^-$** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Temp** | 1 | | | | | | | | | | |
| **pH** | -.964** | 1 | | | | | | | | | |
| **DO** | -0.536 | 0.534 | 1 | | | | | | | | |
| **BOD** | 0.374 | -0.198 | -0.008 | 1 | | | | | | | |
| **Cond** | 0.552 | -0.532 | -0.975** | 0.205 | 1 | | | | | | |
| **TDS** | -0.683 | 0.521 | -0.073 | -0.783 | -0.029 | 1 | | | | | |
| **$PO_4^{3-}$** | 0.325 | -0.395 | 0.559 | 0.1 | -0.541 | -0.495 | 1 | | | | |
| **$NO_3^-$** | -0.434 | 0.348 | 0.659 | -0.689 | -0.81 | 0.308 | 0.408 | 1 | | | |
| **$SO_4^{2-}$** | 0.397 | -0.308 | -0.588 | 0.735 | 0.753 | -0.331 | -0.373 | -.996** | 1 | | |
| **$CO_3^{2-}$** | -0.38 | 0.549 | -0.198 | -0.04 | 0.151 | 0.222 | -0.81 | -0.076 | 0.053 | 1 | |
| $Cl^-$ | 0.169 | -0.202 | 0.369 | -0.466 | -0.526 | -0.158 | 0.594 | 0.803 | -0.824 | -0.201 | 1 |

**. Correlation is significant at the 0.01 level (2-tailed).

## 4. Conclusion

The physicochemical parameters of EtimEkporiverwere found to be within international guidelines such as WHO, EPA and FEPA. The Pearson's correlation coefficient revealed weak correlations amongst the parameters measured, indicating different sources of their input to the water body. Over-all the study revealed a low pollution status of the river under study.

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