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*Research Article*

# Evaluation of the Ecological Impact of Human Settlement on the Water Quality of Lower Cross River, Nigeria

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The ecological impact of human settlement on the water quality of Lower Cross River, Nigeria was evaluated. The physical and chemical conditions of the river water were determined from January to August, 2011. Three stations comprising Itu in Akwa Ibom State with intense human activities (station 2), its upstream (without human settlement) at Cross River State (station 1) and the downstream (station 3) were sampled. The Parametric One Way Analysis of Variance (ANOVA) indicated that of the 17 physical and chemical parameters determined, only water level and COD were found to be significantly different ($P < 0.01$) among stations. The spatial variations in the level of significant correlation of the physical and chemical parameters among the stations and the higher level of interrelationship in downstream station 2 and 3 than station 1 could be attributed to inputs resulting from human settlement. Comparison between some parameters with Standard Organization of Nigeria, and World Health Organization maximum permitted levels for drinking water indicated that the water was not polluted. However, the BOD and COD concentrations of greater than 2 mg/L and 20 mg/L respectively were indicative of pollution.

## 1. Introduction

The lower Cross River which originated from Cameroon is the main river in southeastern Nigeria and gives its name to Cross River State, Nigeria. The river serves as the main source of water for domestic and agricultural purposes, source of shell and fin-fish for the major communities settling along its banks. Human settlements are recognized as ecological systems, in the sense that they are "habitat systems" for human populations, which may be directly comparable with "natural" ecosystems [1]. Clean, safe, and adequate freshwater is vital to the survival of all living organisms and the smooth functioning of ecosystems, communities, and economics. Declining water quality has become a global issue of concern as the growth of human populations, expansion of industrial/agricultural activities, and terrible threats of climate changes alternate the hydrological cycle. Water quality issues are complex and diverse and are deserving of urgent attention and action [2].

Human are adjudged to be the principal drivers of change on the earth's surface. Such impact may shape the earth in small subtle ways and sometimes in big catastrophic ways [3, 4]. Ecosystems are damaged by degraded water quality, among other factors. The biodiversity of freshwater ecosystems has been degraded more than any other ecosystem, including tropical rainforests [5].

Data existing on the assessment of water quality using physical and chemical parameters for coastal rivers with Atlantic tidal effect in Nigeria are scanty. The findings are reported as follows: survey of drinking water quality using spot samples along River Sombreiro, Imo River, and new Calabar River has been conducted [6]. Investigation of seasonal variations in the water quality indices of dissolved oxygen, biochemical oxygen demand, turbidity, total solids, nitrate, phosphate, pH, temperature, and faecal coliforms of Warri River revealed seasonal effects on these parameters [7]. Variations in the physicochemical features of New Calabar River indicated acidic, low alkaline, and soft water with obvious seasonal flux in silica level with higher dry season values than wet season [8]. Temperature, and salinity variations of Qua Iboe River exhibited clearly defined hydrological regimes with bimodal and unimodal peaks, respectively [9]. Further investigation of New Calabar River revealed significant seasonal variations with dry season values higher than wet ones with respect to surface water temperatures, conductivity, transparency, biochemical oxygen demand, total dissolved solids, total hardness, and total alkalinity [10]. Investigation of seasonal variation in water quality of the Cross River system dominated by sampling of the Cross River Estuary indicated that the significant seasonal variations in the physicochemical parameters are mainly attributed to seasonal changes in meteorological events, while the spatial variations are related to tidally-forced mixing processes, local interactions with coastal, and riverine discharges [11, 12]. Baseline ecological studies of the Great Kwa River, one of the major tributaries of the Cross River Estuary have been conducted [13].

The purpose of the present study is to provide baseline data on the water quality of Lower Cross River which is a freshwater system and tidal downstream by using physical and chemical characteristics, to determine the interrelationship between the characteristics, and to give the differences of these characteristics between upstream (station 1 without human settlement), station 2 with intense human activities, and downstream (station 3) with a view to establish significant changes attributable to human settlement.

## 2. Study Area

The Cross River Basin encompasses an area of about 70,000 $km^2$, of which 50,000 $km^2$ lies within Nigeria and 20,000 $km^2$ lies with Cameroun [14]. From observed physiographic, ecological, and zoogeographical discontinuities, the section draining southeastern Nigeria is termed the "Lower Cross", and the Cameroonian section is referred to as the "upper Cross." The Lower Cross River is located between longitudes 7°43′ and 8°22′E and Latitudes 4°28′ and 5°27′N (Figure 1). The main river channel covers a distance of 600 km from source to mouth, where it discharges directly into the Atlantic Ocean at the Bight of Bonny [15]. The estuarine catchment area is 95 $km^2$ [16], thus, resulting in a freshwater basin area of 69,905 $km^2$.

The Lower Cross River Basin lies within a typical tropical humid climate, which is characterized by distinct dry and wet seasons, peak dry seasons occurs in December–February [17]. The drainage basin is generally of low relief and lies almost entirely on the coastal plain of the tropical rainforest belt of southeastern Nigeria which is typified by high temperatures and rainfall with thick forests. The dry season which lasts from November to April is influenced by the hot northeastern continental air mass from the sahara desert and is characterized by fairly high temperature. Relative humidity is usually high throughout the year with a percentage of 80% and much higher towards the coast. Maximum rainfall occurs during the months of June–September [18]. The study area is made up of secondary rainforest which has been deeply subjected to deforestation and other human activities; fishing is a common activity across the entire stretch of the river.

Three stations were selected for sampling. These stations are Itu in Akwa Ibom State with intense human activities

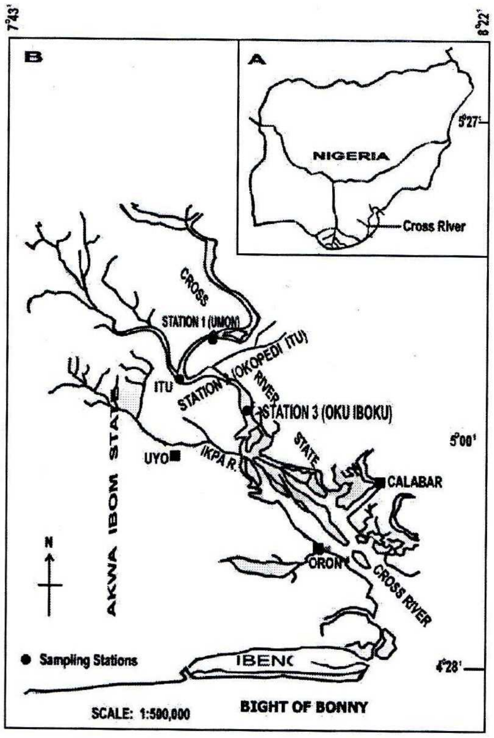


Figure 1: Map of Lower Cross River showing study stations. Inset: map of Nigeria showing Cross River.

(station 2), its upstream (without human settlement) at Cross River State (station 1), and the downstream (station 3).

The description of each station is given below.

*Station 1* is about 4 km from Umon town in Cross River State and without human settlement. The dominant vegetation in this station are palm trees (*Elaeis guineensis*), bamboo (*Bambusa africana*), plantain and banana (*Musa* spp), and guinea grass (*Panicum maximum*). The crops cultivated in the riparian belts are okro (*Abelmoschus esculentus*), garden egg (*Solanum melongena*), and vegetables. The station is characterized by a sandy erosional biotope and a muddy bankroot biotope made up of silt.

*Station 2* which is 18 km from station 1 is located in Itu town, by Mary Slessor hospital. This station is characterized by intense deforestation, dense human settlement resulting in regular bathing, and washing of clothes and utensils in the river. Surface run-off of inputs from domestic wastes is also common at this station during wet season. Okro and vegetables are also cultivated in the riparian areas of this station. The station is associated with sandy erosional biotope and muddy bankroot biotope made up of silt and clay. This station is also characterized by Itu bridge located along Uyo-Calabar highway and is reported to be one of the landmark achievements of the Gowon administration when it was completed in 1975.

*Station 3* is about 21.5 km downstream of station 2. It is located in Oku Iboku, Akwa Ibom State. The dominant vegetation is palm trees. It is characterized by a sandy substratum and basically a muddy bankroot biotope. The station is tidal but the water is fresh. This station is less deforested and associated with human activities than in station 2.

## 3. Materials and Methods

The sampling programme was carried out monthly between 0800 and 1700 h each sampling day, from January to August, 2011. Physical features such as air and surface water temperatures, water level, transparency, and flow velocity were measured *in situ* during each trip. Water samples for other physical and chemical analysis were collected with one litre polyethylene bottle, previously washed, rinsed, and dried in the laboratory. Water samples for dissolved oxygen and biological oxygen demand determination were taken using 250 mL reagent bottles with glass stoppers.

Physical and chemical analysis of water samples was based on [19, 20]. Air and surface water temperatures were measured with OAKTON MIN/MAX memory/digital thermometer, China. Transparency was measured by taking the average of the depth of disappearance and reappearance of a secchi disc. Water level was determined by dipping a string tied to a heavy stone to the bottom of the water at a specific point at the middle of the different sampled stations and the resulting depth measured with a graduated rule. Total dissolved solids (TDS) was determined by filtering a well-mixed sample of the water through a standard glass fibre filter, and the filtrate evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dry weight was taken as the total dissolved solids. The residue retained on the filter was dried to a constant weight at 103 to 105°C. The increase in weight of the filter was taken as the total suspended solids (TSS). The total solids (TS) were summation of TDS and TSS. Flow velocity was measured using the surface float method by floating a ping pong filled with water over a given distance on the water surface at a given time, and the flow velocity calculated in m/s. Electrical conductivity was measured with a battery-operated conductivity bridge (model MC-1 Mark V). pH was measured using digital pH/temperature meter (model 7065). Alkalinity was determined by titration method, using phenolphthalein alkalinity. Dissolved oxygen (DO) was determined by Winkler's titrimetric method. Biochemical oxygen demand ($BOD_5$) was a measure of dissolved oxygen before and after incubation in the dark at 20°C for five days. Chemical oxygen demand (COD) was determined using DRB 200—Reactor and Colorimetric Determination Method 8000. Nitrate ($NO_3^-$), Sulphate ($SO_4^{2-}$), and Phosphate ($PO_4^{3-}$) were determined by using HACH SPECTRO DR 3800.

Past statistical software was used to analyze the following: all measures of central tendency and dispersion to characterize the stations in terms of the physical and chemical conditions, test of significance using parametric One Way Analysis of Variance (ANOVA), and detecting points of significant differences using Tukey's Pairwise comparison. SPSS statistics 17.0 software was used to analyse correlation coefficient among the physical and chemical parameters.

Where available, maximum permitted level of each physical and chemical parameter for drinking water quality was provided for [21, 22].

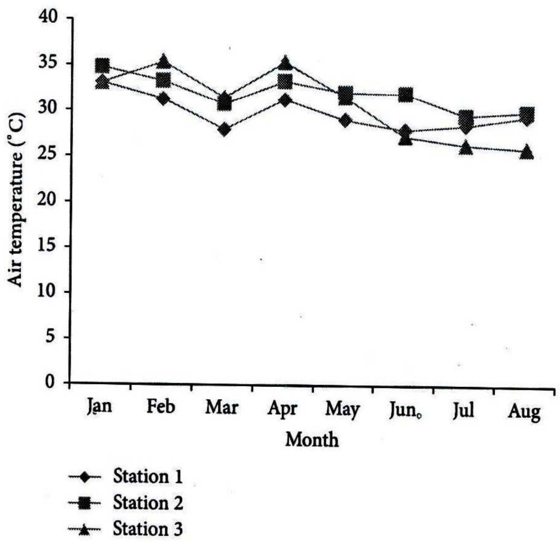


FIGURE 2: Spatial and temporal variations in air temperature at the study stations, Jan–Aug, 2011.

## 4. Results

The physical and chemical parameters of the Lower Cross River study stations are summarized in Table 1, using measures of central tendency and dispersion. The results of statistical analysis to test for significant difference in parameters among the study stations and maximum permitted levels for parameters available are also indicated.

There was no consistent trend in variation between air and water temperatures (Figures 2 and 3, resp.) the air temperature for all stations ranged 26.0 to 35.4°C, with a mean range of 29.89 to 31.99, while that of water was 26.0 to 33.2°C, with a mean range of 29.68 to 30.11. Air and water temperatures during the dry months were predominantly higher than values recorded during the wet months.

The range of transparency for all stations was 0.210 to 2.195 m with a mean range of 0.664 to 1.202. Transparency values in dry months were significantly higher than those recorded in wet months (Figure 4).

The range in water level for all stations was 2.40 to 13.99 m, with mean range of 5.236 to 10.355. Water level was significantly higher in station 3 than in stations 1 and 2. Water level values in wet months were significantly higher than those recorded in dry months (Figure 5).

Total dissolved solids for all stations ranged from 18.0 to 50.0 mg/L, with mean range of 26.0 to 28.0, and higher values in wet months than dry months (Figure 6). Total suspended solid for all (Figure 7) stations ranged from 0.001 to 0.04 mg/L with mean range of 0.0089 to 0.0128. The total solids for all the stations ranged from 20.0 to 50.001 mg/L (Figure 8), with mean range of 26.009 to 28.013. The total solids followed the same trend for total dissolved solids.

Flow velocity for all stations ranged from 0.031 to 0.276 m/s (Figure 9), with mean ranged of 0.1136 to 0.1761. There was no consistent trend in flow velocity.

Electrical conductivity for all stations ranged from 36.0 to 80.0 μS/cm (Figure 10), with mean range of 53.63 to 65.0.

Table 1: Summary of the physical and chemical parameters of the Lower Cross River study stations (January–August, 2011). Values are mean ± SE. The minimum and maximum values are noted in parentheses.

| Parameters | Station 1 | Station 2 | Station 3 | Statistical significance | Maximum permitted levels SON | Maximum permitted levels WHO |
|---|---|---|---|---|---|---|
| Air temperature (°C) | 29.89 ± 0.55 (28.0–33.1) | 31.99 ± 0.63 (29.6–34.3) | 30.84 ± 1.36 (26.0–32.4) | $P > 0.05$ | | |
| Water temperature (°C) | 29.68 ± 0.91 (26.1–32.0) | 29.89 ± 0.94 (26.0–32.3) | 30.11 ± 1.04 (26.0–33.2) | $P > 0.05$ | Ambient | |
| Transparency (m) | 1.022 ± 0.2438 (0.250–2.160) | 1.202 ± 0.3113 (0.400–2.195) | 0.664 ± 0.2501 (0.210–1.550) | $P > 0.05$ | | |
| Water level (m) | 7.178 ± 0.8205 (3.86–10.015)$^{A}$ | 5.236 ± 0.8213 (2.40–9.62)$^{A}$ | 10.355 ± 1.0901 (5.30–13.99)$^{B}$ | $P < 0.01$ | | |
| TDS (mg/L) | 28.0 ± 2.04 (20.0–40.0) | 27.88 ± 3.29 (21.0–50.0) | 26.0 ± 2.37 (18.0–40.0) | $P > 0.05$ | 500 | NHC |
| TSS (mg/L) | 0.0128 ± 0.005 (0.003–0.011) | 0.0096 ± 0.005 (0.001–0.04) | 0.0089 ± 0.004 (0.002–0.03) | $P > 0.05$ | | |
| TS (mg/L) | 28.013 ± 2.044 (20.0–40.01) | 27.885 ± 3.294 (21.0–50.001) | 26.009 ± 2.367 (18.0–40.0) | $P > 0.05$ | | |
| Flow velocity (m/s) | 0.1136 ± 0.0232 (0.047–0.230) | 0.176 ± 0.0287 (0.078–0.276) | 0.1494 ± 0.0339 (0.031–0.262) | $P > 0.05$ | | |
| Electrical conductivity (μS/cm) | 65.0 ± 4.04 (48.0–80.0) | 54.0 ± 4.16 (41.0–80.0) | 53.63 ± 4.59 (36.0–80.0) | $P > 0.05$ | 1000 | |
| pH | 6.75 ± 0.072 (6.30–6.90) | 6.74 ± 0.055 (6.50–7.04) | 6.69 ± 0.099 (6.10–7.06) | $P > 0.05$ | 6.5–8.5 | NHC |
| Alkalinity (mg/L $CaCO_3$) | 6.375 ± 0.572 (3.0–8.5) | 7.255 ± 0.765 (3.0–10.0) | 6.625 ± 0.910 (3.0–9.5) | $P > 0.05$ | | |
| Dissolved oxygen (mg/L) | 8.51 ± 1.92 (4.6–18.2) | 12.25 ± 1.91 (4.0–19.8) | 10.59 ± 1.59 (5.0–13.6) | $P > 0.05$ | | |
| $BOD_5$ (mg/L) | 3.38 ± 0.78 (2.10–7.60) | 3.91 ± 0.77 (1.70–8.20) | 3.86 ± 0.75 (1.75–7.10) | $P > 0.05$ | | |
| COD (mg/L) | 161.63 ± 14.54 (102.45–211.2)$^{A}$ | 116.21 ± 12.27 (67.11–158.14)$^{B}$ | 87.98 ± 10.75 (48.30–127.52)$^{B}$ | $P < 0.01$ | | |
| Nitrate (mg/L) | 5.37 ± 0.90 (2.06–8.17) | 4.36 ± 0.83 (1.13–6.99) | 3.04 ± 0.52 (1.01–4.85) | $P > 0.05$ | 50 | 50 |
| Sulphate (mg/L) | 3.51 ± 0.62 (1.2–5.9) | 2.69 ± 0.569 (0.4–4.7) | 1.60 ± 0.418 (0.0–3.2) | $P > 0.05$ | 100 | NHC |
| Phosphate (mg/L) | 0.348 ± 0.099 (0.00–0.71) | 0.20 ± 0.061 (0.00–0.45) | 0.124 ± 0.042 (0.00–0.29) | $P > 0.05$ | | |

Similar letters indicate means that are not significantly different from each other.
NHC means not of health concern at levels found in drinking water.
$P > 0.05$: not significant; $P < 0.01$: significant.

There was no consistent trend in electrical conductivity values recorded.

Hydrogen ion concentration (pH) ranged from 6.10 to 7.06 (Figure 11), with a mean range of 6.69 to 6.75. There was no consistent trend in pH values.

Alkalinity for all stations ranged from 3.0 to 10.0 mg/L $CaCO_3$ (Figure 12), with a mean range of 6.375 to 7.255. There was no consistent trend in alkalinity.

Dissolved oxygen ranged from 4.0 to 19.8 mg/L, with a mean range of 8.51 to 12.25 mg/L. Higher dissolved oxygen values were recorded during the dry months and onset of wet months than wet months (Figure 13). $BOD_5$ followed the same trend as dissolved oxygen (Figure 14). $BOD_5$ ranged from 1.70 to 8.20 mg/L, with a mean range of 3.38 to 3.91. COD ranged from 48.30 to 211.2 mg/L, with a mean range of 87.98 to 161.63. Higher COD values were recorded in wet months than dry months (Figure 15).

Nitrate, sulphate, and phosphate at all stations followed the same trend of higher values at wet months than dry months. Nitrate ranged from 1.01 to 8.17 mg/L (Figure 16),

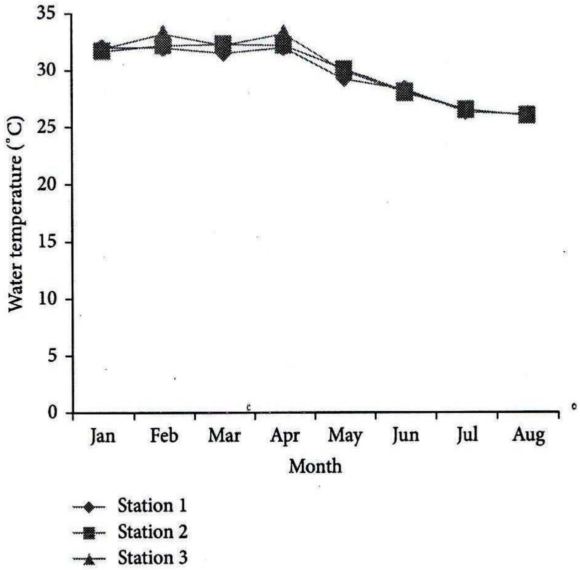


Figure 3: Spatial and temporal variations in water temperature at the study stations, Jan–Aug, 2011.

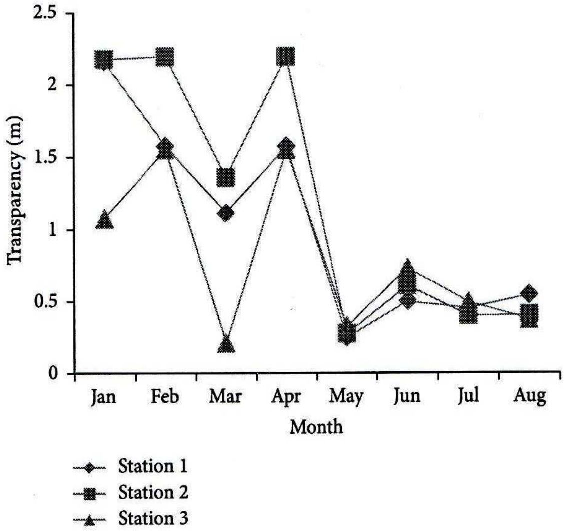


Figure 4: Spatial and temporal variations in transparency at the study stations, Jan–Aug, 2011.

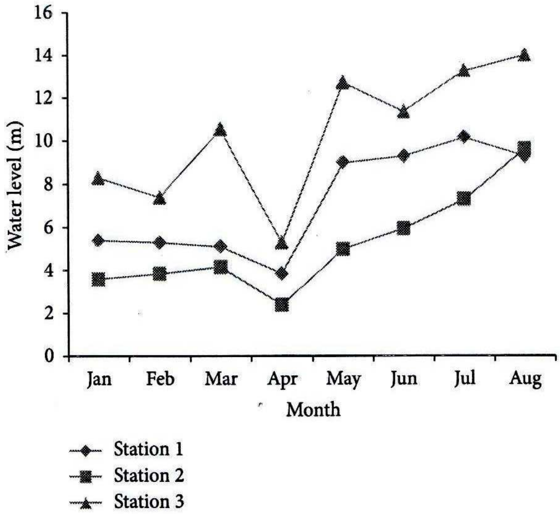


Figure 5: Spatial and temporal variations in total dissolved solids at the study stations, Jan–Aug, 2011.

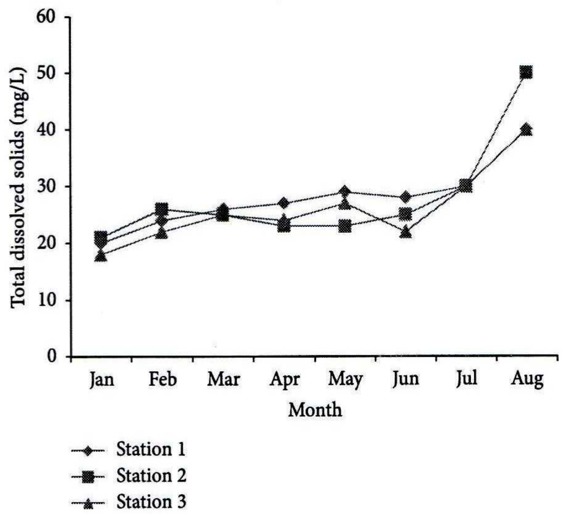


Figure 6: Spatial and temporal variations in total dissolved solids at the study stations, Jan–Aug, 2011.

with a mean range of 3.04 to 5.37. Sulphate ranged from 0.0 to 5.9 mg/L (Figure 17), with a mean range of 1.60 to 3.51. Phosphate ranged from 0.00 to 0.71 mg/L (Figure 18), with a mean range of 0.124 to 0.348.

The interrelationship among the physical and chemical parameters of the Lower Cross River study stations are shown with the values of correlation coefficient ($r$) in Tables 2(a)–2(c). The $r$ values were either not significant or significant at $P < 0.05$ or $P < 0.01$. The values ranged among all the parameters from −0.024 to 1.000 for all the stations.

Water temperature correlated significantly with TDS and TS ($P < 0.05$), COD, nitrate, sulphate, and phosphate ($P < 0.01$) for all stations; transparency ($P < 0.05$) and water level ($P < 0.01$) in station 1 and 2; flow velocity ($P < 0.05$) in station 1; and electrical conductivity ($P < 0.01$) in station 2 and 3.

Transparency correlated significantly with nitrate, sulphate, and phosphate ($P < 0.01$) in station 1 and 2; water level and COD ($P < 0.01$) in station 1; water level, dissolved oxygen, and COD ($P < 0.05$) in station 2. There was no correlation between transparency and other parameters in station 3.

Water level correlated significantly with sulphate and phosphate ($P < 0.01$) in station 1 and 2; flow velocity ($P < 0.05$), COD, and nitrate ($P < 0.01$) in station 1, TDS, dissolved oxygen, COD and nitrate ($P < 0.05$), and TS and electrical conductivity ($P < 0.01$) in station 2; electrical conductivity ($P < 0.01$) in station 3.

TDS correlated significantly with TS for all stations, COD, sulphate and phosphate ($P < 0.01$), flow velocity, and

Table 2: (a) Pearson correlation coefficient among the physical and chemical parameters of the Lower Cross River at station 1 (January–August, 2011). (b) Pearson correlation coefficient among the physical and chemical parameters of the Lower Cross River at station 2 (January–August, 2011). (c) Pearson correlation coefficient among the physical and chemical parameters of the Lower Cross River at station 3 (January–August, 2011).

(a)

| Parameters | Water temperature | Transparency | Water level | TDS | TSS | TS | Flow velocity | Electrical conductivity | pH | Alkalinity | Dissolved oxygen | BOD | COD | Nitrate | Sulphate | Phosphate |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Water temperature | 1 | | | | | | | | | | | | | | | |
| Transparency | 0.822** | 1 | | | | | | | | | | | | | | |
| Water level | −0.931** | −0.868** | 1 | | | | | | | | | | | | | |
| TDS | −0.811* | −0.702 | 0.621 | 1 | | | | | | | | | | | | |
| TSS | 0.354 | 0.279 | −0.271 | −0.273 | 1 | | | | | | | | | | | |
| TS | −0.806* | −0.697 | 0.617 | 0.999** | −0.239 | | | | | | | | | | | |
| Flow Velocity | −0.890** | −0.578 | 0.793* | 0.768* | −0.361 | 0.762* | 1 | | | | | | | | | |
| Electrical conductivity | −0.411 | −0.391 | 0.267 | 0.684 | 0.039 | 0.692 | 0.296 | 1 | | | | | | | | |
| pH | 0.263 | −0.027 | −0.059 | −0.632 | −0.219 | −0.646 | −0.448 | −0.415 | 1 | | | | | | | |
| Alkalinity | −0.662 | −0.568 | 0.610 | 0.602 | −0.825* | 0.578 | 0.646 | 0.185 | −0.158 | 1 | | | | | | |
| Dissolved oxygen | 0.575 | −0.302 | −0.362 | −0.577 | −0.151 | −0.589 | −0.396 | −0.450 | 0.483 | −0.102 | 1 | | | | | |
| BOD | 0.029 | −0.442 | 0.075 | 0.139 | −0.130 | 0.143 | −0.144 | 0.263 | 0.221 | −0.169 | 0.363 | 1 | | | | |
| COD | −0.928** | −0.900** | 0.856** | 0.850** | −0.398 | 0.843** | 0.748* | 0.612 | −0.163 | 0.644 | −0.478 | 0.249 | 1 | | | |
| Nitrate | −0.939** | −0.909** | 0.911** | 0.799* | −0.351 | 0.793** | 0.764* | 0.576 | −0.121 | 0.626 | −0.437 | 0.240 | 0.989** | | | |
| Sulphate | −0.962** | −0.862** | 0.875** | 0.863** | −0.370 | 0.857** | 0.800* | 0.605 | −0.231 | 0.647 | −0.559 | 0.128 | 0.990** | 0.984** | 1 | |
| Phosphate | −0.965** | −0.858** | 0.885** | 0.846** | −0.370 | 0.840** | 0.822* | 0.577 | −0.203 | 0.628 | −0.526 | 0.149 | 0.988** | 0.986** | 0.996** | 1 |

*Correlation is significant at the 0.05 level.
**Correlation is significant at the 0.01 level.

(b)

| Parameters | Water temperature | Transparency | Water level | TDS | TSS | TS | Flow velocity | Electrical conductivity | pH | Alkalinity | Dissolved oxygen | BOD | COD | Nitrate | Sulphate | Phosphate |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Water temperature | 1 | | | | | | | | | | | | | | | |
| Transparency | 0.817* | 1 | | | | | | | | | | | | | | |
| Water level | −0.939** | −0.788* | 1 | | | | | | | | | | | | | |
| TDS | −0.714* | −0.469 | 0.865* | 1 | | | | | | | | | | | | |
| TSS | −0.024 | −0.185 | −0.039 | −0.221 | 1 | | | | | | | | | | | |
| TS | −0.714* | −0.469 | 0.865** | 1.000** | −0.220 | 1 | | | | | | | | | | |
| Flow Velocity | −0.171 | −0.423 | 0.294 | 0.136 | −0.226 | 0.136 | 1 | | | | | | | | | |
| Electrical conductivity | −0.817* | −0.616 | 0.901** | 0.965** | −0.161 | 0.965** | 0.099 | 1 | | | | | | | | |
| pH | 0.473 | −0.396 | −0.616 | −0.778* | 0.015 | −0.778** | 0.076 | −0.807* | 1 | | | | | | | |

(b) Continued.

| Parameters | Water temperature | Transparency | Water level | TDS | TSS | TS | Flow velocity | Electrical conductivity | pH | Alkalinity | Dissolved oxygen | BOD | COD | Nitrate | Sulphate | Phosphate |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alkalinity | −0.353 | −0.254 | 0.393 | 0.473 | −0.110 | 0.473 | 0.545 | 0.450 | −0.122 | 1 | | | | | | |
| Dissolved oxygen | 0.873** | 0.751* | −0.798* | −0.458 | −0.243 | −0.458 | −0.090 | −0.562 | 0.399 | 0.006 | 1 | | | | | |
| BOD | 0.524 | −0.350 | −0.472 | −0.130 | −0.308 | −0.130 | −0.047 | −0.108 | −0.182 | 0.126 | 0.708* | 1 | | | | |
| COD | −0.903** | −0.908* | 0.821* | 0.607 | 0.107 | 0.607 | 0.123 | 0.782* | −0.562 | 0.274 | −0.761* | −0.234 | 1 | | | |
| Nitrate | −0.904** | −0.921** | 0.814* | 0.574 | 0.117 | 0.574 | 0.135 | 0.753* | −0.529 | 0.244 | −0.781* | −0.268 | 0.998* | 1 | | |
| Sulphate | −0.904** | −0.890** | 0.820** | 0.622 | 0.143 | 0.623 | 0.104 | 0.795* | −0.575 | 0.317 | −0.750* | −0.223 | 0.997** | 0.992** | 1 | |
| Phosphate | −0.968** | −0.846** | 0.898** | 0.715* | 0.035 | 0.715* | 0.126 | 0.856** | −0.586 | 0.362 | −0.808* | −0.318 | 0.971** | 0.965** | 0.975** | 1 |

*Correlation is significant at the 0.05 level.
**Correlation is significant at the 0.01 level.

(c)

| Parameters | Water temperature | Transparency | Water level | TDS | TSS | TS | Flow velocity | Electrical conductivity | pH | Alkalinity | Dissolved oxygen | BOD | COD | Nitrate | Sulphate | Phosphate |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Water temperature | 1 | | | | | | | | | | | | | | | |
| Transparency | 0.634 | 1 | | | | | | | | | | | | | | |
| Water level | −0.702 | −0.392 | 1 | | | | | | | | | | | | | |
| TDS | −0.713* | −0.627 | 0.695 | 1 | | | | | | | | | | | | |
| TSS | −0.164 | −0.532 | 0.111 | 0.136 | 1 | | | | | | | | | | | |
| TS | −0.714* | −0.627 | 0.695 | 1.000** | 0.139 | 1 | | | | | | | | | | |
| Flow Velocity | −0.421 | −0.374 | 0.704 | 0.299 | 0.161 | 0.299 | 1 | | | | | | | | | |
| Electrical conductivity | −0.791* | −0.583 | 0.801* | 0.914** | 0.042 | 0.914** | 0.316 | 1 | | | | | | | | |
| pH | 0.558 | 0.345 | −0.645 | −0.896** | 0.108 | −0.895** | −0.057 | −0.857** | 1 | | | | | | | |
| Alkalinity | −0.638 | −0.695 | 0.507 | 0.655 | 0.226 | 0.655 | 0.214 | −0.815* | −0.466 | 1 | | | | | | |
| Dissolved oxygen | 0.612 | 0.378 | −0.662 | −0.601 | −0.290 | −0.601 | −0.060 | −0.804* | 0.620 | −0.762* | 1 | | | | | |
| BOD | 0.407 | −0.046 | −0.501 | 0.069 | 0.081 | 0.069 | −0.750* | −0.105 | −0.225 | −0.082 | 0.063 | 1 | | | | |
| COD | −0.909** | −0.625 | 0.532 | 0.781* | 0.145 | 0.781* | 0.104 | 0.852** | −0.645 | 0.787* | −0.723* | −0.102 | 1 | | | |
| Nitrate | −0.925** | 0.698 | 0.544 | 0.773* | 0.214 | 0.773* | 0.134 | 0.842** | −0.638 | 0.783* | −0.720* | −0.090 | 0.992** | 1 | | |
| Sulphate | −0.911** | −0.663 | 0.585 | 0.802* | 0.147 | 0.802* | 0.169 | 0.890** | −0.665 | 0.838** | −0.749* | −0.129 | 0.994** | 0.988** | 1 | |
| Phosphate | −0.944** | −0.597 | 0.655 | 0.821* | 0.129 | 0.821* | 0.215 | 0.893** | −0.708* | 0.754* | −0.747* | −0.192 | 0.986** | 0.978** | 0.989** | 1 |

*Correlation is significant at the 0.05 level.
**Correlation is significant at the 0.01 level.

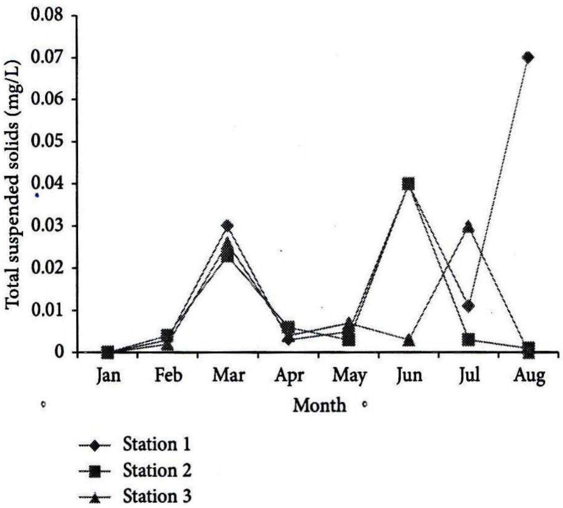


Figure 7: Spatial and temporal variations in total suspended solids at the study stations, Jan–Aug, 2011.

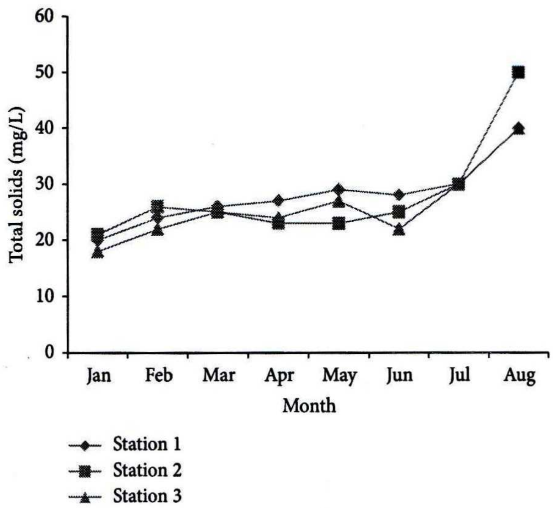


Figure 8: Spatial and temporal variations in total solids at the study stations, Jan–Aug, 2011.

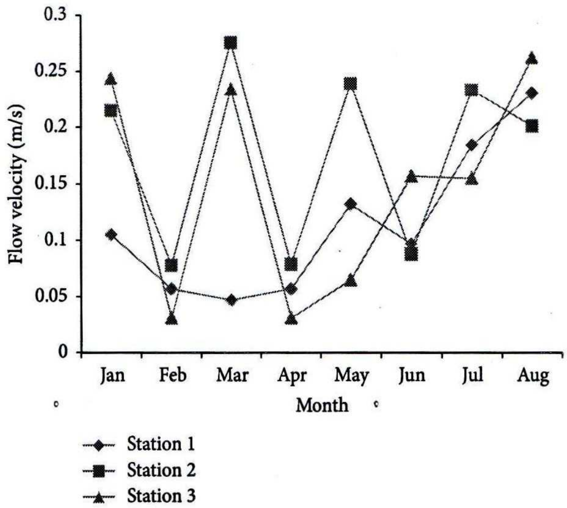


Figure 9: Spatial and temporal variations in flow velocity at the study stations, Jan–Aug, 2011.

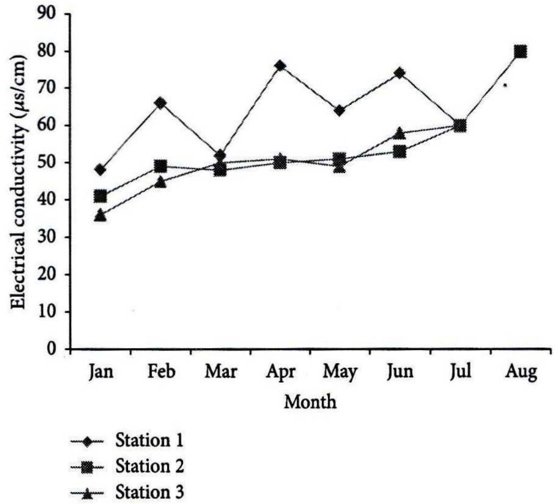


Figure 10: Spatial and temporal variations in electrical conductivity at the study stations, Jan–Aug, 2011.

nitrate ($P < 0.05$) in station 1; pH ($P < 0.05$) in station 2; electrical conductivity ($P < 0.05$) in stations 2 and 3; COD, nitrate, and sulphate ($P < 0.05$) in station 3; TSS correlated significantly with alkalinity ($P < 0.05$) in station 1, but there was no significant correlation between TSS and other parameters in stations 2 and 3. TS correlated significantly with flow velocity ($P < 0.05$), COD, nitrate, sulphate, and phosphate ($P < 0.01$) in station 1; electrical conductivity and pH ($P < 0.01$), phosphate ($P < 0.05$) in stations 2 and 3; COD, nitrate, and sulphate in station 3.

Flow velocity correlated significantly with COD, nitrate, sulphate and phosphate ($P < 0.05$) in station 1, and BOD ($P < 0.05$) in station 3.

Electrical conductivity correlated significantly with pH, COD, nitrate and sulphate ($P < 0.05$) and phosphate ($P < 0.01$) in station 2, pH, COD, nitrate, sulphate and phosphate ($P < 0.01$) and dissolved oxygen ($P < 0.05$) in station 3.

pH correlated significantly with phosphate ($P < 0.05$) in station 3. Alkalinity correlated significantly with dissolved oxygen, COD, nitrate, phosphate ($P < 0.05$) and sulphate ($P < 0.01$) in station 3.

Dissolved oxygen correlated significantly with COD, nitrate, sulphate, and phosphate ($P < 0.05$) in stations 2 and 3; and BOD ($P < 0.05$) in station 2.

COD correlated significantly with nitrate, sulphate, and phosphate ($P < 0.01$) for all stations.

Nitrate correlated significantly with sulphate and phosphate ($P < 0.01$) for all stations. Sulphate also correlated significantly with phosphate ($P < 0.01$) for all stations.

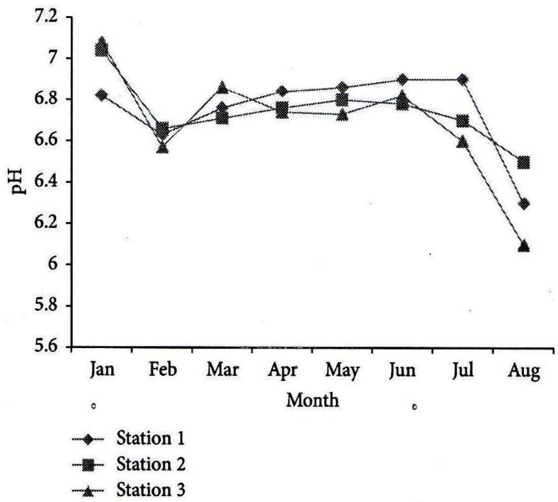


FIGURE 11: Spatial and temporal variations in hydrogen ion concentration (pH) at the study stations, Jan–Aug, 2011.

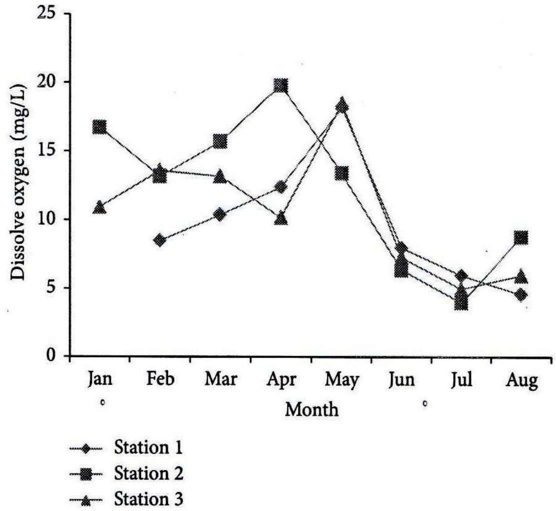


FIGURE 13: Spatial and temporal variations in dissolved oxygen at the study stations, Jan–Aug, 2011.

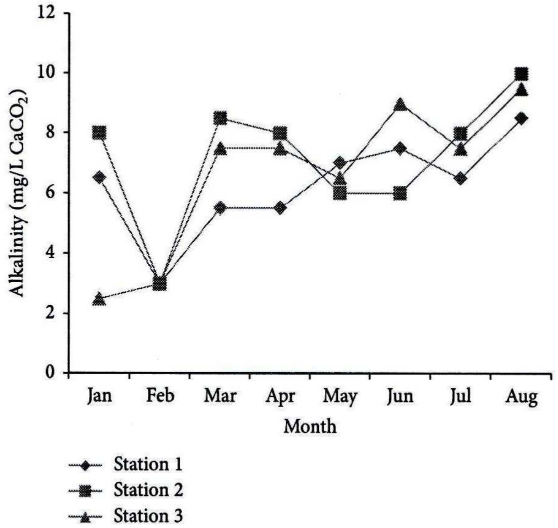


FIGURE 12: Spatial and temporal variations in alkalinity at the study stations, Jan–Aug, 2011.

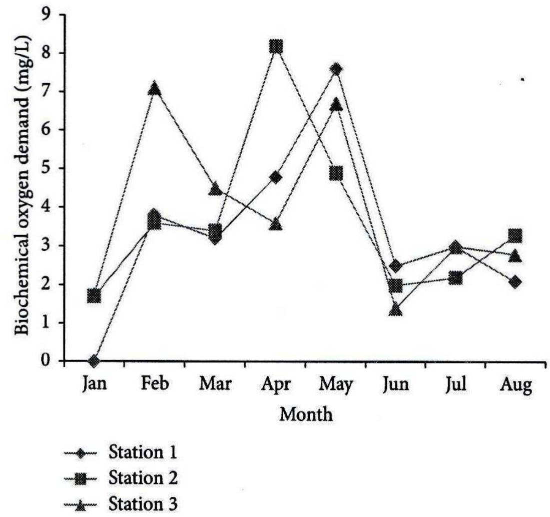


FIGURE 14: Spatial and temporal variations in $BOD_5$ at the study stations, Jan–Aug, 2011.

In all stations, significant positive correlation (station 1 = 27, station 2 = 25, and station 3 = 26) dominated significant negative correlation (station = 14, station 2 = 21, station 3 = 19).

## 5. Discussion

Physical and chemical characteristics of river water affect the biological characteristics and indicate the status of water quality [23]. Domestic use, agricultural production, mining, industrial production, power generation, forestry practices, and other factors can alter the chemical, biological, and physical characteristics of water in ways that can threaten ecosystem integrity and human health [2]. The major sources of water pollution are from human settlements, industrial, and agricultural activities [24].

The Parametric One Way Analysis of Variance (ANOVA) indicated that anthropogenic activities such as deforestation, fishing, subsistence agriculture, bathing and washing, and inputs from surface run-off associated with human settlement in the present study were not found to have significant impact on the physical and chemical characteristics of the Lower Cross River, Nigeria. Of the 17 physical and chemical parameters investigated, only water level and COD were found to be significantly different ($P < 0.01$) among stations. The significant difference in water level could be attributed to tidal action in station 3 which was found to be the cause of the significant difference by Tukey's pairwise comparison. Factors change in response to tidal, diel, and seasonal cycles as

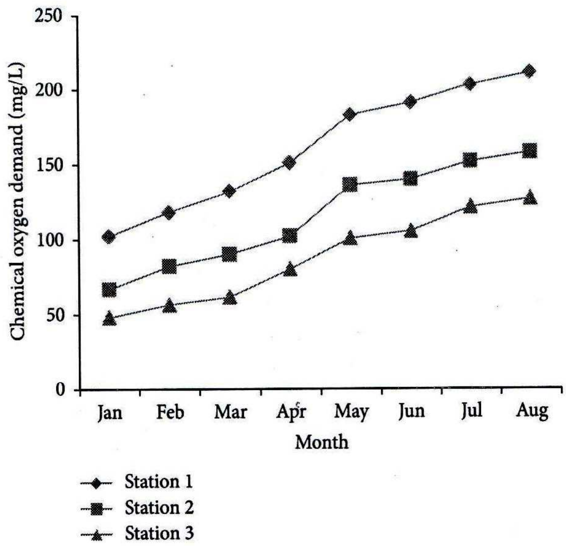


Figure 15: Spatial and temporal variations in COD at the study stations, Jan–Aug, 2011.

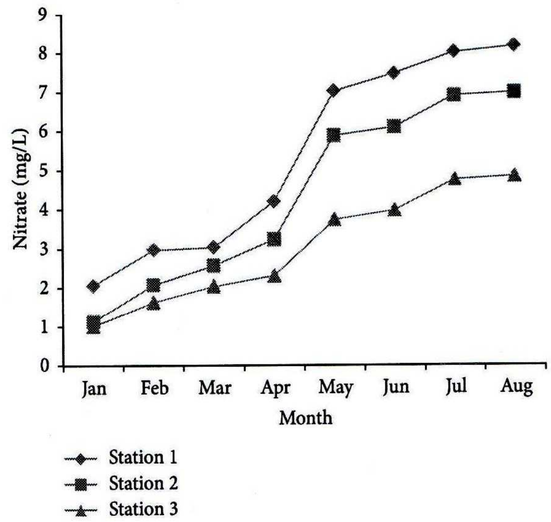


Figure 16: Spatial and temporal variations in the concentration of nitrate at the study stations, Jan–Aug, 2011.

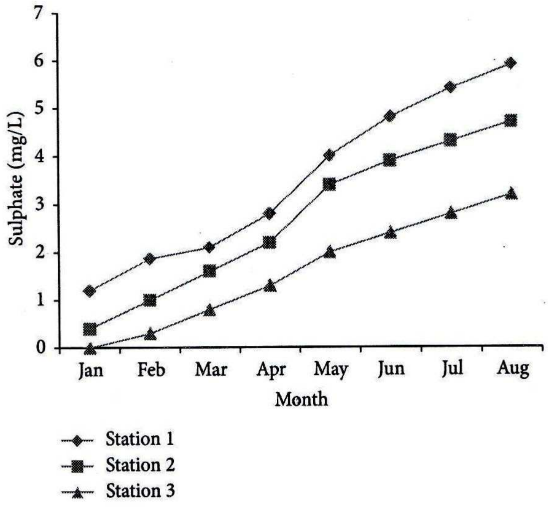


Figure 17: Spatial and temporal variations in the concentration of sulphate at the study stations, Jan–Aug, 2011.

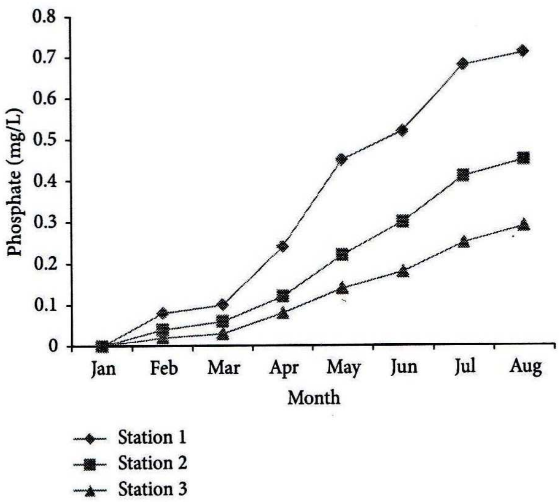


Figure 18: Spatial and temporal variations in concentration of phosphate at the study stations, Jan–Aug, 2011.

well as to sporadic variations caused by storms and mankind's intervention [25]. The significant difference ($P < 0.01$) in COD is due to the significantly higher values recorded in station 1 than in stations 2 and 3, meaning that there could be discharge of industrial effluents upstream of the river. For effective maintenance of water quality through appropriate control measures, continuous monitoring of a large number of quality parameters is essential, but since regular monitoring is a very difficult and laborious task, an alternative approach based on statistical correlation has been used to develop mathematical relationship for comparison of physical and chemical parameters in recent years [26, 27]. The spatial variations in the level of significant correlation of the physical and chemical parameters among the stations and the higher level of interrelationship in downstream stations 2 and 3 than in station 1 could be attributed to inputs resulting from human settlement. Comparison between TDS, electrical conductivity, pH, nitrate, and sulphate values of the present study and maximum permitted levels of [21, 22] indicated that the water was not polluted. However, BOD and COD concentrations of greater than 2 mg/L and 20 mg/L, respectively, for the Lower Cross River study stations were indicative of pollution. Generally, unpolluted waters typically have BOD values of 2 mg/L $O_2$ or less, and those receiving wastewaters may have values up to 10 mg/L $O_2$ or more, while COD in unpolluted surface waters range from 20 mg/L $O_2$ or less to greater than 200 mg/L $O_2$ in waters receiving effluents [28, 29]. COD is a reliable parameter for guiding the extent of pollution in water [30, 31].

The high COD recorded in the present study is similar to the range of 75–203 mg/L reported for River Pompom which is within area of mine work in Nigeria [32]. These values are at variance with COD of other Southern Nigeria waters which are characterized by low values indicative of unpolluted waters. For instance, a range of 14.20 to 15.52 mg/L has been reported for New Calabar River [29] and 2.22 to 4.05 mg/L for Warri River [33].

The records of other physical and chemical parameters investigated in this study were within the levels reported for similar rivers with Atlantic tidal effect in southern Nigeria [10, 33–36].

## 6. Conclusion

Although the Parametric One Way Analysis of Variance (ANOVA) of the physical and chemical parameters investigated indicated that human settlement in the study area did not have any significant impact on the Lower Cross River water quality, the spatial variations in the level of significant correlation of the physical and chemical parameters among the stations and the higher level of interrelationship in downstream stations 2 and 3 than in station 1 could be attributed to inputs resulting from human settlement. However, this investigation could serve as a baseline for the study area, since there is absence of industrial activities in the area at present. This could be due to the absence of industrial activities in the area. This investigation could, therefore, serve as a baseline for the study area. Also, the BOD and COD values highly above recommended maximum permitted levels require further investigation of the water quality of the river, particularly upstream of the study area. This study will be followed by assessment of the biological characteristics of the present study area of the river.

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