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Seasonality, Collinearity and Quality Assessment of the Physicochemical Properties of Okoro River Estuary, South Eastern Nigeria

John Ukpatu[1*], Enenwan Udoinyang[2] and Lawrence Etim[1]

[1]Department of Fisheries and Aquaculture, Akwa Ibom State University (AKSU), Nigeria.
[2]Department of Animal and Environmental Biology, Faculty of Science, University of Uyo, P.M.B 1017, Uyo, Nigeria.

Authors' contributions

This work was carried out in collaboration between all authors. Author JU designed the study, wrote the protocol and wrote the first draft of the manuscript. Author LE managed the literature searches and analyses of the study. Author EU managed the experimental process. All authors read and approved the final manuscript.

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ABSTRACT

Aim: To decipher the effect of season on the water quality of Okoro River estuary.
Study Design: The study was designed to cover two wet and two dry seasons for 24 months. Triplicate samples were taken per month and mean taken to represent each month. Fifteen (15) physicochemical parameters were measured for 24 months.
Place and Duration of Study: The study was carried out in Okoro River estuary, Southeastern Nigeria between April 2011 and March 2013.
Methodology: The analyses of physicochemical properties followed standard protocol in American Public Health Association (APHA).
Results: Nine physicochemical variables: temperature, pH ,TSS, TDS , DO, water hardness, Na and rainfall varied significantly between rainy and dry season ($p<0.05$), while six variables: BOD_5 THC, Ni, K, Cu and Zn were not significantly different ($p>0.05$) between the two seasons. The

*Corresponding author: E-mail: etitigwun@yahoo.com;

result also showed collinerity among the physicochemical parameters. Salinity fluctuated from 24.10‰ in the rainy season to 30.90‰ in the dry season. Temperature ranged from 24.7°C to 34.4°C with mean annual water temperature of 28± 1.934°C. Water temperature decreases with increase in rainfall. The pH values indicate slightly alkaline nature with mean of 7.38± 0.58. The geochemical indices of the three metals (Ni, Cu and Zn) ranged between 0.06 – 0.26 mg/l and showed signs of trace metal pollution. BOD ranged from 2.01 – 4.22 mg/l with a mean value of 3.04± 0.54 while DO ranged from 6.1 – 8.24 mg/l with a mean value of 7.24± 0.72 mg/l. The maximum value of 716.0 mg/l recorded for sodium indicated saline intrusion in the estuary. The total hydrocarbon content (THC) level of 0.01-2.65 mg/l indicated that the estuary is suffering from oil pollution. The pollution content in the estuary was as a result of anthropogenic perturbation. The water of the estuary was found to be hard (418.68 ± 90.6 mg/l) and may not serve as good source of drinking for the community since the value is higher than 300 mg/l recommended by WHO, 2011 but could serve as an excellent source of natural resources development.

Conclusion: The results revealed that most of the physicochemical parameters were significantly different at (p=0.05) between the dry and rainy seasons. Positive and negative associations indicated natural selection and connection of the physicochemical and environmental parameters in the ecological system.

Keywords: Anthropogenic perturbation; ecological wellbeing; oil pollution; riverine flow; water quality status.

1. INTRODUCTION

Water quality is an index of health and well being of the ecosystem and has direct impact on the water resources and human health [1]. Water quality plays an important role in increasing the productivity of the ecosystem. It provides nutritional balance and enhances healthy environment to aquatic organisms [2]. Physicochemical parameters of water ultimately govern the healthy survival of those organisms in an aquatic ecosystem [3]. Good water quality depends on the ecological integrity and to a large extent on the physicochemical characteristics of the water, the magnitude and source of any pollution load [4]. Industrialization, urbanization and modern agriculture practices have direct impact on the water quality. These factors according to the report on the implementation of Akwa Ibom State University of Technology [5] influence the water resources quantitatively and qualitatively. The evaluation of river water quality is a critical element in the assessment of water resources and community structure in an estuary. Besides, the monitoring and assessment of the variation in water parameters are essential for assessing water quality at any given location [10,11].

Researches have been carried on different water system at different locations such as Bonny estuary, Nigeria [6] Lower Cross River, Nigeria [7] Calabar River, Nigeria [8] New Calabar River, Nigeria [9] Lower Cross River estuary, Nigeria [10] Lagos Lagoon, Nigeria [11] Tarkwa Bay, Nigeria [12] Nkoro River, Niger Delta, Nigeria [13] River Benue Nigeria [14] [15] and [2] Pondicherry coast India [16] Uppanar estuary of Cuddalore Southeast coast of India [3] Tapi estuary west coast of India [17] Mumbai coast India [18] Ganga Basin, India; [19] and Gurjat Coast, Pakistan [20].

The seasonal variations in the physicochemical characteristics and nutrient budget in the network of water bodies across the globe have also been studied. These studies included various types of water bodies such as rivers, lakes, lagoons, estuaries, and oceans. An assessment of seasonal changes in water quality is an important aspect for evaluation of temporal variations of water pollution due to natural or anthropogenic inputs [46].

Okoro River estuary is a unique aquatic environment in the tropical belt with marked maritime inference due to riverine flow, vertical mixing, coastal nutrient enrichment, oil pollution and other anthropogenic sources. It is also one of the ecologically and economically rich marine ecosystems in the Southeastern region of Nigeria, providing breeding grounds for a variety of fish/ shrimp species. Numerous activities such as oil exploitation and exploration, laundry/fuel wood exploitation and fisheries activities take place in the estuary.

However, paucity of information is available in relation to physicochemical characteristics of the water quality and environmental conditions of Okoro River estuary, Southeastern Nigeria. Consequently, this study can fill the spatial gap and provide baseline information on the pollution levels in the estuary and its environment. It can also supplement any comprehensive coastal strategy for addressing the potential environmental problems associated with estuarine disturbance and coastal nutrient enrichment in the oil region of Nigeria.

2. MATERIALS AND METHODS

2.1 Description of the Study Area

The study was carried out in Okoro River estuary, Southeastern Nigeria located (4°33'N - 4°55' N; 7°45'E -7°55'E) about 650 m above sea level in the tropical mangrove forest belt east of the Niger Delta between the lower Imo and Qua Iboe River estuaries (Fig. 1). The tidal range in the area is about 0.8 m at neap tides and 2.20 m during spring tides with little fresh water input joined by numerous tributaries as they empty into the Atlantic Ocean [21]. The climate of the area is tropical with distinct rainy (April to October) and dry seasons (November to March) with a high annual rainfall averaging 2500 mm [22] [5]. The mean water temperature of the study area is 28.2°C [23].

2.2 Vegetation and Mineral Resources

The area is characterized by an expensive mangrove swamp dominated with mangrove species: *Rhizohora racemosa, Avicennia germinas, Conocarpus eractus*, interspersed with *Nypa fruticans* with inter-tidal mud flats influenced by the semi-durnal tidal regime of the estuary. Fishing and farming are the main economic activities in this study area. Oil palm (*Elaeis guineensis*) and coconut palm (*Cocus mueifera*) are also widely distributed in the surrounding villages. The area is also an oil-producing area with several oil exploration wells and oil pipelines.

Fig. 1. Okoro River estuary, Southeastern Nigeria
(Source: Google earth)

2.3 Physicochemical Analysis of Water (April, 2011 – March, 2013)

Surface water temperature, pH (hydrogen ion concentration), salinity and total dissolved solids (TDS) were measured insitu with the multi-parameters monitoring instrument (Model- EXTECH, EC, 500). Dissolved Oxygen was measured with DO meter – Model – EXTECH 11, DO 600, while biochemical oxygen demand (BOD_5) was determined with DO –meter Model – EXTECH 11, DO 600 after 5 days incubation @ 20°C . Similarly, total suspended solids (TSS) was determined using Gravimetric method. Water hardness (HAR) was determined by complexometric titration- with EDTA. Total hydrocarbon content (THC) was extracted with carbon tetrachloride (CCL_4) in a separating funnel at pH 5 and absorbance read from the Fisher Electrophotometer at 450 nm wave length after appropriate treatment and digestion with H_2SO_4 and diethyl ether. Sodium and potassium concentrations were determined by emission photometry using flame photometer (APHA, 1998) while copper, zinc, nickel was determined using atomic absorption spectro- photometer (AAS)- Perkin- Elmer Model 2380 [24]. Rainfall data was collected from the Meteorological Unit, Department of Geography, University of Uyo, Nigeria.

2.4 Statistical Analyses

Means, range and standard deviations were calculated for each parameter. T-test was used to analyze the significant differences of each parameter between seasons. Coefficient of correlation (r) was worked out to understand the co-linearity and the degree of association between various parameters and the significance level was tested at $p< 0.05$ [25]. All these statistical analyses were performed using SPSS Statistical Tools (version 19.0). The Microsoft Excel 2007 was used for the graphical presentation of data.

3. RESULTS

3.1 Seasonality

The ranges and means of physicochemical parameters determined in the rainy and dry seasons in the Okoro River estuary are presented in Table 1. The range obtained for temperature was higher in the dry season (28.50 - 34.20°C) and lower in the rainy season (24.70 - 32.40°C). The pH value showed significant fluctuations during the dry and rainy seasons and was higher in the dry season (7.58 - 8.24) than in the rainy season (6.12 - 7.86). Total suspended solids (TDS) had higher mean value in the dry season and ranged from (201.50 – 386.5 mg/l, rainy season) and 304.20 – 376.0 mg/l, dry season). Total dissolved solids (TDS) recorded higher range in the dry season (20112.50 - 25811.00 mg/l) and ranged from (13400.50- 23532.50 mg/l) in the rainy season. Dissolved oxygen ranged from (6.69 – 8.80 mg/l, rainy season) and 6.10 – 7.80 mg/l, dry season).

The range of BOD_5 (2.50 – 4.22 mg/l) in the dry season was higher compared to a minimum and maximum (2.010 – 3.28 mg/l) values in the rainy season. Salinity was optimum during the dry season (22.80 – 30.90‰) compared to a lower range during the rainy season (19.80 – 27.40‰). THC ranged between (0.05 – 2.65 mg/l) in the dry season compared to a reduced range of 0.010 -2.190 mg/l) in the rainy season. Water hardness (HAR) was higher (312.50 - 596.20 mg/l) in the dry season and lower in the rainy season (220.50 – 453.00 mg/l). Na showed higher values and ranged from (514.50 – 716.00 mg/l in the dry season and lower values (382.0 – 709.00 mg/l in the rainy season. Other parameters that had higher range in the dry season than in the rainy season include: Ni (0.110 – 0.260 mg/l, rainy season) and 0.110 - 0.250 mg/l dry season), Cu (0.120 – 0.210 mg/l, dry season) and (0.070 – 0.190 mg/l, rainy season) and Zn (0.120 – 0.240 mg/l, dry season) and (0.05 – 0.23 mg/l). However, the parameters that had wider range in the rainy season than in the dry season include: potassium (K) (300.40- 605.20 mg/l, rainy season) and 265.50- 593.40mg/l, dry season) and rainfall (133.30 - 918.20 mm), rainy season and (0.00 - 267.50 mm) dry season. Total rainfall value (31084 mm) recorded in the rainy season was higher than that of the dry season (281.8 mm). Similarly, the mean value of temperature was higher in the dry season (30.20±2.16) than in the rainy season (26.85 ±1.79). The mean value for pH was higher in the dry season (7.58 -8.24 mg/l) than in the rainy season (6.12 - 7.86 mg/l). Other parameters that had higher mean value in the dry season include: BOD_5, Salinity, water hardness and Sodium (Na). Among the heavy metals, Cu and Zn had higher mean value in the dry season than in the rainy season. On the other hand, Rainfall, DO, TSS had higher mean value in the rainy season than in the dry, while Ni and K recorded higher mean values in the rainy season than in the dry season.

Table 1. Seasonal variation in the physicochemical parameters and the t-values of the student's T-test in Okoro River estuary, Southeastern Nigeria

Parameters	Rainy season	Dry season	T-test	p	Decision rule
	Mean ± SD (Min –Max)	Mean ± SD Min –Max	t-values		
Temperature (^oC)	26.85±1.79 (24.70 - 32.40)	30.20 ± 2.16 (28.50 -34.20)	17.073	.001*	S (p < 0.05)
pH	7.21 ± 0.54 (6.12 - 7.86)	7.97 ± 0.27 (7.58 -8.24)	15.740	.001*	S (p < 0.05)
TSS (mg/l)	272.957±60.42 (201.50 - 386.50)	329.28 ± 29.86 (304.20 -376.00)	7.336	.013*	S (p < 0.05)
TDS (mg/l)	19585.79±3415.11 (13400.50-23532.50)	23512.70±1643.06 (20112.50-25811.00)	11.250	.003*	S (p < 0.05)
DO (mg/l)	7.75±0.594 (6.69 - 8.80)	6.748 ± 0.50 (6.10 – 7.80)	19.018	.000*	S (p < 0.05)
BOD_5 (mg/l)	2.75± 0.38 (2.01 - 3.28)	3.08 ± 0.50 (2.50 -4.22)	3.297	.083	NS (p >0.05)
Salinity ‰	23.685± 2.15 (19.80 - 27.40)	27.20 ± 2.38 (22.80 – 30.90)	14.195	.001*	S (p < 0.05)
THC (mg/l)	1.15 ± 0.89 (0.01 - 2.19)	1.36 ± 0.83 (0.05 -2.65)	.368	.550	NS (p >0.05)
Water_hardness (mg/l)	366.24± 59.33 (220.50 - 453.00)	438.21 ± 90.58 (312.50 – 596.20)	5.557	.028*	S (p < 0.05)
Ni (mg/l)	0.16± 0.043 (0.11 - 0.26)	0.180 ± 0.05 (0.11 -0.25)	.741	.399	NS (p >0.05)
Na (mg/l)	487.21 ± 93.97 (382.00 -709.00)	627.15 ± 66.22 (514.50 – 716.00)	16.290	.001*	S (p < 0.05)
K (mg/l)	497.81 ± 84.12 (300.40 -605.20)	476.78 ± 97.20 (265.50 – 593.40)	.321	.577	NS (p > 0.05)
Cu (mg/l)	0.13 ± 0.03 (0.07 -0.19)	0.152 ± 0.02 (0.12 -0.21)	.790	.384	NS (p > 0.05)
Zn (mg/l)	0.14 ± 0.06 (0.05 -0.23)	0.188 ± 0.03 (0.12 – 0.24)	3.329	.082	NS (p > 0.05)
Rainfall (mm)	395.80 ± 244.68 (133.30 -918.20)	83.95 ± 94.42 (0.00 – 267.50)	14.536	.001*	S (p< 0.05)

S = significant at p < 0.05, NS = not significant at p> 0.05

Nine physicochemical variables: temperature, pH, TSS, TDS, DO, water hardness Na and rainfall varied significantly between rainy and dry season (p<0.05), while six variables: BOD_5 THC, Ni, potassium, Cu and Zn were not significantly different (p>0.05) between the two seasons.

The results obtained were pooled into monthly average values to get a clear picture of the seasonal variation of the physico-chemical parameters variables (Fig. 2a-o).

3.2 Collinearity

The correlations among the physicochemical properties and their level of significance are presented in Table 2. Positive and negative associations indicated natural selection and connection of the physicochemical and environmental parameters in the ecological system.

3.3 Quality Assessment

Table 3 shows the overall mean values, range and descriptive statistics for the fifteen (15) physicochemical and environmental variables determined in Okoro River estuary. The values were compared with standard for proper quality assessment of the physicochemical properties and ecological wellbeing of Okoro River estuary.

4. DISCUSSION

4.1 Seasonality

Surface water temperature is an indispensable ecological factor that regulates the physiological behaviour and distribution of aquatic organisms. The water temperature profile of the estuary varied significantly ($p < 0.05$) and ranged from (24.70°C – 34. 40°C) between dry and rainy seasons. Temperature recorded in this study was lower during the rainy season and higher during the dry season. According to [26] the wet season brings about reduced water temperature, while the dry season results in elevated temperature.

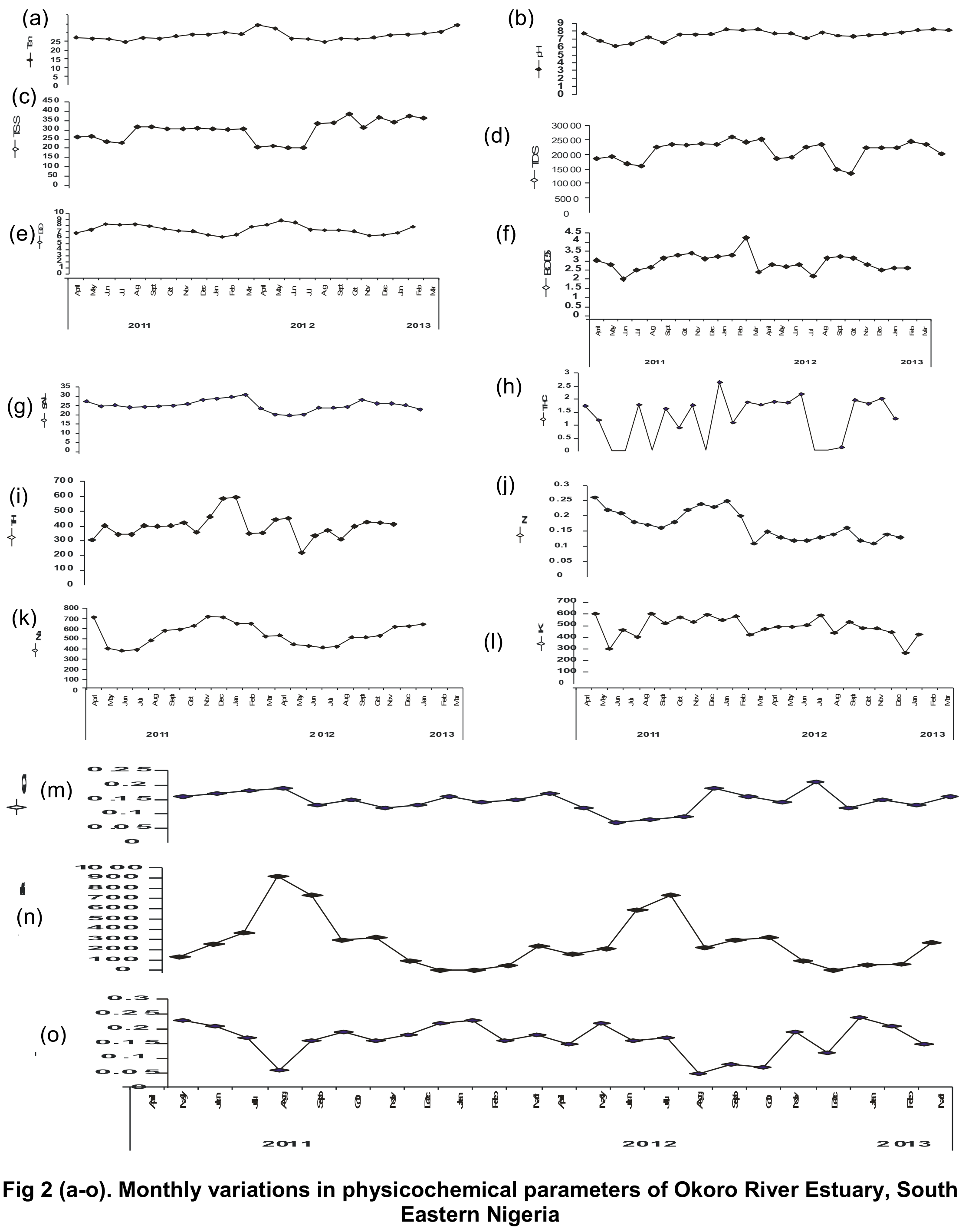

Fig 2 (a-o). Monthly variations in physicochemical parameters of Okoro River Estuary, South Eastern Nigeria

Table 2. Pearson correlation and linear relationship among physicochemical parameters in Okoro River estuary

	Temp	pH	TSS	TDS	DO	BOD5	SAL	THC	HAR	Ni	Na	K	Cu	Zn	RNF
Temp	1.000														
pH	.791	1.000													
TSS	.546	.606	1.000												
TDS	.754	.755	.935	1.000											
DO	-.736	-.871	-.384	-.590	1.000										
BOD5	.822	.786	.650	.773	-.714	1.000									
SAL	.874	.784	.354	.585	-.874	.692	1.000								
THC	.312	.513	.380	.281	-.464	.299	.339	1.000							
HAR	.847	.606	.497	.673	-.623	.701	.695	.304	1.000						
Ni	.297	.511	-.113	.035	-.714	.119	.583	.427	.080	1.000					
Na	.591	.827	.618	.707	-.784	.694	.724	.369	.306	.504	1.000				
K	.110	.442	.520	.423	-.232	.109	.221	.444	-.057	.208	.645	1.000			
Cu	-.360	-.591	-.814	-.749	.236	-.514	-.103	-.339	-.320	.201	-.472	-567	1.000		
Zn	.281	.404	.400	.411	-.491	.285	.402	.189	.013	.529	.586	.267	-.191	1.000	
RNF	-.662	-.653	-.473	-.628	.778	-.568	-.695	-.260	-.414	-.644	-.730	-.235	.235	-.768	1.000

*Keys: Temp = Temperature, pH = Hydrogen Ion, TSS= Total Suspended Solids, TDS = Total Dissolved Solids, BOD5 = Biological Oxygen Demand, SAL = Salinity, THC = Total hydrocarbon Content, HAR = Water hardness, Ni= Nickel, Na= Sodium, K = Potassium, Cu= Copper, Zn=Zinc, RNF= Rainfall pattern. *Correlation Rating: Component loading > 0.75 is very strong (significant); 0.50-0.75 is strong (significant); 0.40-0.50 is moderate and (r) < 0.40 is weak insignificant association. Intensities of association: (+) = positive, (-) = inverse or negative relationship*

Table 3. Overall mean values and descriptive variation of physicochemical parameters in Okoro River Estuary, Southeastern Nigeria

Parameters	Min	Max	Mean ±SD	Coefficient of Variation (CV)	WHO,2011
Temp (°C)	24.7	34.4	28.00 ± 1.934	0.069	<40°C
pH	6.12	8.24	7.38 ± 0.759	0.102	6-8.5
TSS (mg/l)	231.2	316.3	289.07 ± 30.72	0.106	<500 mg/l
TDS (mg/l)	16080.5	25811	21879.87± 3300.49	0.15	2000 mg/l
DO (mg/l)	6.1	8.24	7.24 ± 0.728	0.10	>5mg//l
BOD_5(mg/l)	2.01	4.22	3.04 ± 0.545	0.157	10 mg/l
SAL (‰)	24.1	30.9	26.59 ± 2.299	0.086	10-25 mg/l
THC (mg/l)	0.1	2.65	1.07 ± 0.885	0.826	10 mg/l
HAR (mg/l)	308.1	596.2	418.68 ± 90.6	0.216	300 mg/l
Ni (mg/l)	0.16	0.26	0.21 ± 0.032	0.117	0.05 mg/l
Na (mg/l)	382.0	716.0	574.25 ± 127.6	0.188	5 mg/l
K (mg/l)	300.4	605.2	511.68 ± 96.43	0.222	0.5 mg/l
Cu (mg/l)	0.12	0.18	0.15 ± 0.019	0.128	0.01mg/l
Zn (mg/l)	0.06	0.23	0.17 ± 0.046	2.56	0.1 mg/l
RNF (mm)	0.0	918.1	282.60 ±84.45	1.006	

Keys: Temp= Temperature, pH=Hydrogen Ion, TSS= Total Suspended Solids, TDS= Total Dissolved Solids, BOD_5 = Biological Oxygen Demand, SAL= Salinity, THC= Total hydrocarbon Content, HAR= Water hardness, Ni= Nickel, Na= Sodium, K= Potassium, Cu= Copper, Zn=Zinc, RNF= Rainfall pattern

The pH regime varied significantly in terms of season ($p<0.05$) in the water body throughout the study period and ranged from 6.12 to 8.24. In terms of seasonal variation, the low pH observed during the rainy season could be attributed to some factors such as the increase of CO_2 by respiration through bicarbonate degradation, the dilution of sea water by the freshwater influx and the decomposition of organic material. The high pH values recorded during the dry season might be due to the influence of seawater penetration and high photosynthetic activity. The strong inverse relationship ($r = - 0.871$, $p < 0.01$) between pH and dissolved oxygen (DO) testified to this fact. The seasonal variation of pH values observed in this study is in agreement with results of previous studies conducted by [6] in Bonny River, Nigeria where the highest pH values were recorded in the dry season and lower values of pH in the rainy season. Similar trend was reported by [9] in the New Calabar River; [10] in the Lower Cross River estuary.

The study recorded higher values of TDS in the rainy season. The higher TDS values could be associated with large surface runoff to a decrease of pH and input of materials from rainfall, mangrove vegetation, bedrocks and mud flats. Similarly, high concentrations of TDS may also reduce water clarity and contribute to a decrease in photosynthetic process. The seasonal variation of the dissolved oxygen content showed maximum value during June to September (rainy season) and the minimum during January to April (dry season). This could be ascribed to the fact that the impact of the waste discharged into the estuary is more pronounced during the dry season as compared to the rainy season due to the surface runoff and the waste discharge can also influence pH values. The results revealed that the estuarine zone was significantly influenced by freshwater input during the rainy season. Dissolved oxygen (DO) was relatively high, whereas salinity was low during the rainy season. The range of BOD_5 in the dry season (2.50 -4.22 mg/l) in the study area was high compared to the range (2.01 -3.28 mg/l) in the rainy season respectively. The variation was as a result of increased dilution and influx of fresh water during the rainy season and evaporation process and is also as a result of the increasing pollution during the dry season. The seasonal variation result showed that BOD was increasing during the rainy season as compared to the dry season. This result agrees with the findings of other studies [13,14,2].

The monthly values of salinity varied between 19.80 – 27.40‰ in the rainy season (April - October) and 22.80 – 30.90‰ in the dry season (November - March). The estuary represents a typical brackish water milieu with salinity ranging from 19.80 – 30.90 ‰. Salinity in the Okoro River estuary showed a clear unimodal oscillatory rhythm with a peak during dry season and a trough during the rainy season. During the rainy season (April-October), the salinity remained comparatively low. The lower salinity value in the rainy season may be due to heavy rainfall especially in July which had resulted in large quality of fresh water inflow into the estuary. Thus, salinity in the estuary was influenced by continental run –off from high precipitation. This corroborates the report of [6] that the influx of water mainly due to rainfall has been a major factor controlling seasonal variations in salinity gradient in estuaries of the Niger Delta region. Sodium (Na) concentrations varied from 382.0 mg/L to 716.0mg/L with mean value of 574.25 mg/l. Potassium (K) values was lowest (265.50-593.40 mg/l) in the dry season and highest (300.40- 605.20 mg/l) in the rainy season, with mean value of (511.68 mg/l). Seawater intrusion could be the cause of high sodium and potassium during the rainy season in the study area. Thus, tidal variation has a great influence on Okoro River estuary environment.

Monthly rainfall pattern ranged between 0.00 mm (dry season) and 918.6 mm (rainy season). In Okoro River estuary for instance, sea rise and seasonal variation of physicochemical properties in respect to season are largely influenced by rainfall pattern. This is evidenced by the tremendous rise in rainfall value (918.6 mm) during the month of July (the peak of the rainy reason) and 0.00 mm in December and January (the peak of the dry season). Rainfall could cause dilution of estuaries and cause reduction in salinity profile, while heat generated by sunlight in dry season months would cause evaporation of the surface water making it saltier and hence more saline [49].

4.2 Collinearity

Temperature profile showed a negative correlation with dissolved oxygen (DO) ($r = -0.766$, $p < 0.05$). This implies that the higher the temperature, the lower the dissolved oxygen. In aquatic systems, the level of oxygenation is the result of an imbalance between the process of photosynthesis, degradation of organic matter and physicochemical properties of water. Thus, the negative correlation between temperature and dissolved oxygen showed an imbalance condition between photosynthesis and degradation of organic matter in the water The significant positive correlation obtained between water temperature and salinity ($r = 0.764$, $p < 0.05$) also indicates that salinity is largely influenced by temperature. Variations in salinity in the study area were mainly influenced by the positive relationship with temperature and the inverse relationship with rainfall and entry of freshwater into the estuary. This could influence biodiversity abundance. This supports [27,11] who stated that temperature is a stable environmental factor in the shallow brackish environments and that it influences species abundance in the West African Coast. Thus, the seasonal variation in temperature in this area constitutes an important environmental forcing function in an ecological system.

The strong positive correlation between Na and pH ($r = 0.834$, $p<0.001$) indicates that the estuary is alkaline in nature. Alkalinity of the water of Okoro River estuary may be due to carbonate and bicarbonate of sodium (Na) and the vertical mixing of freshwater and seawater in the exchange zone. Similar changes in pH due to precipitation and freshwater input have been reported by [26] in his study of the Cross River estuary. Positive correlation ($r= 0.501$ $p< 0.05$) between TSS and temperature indicates that high TSS can also cause an increase in surface water temperature because the suspended particles absorb heat from sunlight. The implications of this result is that higher TSS and temperature cause dissolved oxygen levels to fall because warmer water can hold less dissolved oxygen, while fast running water carries more particles and larger-sized sediment. Also, the decrease of DO can be related to the increase of decomposition rates. Positive relationship ($r = 0.673$, $p< 0.05$) between TDS and water hardness and the strong positive correlation between TDS and Na^+ ($r = 0.707$, $p < 0.05$) and moderate correlation between TDS and Potassium (K^+) ($r = 0.423$) and TDS and Zn^+ ($r = 0.411$) respectively indicated that total dissolved solids have a relationship with K^+, Na^+ and Zn^{2+}, signifying existence of a large cation exchange capacity in the estuary. The result indicated also that level of TDS in the estuary contributes to the salt content. TDS correlated positively with salinity ($r = 0.585$). Salinity in the estuary is influenced by freshwater and sea water mix. There is greater variability of the water quality in the estuary, particularly in respect to nutrient, salinity and pH. The monthly output of total suspended solids is similar to that of total dissolved solid. It testifies to the suspended solids enrichment in oxidization basin and their participation in the chemical processes within the estuary. These solids accentuate the oxygen demand and limit reserves for the oxidation of dissolved and colloidal matter.

The correlation between DO and salinity showed an inverse relationship ($r = - 0.892$, $p < 0.001$).

This implies that DO concentration in this coastal water was largely dependent on the freshwater influx. During the present study, salinity was found to be the most important factor that controls the level of DO in the water of Okoro River estuary. Also, the major factor controlling dissolved oxygen concentration in Okoro River estuary is biological activity. This is contrary to the findings of [28] that the decomposition of organic material by micro-organisms such as bacteria did not deplete DO saturation level in freshwater stream in Calabar, Southeastern Nigeria. The decay of mangrove leaves (litter fall), woody debris, dead plants and the decay of carcasses of animals influenced the dissolved oxygen of Okoro River estuary which is evident in the strong inverse relationship ($r = -0.714$, $p < 0.05$) between BOD and DO and that organic matter decomposition influence DO saturation level. This implies that the higher the BOD, the lower the DO. The positive correlation ($r = 0.778$, $p < 0.05$) between dissolved oxygen (DO) and rainfall pattern of the study area showed that rainfall increases the velocity of running water of the estuary, thereby dissolving more oxygen than still water. The strong inverse relationship between DO and temperature ($r = - 0.736$, $P < 0.05$) is a natural process because warm water easily becomes saturated with oxygen and thus can hold less DO. This observation corroborates the findings of [16] in the Pondicherry Coast India. The result of this study revealed that BOD_5 was negatively correlated with DO ($r = - 0.740, p<0.05$). This indicates that the lower the Oxygen demand (DO) the higher the Biochemical oxygen demands (BOD) in the natural system. The result is similar to the findings of [26] who reported weak negative association between DO and BOD. [15] stated that BOD in River Benue, Makirdi increases as DO decreases and BOD increases as the bio-degradable organic content increases in water. The positive correlation ($r = 0.657$, $p< 0.05$) between BOD and temperature indicates that temperature influences the level of BOD in water.

The strong positive correlation between pH and salinity ($r = 0.830$, $p< 0.001$) suggests that an increase in pH of water is associated with increase in salinity regime. The relationship between salinity and pH also indicates an alkaline condition arising due to coastal sea-water influence. Negative association was recorded between salinity and DO ($r = - 0.628$, $p< 0.05$). This indicates that increase in salinity by evaporation in dry season in the near-shore coastal water of Okoro River estuary remains well oxygenated. Therefore salinity can be readily measured and used as a surrogate indicator for the presence of DO, TSS, TDS and pH. A strong positive correlation was observed between water hardness and TDS ($r = 0.673$, $p < 0.05$). Similar relationships were also reported by [29] for Paper Mill area of India. Positive relationship between water hardness and TDS was also established by [19] for Central Ganga Basin of India. The implication of the high water hardness in Okoro River estuary is that the greater the hardness, the harder it is for toxic metals to be absorbed through the gills of fish. This could be established from the low and insignificant relationship between water hardness and Ni ($r = 0. 06$), Na ($r = 0. 306$), Zn ($r = 0.013$) and negative correlation with Cu, $r =- 0.320$ respectively. Thus, the level of water hardness reported in this study can support a thriving phytoplankton and zooplankton community. The positive correlation between Cu, Ni and Zn was also reported by [20] for Pakistan Coast. Similar observations had been made from other estuarine water bodies: [30] coastal water off Devi estuary India; [17] West Coast of India. The positive association of Zn, Ni and Cu ($r = 0.529$; $r= 0.201$) could imply that Zn is essential in neutralizing the toxic effects of Cu and Ni.

Rainfall also causes the leaching of acid and metals concurrently into the water, which can have an immediate or long-term effect of influencing the chemical composition and pH fluctuations of an area [3] This explains why rainfall and pH have strong inverse relationship in Okoro River estuary ($r = - 0.557$, $P< 0.05$). The inverse relationships between TSS/TDS and rainfall could also be governed by suspended sediments transportation with the fresh water influx into the estuary during the rainy season.

4.3 Water Quality Assessment

The range of temperatures obtained in this study falls within the range (26.2°C to 30.1°C) obtained by [30] from the coastal waters of Devi estuary, Orissa, India. The finding also agrees with earlier reported works by [31] between 26.3°C to 30.4°C; [32] 25.9°C to 32.4°C. It is also similar to the values of 23.5°C to 33.5°C obtained in Tapi estuary of West coast India [17] and 27.0°C to 31.0°C in Nkoro River Niger Delta Nigeria [13] but lower than 28°C to 36°C reported by [33] for coastal waters of Malaysia. The mean value of 28.0± 1.9°C recorded in this study is closer to 28.2±0.06°C [14] and 28.74±0.17°C [15]. However the ranged of temperature 24.70°C -

$34.40^{o}C$ can support phytoplankton community which is an index that would provide the primary production potential of an ecosystem upon which biodiversity biomass and carrying capacity of the estuary depend.

The temporal distribution of pH ranging from 6.12 – 8.24 is characteristic of a tidal brackish water environment as noted by [34]. The range of pH value is closer to the range of 5.5 – 8.5 obtained by [33] for Malaysian coastal waters. The pH values are also within the range obtained in Pondicherry Coast of India [16]. This was also similar to the report of [17]. The result of this study disagrees with that of [13] in Nkoro River; [35] in Challawa River in Kano State, Nigeria; [14] in River Benue at Makurdi, Nigeria and [20] for the Gujrat River, Pakistan Gulf. Higher pH values recorded in this study may be due to saline intrusion and pollutant load in Okoro River estuary, Southeastern Nigeria. Generally, the obtained pH values fall within the World Health Organization limit of 6.5 – 8.5 and the water quality range of 6.5 to 8.5 for full contact recreation and animal health [36] [1] The European Union (EU) also set pH protection limit of 6.0 to 9.0 for aquatic life and fisheries development. The pH values recorded in this study were well within the preferred pH level of 6.5 to 9.0 recommended for optimal fish production [37] Thus, the pH values obtained in Okoro River estuary are capable of sustaining aquatic life. Again, water of Okoro River estuary was found to be slightly alkaline with the mean pH value of 7.3.

Total Suspended Solids (TSS) varied from 231.20 mg/l in February - March to 316 mg/l in August - September, with mean value of 289.07$\pm$ 8.869 mg/l. The mean value obtained for TSS in this study is lower than those reported by [38] in oxidation pond, Makurdi and that of Longe and Omole, 2008 in River Illo, Ota Nigeria. However, TSS levels were much higher than those reported by other researchers: [39] for Porto Novo Creek, [14,15] for River Benue, Makurdi. Thus, the total suspended solids (TSS) of the Okoro River estuary showed that the water is highly turbid. This is because turbidity in water is caused by suspended solids that interfere with the passage of light through water. This report supports [24,40] which held that turbidity is closely related to TSS. Turbidity in the water may be due to organic and inorganic constituents of the study. Also, turbidity is often determined and used as surrogate measure of total suspended solids [41,42] pointed out that if suspended solids are chemically inert; they may damage ecosystems by clouding water so that game fish and other animals that depend on vision while hunting are unable to find prey. Total Dissolved Solids (TDS) is a measure of total ions in solution and it ranged from 16080.50 mg/l - 25811.00 mg/l with a mean value of 21879.87 ±3300.49 mg/l in Okoro River estuary. This is higher than other results in other locations: River Benue, Markudi [14] drainage channel in Southwestern Nigeria [43]. This higher value may be due to weathering and dissolution of minerals from local sediment (mud particles) that is a major characteristic of the study area. This supports the findings of [33] that dissolved solid concentrations in natural waters are the result of weathering and dissolutions of minerals from local soil and bedrocks. It also supports the findings of [15] that total dissolved solids (TDS) in water consist of inorganic salts and dissolved minerals. However, rainfall facilitates the dissolution processes as can be seen in the inverse relationship between rainfall, TSS and TDS. Dissolved Oxygen (DO) ranged from 6.10 mg/l to 8.24 mg/l with a mean value of 7.24±0.210 mg/l. [13] reported DO in the range of 3.2±0.1 to 7.3 ±0.16 mg/l in Nkoro River Niger Delta, Nigeria. The result of this study also varied from 5.27± 0.24 mg/l [44] 1.80 ± 0.06 mg/l [14] and 4.33 ± 0.53 mg/l [2].

The results showed that the monthly BOD_5 oscillates between 2.01 to 4.22 mg/l with a mean value of 3.04± 0.15 mg/l. This implies that relatively stable biological activity occurs in the estuary. The mean monthly value of 3.04 mg/l is an indication of a good mineralization of organic biodegradable compound in the oxidation basin because BOD exceeding 5.00 mg/l generally indicates pollution [45]. According to [46], BOD_5 has been a very fair measure of cleanliness of any water on the basis that the values less than 1 -2 mg/l are clean. Thus, the values of 2.01– 4.22 mg/l indicate signs of pollution of Okoro River estuary. However, the values are lower than the range of 1.32 – 6.8 mg/l obtained by [9] from the New Calabar River, Nigeria; 12.47 mg/l by [35] in River Challawa in Kano State and 8.23 ±0.40 mg/l obtained by [14] in River Benue Nigeria, but higher than the BOD_5 of 0.15 – 0.92 mg/l used by [47] to affirm the fair measure of cleanliness of Port Harcourt River, Nigeria. The result of the BOD_5 level of Okoro River can be used as an indicator of the degree of organic pollution of water quality of the area. The consequences of high BOD_5 are the same as those for low dissolved oxygen: aquatic organisms may be stressed, suffocate and die at a low DO and high BOD. According to [2] high BOD values may be harmful to the biological community in the aquatic system if the oxygen consumption is great enough to cause anaerobic conditions.

The range of salinity values from this study were almost the same with the salinity values of Tarkwa Bay, Nigeria as reported by [12]. However, the range is wider than the values of Lagos, Nigeria (3.2-6.03‰) reported by [11] and wider than the value of 0.16 – 0.48‰ obtained by [26] for the Lower Cross River estuary, Nigeria. The differences could be due to estuary and freshwater ecosystem function. Tidal regime could influence the salinity differences between the two localities. Apart from tidal regime, seawater intrusion also influenced the higher salinity regime of the Okoro River estuary. These actions are largely governed by the tidal variation and nutrient dynamics. Besides, tides are the main ecological factor serving as major energy input in the estuary. Tidal variation and nutrient dynamics are more pronounced in the estuary and has strong relationship with sodium content of the area. The high degree of linkage with freshwater and marine ecosystems makes the estuary highly vulnerable to external perturbations. Besides, the salinity of the water increases toward the estuary mouth and is concomitant with pH fluctuations.

The total hydrocarbon content (THC) level of 0.01-2.65 mg/l recorded in Okoro River estuary indicates that the estuary may be suffering from chronic oil pollution. The pollution content of the Okoro River estuary could also be caused by the anthropogenic discharge of oil, gasoline and grease. This agrees with [48,4,23] who observed that the bulk of THC in the QIR and Eastern Obolo estuarine water were associated with crude oil pollutants and particulate matter. This has serious implications for the estuarine biota. Further, total hydrocarbon content of Okoro River estuary may come from oil pipelines and oil spills of boats, which can affect the growth of aquatic plants, thus affecting the photosynthetic rate resulting in low DO. However, the range 0.01 - 2.65 mg/l is not out of the tolerance limit of (0.01 – 2.78 mg/l for all crustaceans in their surrounding habits and other aquatic organisms [48].

Oxygen is removed from the water as organic matter decays. Microbial respiration can also deplete the water column of dissolved oxygen in the presence of organic matter [33]. The photosynthetic activities of aquatic plants in this area can be hindered by the anthropogenic pollutants which can lower the pH and DO of the estuary. Besides, Okoro River is an estuary in a mangrove forest zone. Therefore, the respiration rate of the aquatic organisms will be higher thus causing the pH to be lowered. Thus, the strong inverse relationship between DO and pH ($r = -0.894$, $P< 0.001$).

The wide ranges of concentrations of trace metals found in the samples showed signs of trace metal pollution. The result revealed that Cu ranged from 0.12-0.18 mg/l. These values are wider compared to 0.024 to 0.143 mg/l as reported by [33] for Malaysian coastal waters. The finding simply means that heavy metal pollution is severe in Malaysian coastal waters than that of Okoro River estuary, Southeastern Nigeria. The mean copper concentration of 0.15±0.01 mg/l was higher than 0.056 mg/l recorded by [14,15] in River Benue at Makurdi, Nigeria. Apart from its function as a biocatalyst, Cu is necessary for body pigmentation in addition to Fe and is interrelated with the functions of Zn in the body of aquatic organisms [33]. For dissolved Ni, it ranged from 0.16 -0.26 mg/l and had a mean value of 0.21 mg/l. This is smaller compared to the range of 0.027 – 0.651 mg/l reported by [33] for Malaysian coastal water. Zinc (Zn) ranged from 0.06 – 0.23. (Zn) is an essential element for plants and animals acting as an antioxidant [33]. Zinc levels were lower than the range (0.10 – 0.40 mg/l) obtained by [9] from the New Calabar River, Nigeria. However, regular check on the impact of trace metal and oil effluent discharge in Okoro River system is emphasized.

5. CONCLUSION

Changes in the physicochemical parameters synchronized with seasonal influence. Physicochemical factors interconnect with each other to enhance the process of energy fixation, accumulation of biomass, decomposition of dead organic matter and nutrient cycling in the Okoro River estuary. The distribution of nutrient in the area is influenced by factors like tidal amplitudes, salinity and rainfall. Seawater intrusion and oil pollution are major sources of perturbation in the estuary.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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