World Journal of Advanced Research and Reviews
eISSN: 2581-9615 CODEN (USA): WJARAI
Cross Ref DOI: 10.30574/wjarr
Journal homepage: https://wjarr.com/

(Research Article)

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Seasonal and Tidal variations of DO, BOD, and Nutrients in Major Rivers within Eastern Niger Delta, Nigeria

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World Journal of Advanced Research and Reviews, 2023, 20(01), 243–257

Publication history: Received on 22 August 2023; revised on 03 October 2023; accepted on 05 October 2023

Article DOI: https://doi.org/10.30574/wjarr.2023.20.1.2014

Abstract

River channels within the Oil producing Area of Nigeria are highly impacted by the activities of the Oil Companies. This work examined the Dissolved oxygen (DO), Biochemical oxygen demand (BOD), Nitrate (NO_3^-), Phosphate (PO_4^{3-}), and sulphate (SO_4^{2-}) in Calabar, Cross River, Imo, Great Kwa, and Qua-Iboe Rivers using standard procedures. Results showed that, DO, BOD, NO_3^-, and SO_4^{2-} were within their limits by NESREA whereas, PO_4^{3-} was higher than the limit. Mean levels of NO_3^-, PO_4^{3-}, and SO_4^{2-} were higher during the dry season and low tidal regime while DO and BOD showed higher levels in wet season and high tidal regime. Results also indicated that, DO belong to the slightly polluted class, BOD, NO_3^-, and SO_4^{2-} belong to the non-polluted class whereas, PO_4^{3-} varied between moderately polluted and the severely polluted classes in the studied aquatic channels. Generally, the relationships among the parameters varied from one parameter to the other. Principal component analysis (PCA) identified mainly the anthropogenic factor and moderately the natural factor as being responsible for the levels of the parameters assessed in the studied rivers. Hierarchical clusters analysis (HCA) recorded common associations and sources for the DO and BOD, PO_4^{3-} and SO_4^{2-} while NO_3^- had a separate and personal cluster. The study revealed the existing relationships among the studied parameters and their related impact on the health of the aquatic ecosystems investigated.

Keywords: Water pollution; Eutrophication; Niger Delta; Anthropogenic activities; Nigeria

1. Introduction

Clean water is vital for the existence of human beings on earth however; in developing countries such as Nigeria, most people cannot have access potable water source [1]. Consequently, majority of Africans are depending mainly on unsafe water sources hence; constantly exposed to water-borne ailments [2]. Wastes from industrial, agricultural, commercial, domestic sector and runoff from farms are the major sources of contaminants in water channels within the developing countries [3, 4, 5].These wastes have the tendency of affecting the nutrients and oxygen contents of the aquatic ecosystem [6,7]. Reports have also shown that, high nutrients content in aquatic ecosystem can reduce the level of oxygen available for aquatic organisms [8.9]. The oil activities in the Niger Delta Area of Nigeria have increased the levels of organic, inorganic and microbial contaminants in surface water bodies in the area [10, 11]. Consequently, it has resulted in strange and common ailments among the inhabitants due to exposure to these toxic substances over time [12, 13, 14]. It has also caused the extinction of some aquatic organisms, which hitherto were common in the region [15, 16].Prolonged human exposure to unclean water has high tendency to cause both the carcinogenic and non-

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carcinogenic risks on the consumers [17, 18]. Exposure to unclean water also has the potential of killing more of the consumers higher than other causes of death [19, 20].

Notwithstanding the human and environmental problems associated with elevated contaminants in aquatic ecosystem, high levels of toxic substances have been reported in surface water channels within the area investigated [21, 22, 23]. This may be due to the intensive oil and oil-related activities within the area [24].

Dissolved oxygen (DO) and **B**iochemical oxygen demand (BOD) are the livewire of the aquatic ecosystem hence; any alteration to these parameters can adversely affect the aquatic organisms [25, 26, 27]. Anthropogenic activities such as gas flaring and combustion of fossil fuels increase the levels of nitrate, phosphate, and sulphate in rivers within the study area [28, 29, 30]. According to Bijay-Singh and Craswell, [31] the major source of nitrate in surface water is runoffs from farms with nitrate-containing fertilizers. Excessive nitrate in a drinking water source can cause birth defects, cancer, and other serious health problems on the consumers [32, 33]. Elevated nitrate and phosphate in a water channel may also result in eutrophication and excessive growth of algae [34]. Human exposure to phosphate through drinking water can cause intestinal problems over time [35]. The level of sulphate in a river channel could be elevated by the organic matter contents [36]. Organic matter contents in a water body can also influence the level of phosphate within the aquatic environment [37]. Invariably, high level of decaying plants and animal bodies can increase the phosphate and sulphate contents of the water system. Prolonged exposure to high level of sulphate in water can cause diarrhea, intestinal problems, and dehydration [38, 39]. However, low concentrations in an aquatic ecosystem can adversely affect the growth **of** algae [40].

Consequently, monitoring of these parameters and their relationships in water channels is necessary for the health of human and aquatic lives [41]. It will also forestall severe damage to the food chain and assist in the proper planning by the government [42]. Although reports have shown that, high level of nutrients in aquatic ecosystem can reduce the level of oxygen available for aquatic organisms [8, 9]. Studies on the relationship between oxygen content and nutrients in the studied aquatic ecosystem are limited. Thus, this aimed at assessing the levels of DO, BOD, and nutrients in the studied river channels. It also intended to evaluate the relationships existing among these parameters and establish the existing and future effects on the studied rivers. The outcome of this investigation will disclose the negative impact of dumping organic wastes on the health status of the studied aquatic ecosystems.

2. Materials and methods

2.1. Study area

The study covers an area from latitude 4°33’N - 5°10’N to longitudes 7°31’E - 8°23’E in oil producing area of Nigeria (Figure 1). Rivers studied include Calabar, Cross River, Imo, Great Kwa, and Qua-Iboe Rivers. The areas under investigation are under the tropical rainforest area [43]. The region has dry season that starts from November and terminates in March and wet season running from April to October [44]. The highest temperature of the area is experienced in February while the lowest is July and August [45]. The highest and lowest humidity of the study area is in July and January, respectively [46].

Table 1 Site location and Coordinates

S/N	River System	Longitude	Latitude
1	Great Kwa River	8° 23' E	4° 56' N
2	Calabar River	8° 19' E	4° 58' N
3	Cross River	8° 04' E	5° 10' N
4	Imo River	7° 31' E	4° 40' N
5	Qua Iboe River	7° 56' E	4° 33' N

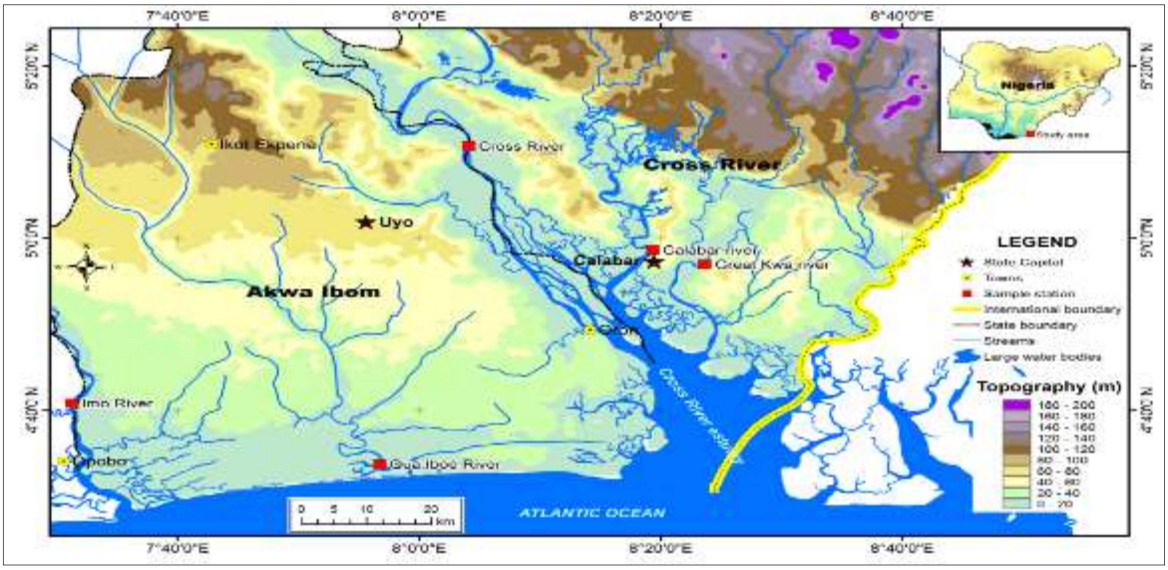

Figure 1 Map showing the studied rivers

2.2. Sample collection and treatment

Water samples were collected from Calabar, Cross River, Great Kwa, Imo, and Qua Iboe Rivers during the two distinct seasons and tidal regimes of the studied rivers. The collection of water at the upper 20 cm of each water system investigated with clean 25-liter plastic containers followed the procedures of APHA [47] and Moussa *et al*. [48]. The study was carried out from April to June 2011 and December to February, 2012 to cover the two seasons (dry and wet) and tidal regimes (low and high). A total of sixty (60) samples were obtained for the study. The dissolved oxygen (DO) content in the studied rivers was determined in situ with DO Meter (Hanna Model) according to the methods of APHA, [49]. Water samples for the determination of biochemical oxygen demand (BOD) were collected with dark brown BOD bottles and 2 mL of alkaline KI was added [49]. BOD in the studied rivers was analysed by the incubation method by APHA, [50].

2.3. Water Quality index (WQI) assessment

A single-factor pollution index (Pi) was employed **for** the assessment of the quality of the studied rivers according to the methods Yan *et al*. [51]. The Pi for the properties of rivers investigated was estimated using Equation (1).

$$Pi = \frac{Ci}{Si} ------------------------------------ (1)$$

Pi is classified as follows: 0-0.20 is clean; 0.21-0.4 is sub clean; 0.41- 1.00 = slightly polluted; 1.01 - 2.0 signifies moderately polluted; and ≥ 2.01 is severely polluted [52].

2.4. Analysis of Data

Results obtained were subjected to statistical analysis using IBM SPSS Statistics 20 (IBM USA). Principal component and Cluster analyses were carried out by Duncan's multiple range tests at 0.01 confidence limits. Factor analysis was carried for the five (5) parameters determined, and values from 0.875 and higher were deemed significant. The Cluster analysis was achieved with Dendrograms to classified groups with common source and properties.

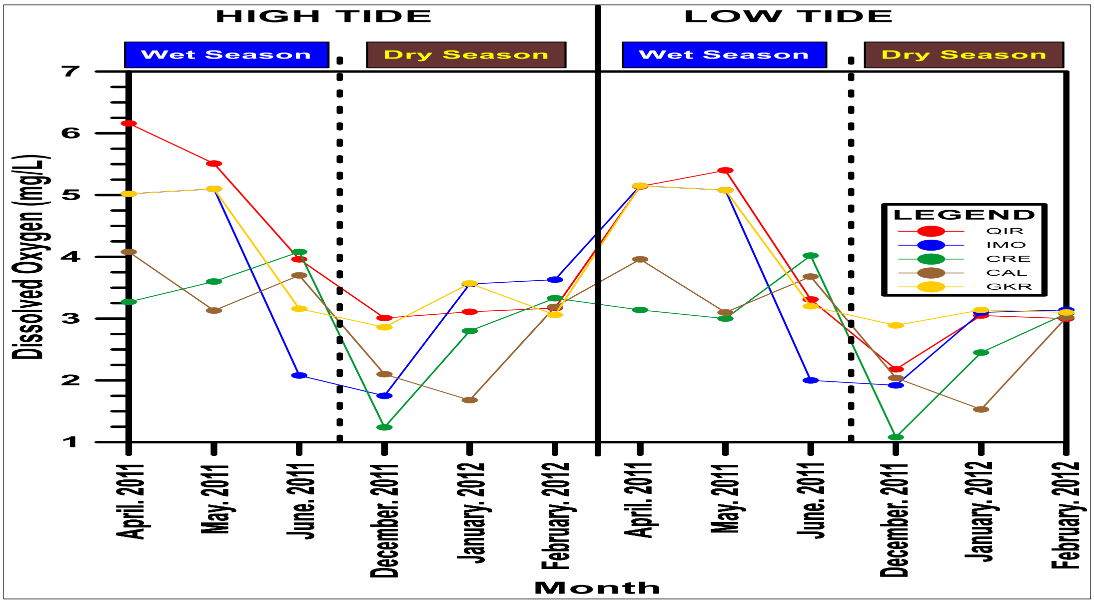

Figure 2 Seasonal and Tidal variations in dissolved oxygen of the studied rivers

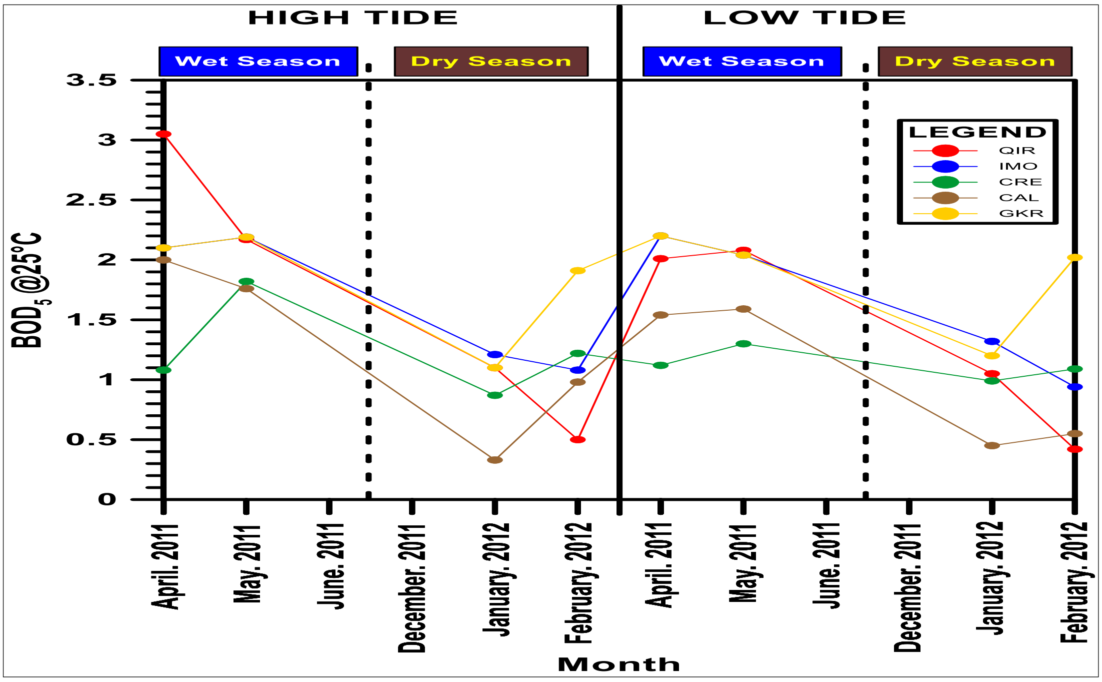

Figure 3 Seasonal and Tidal variations in biochemical oxygen demand of the studied rivers

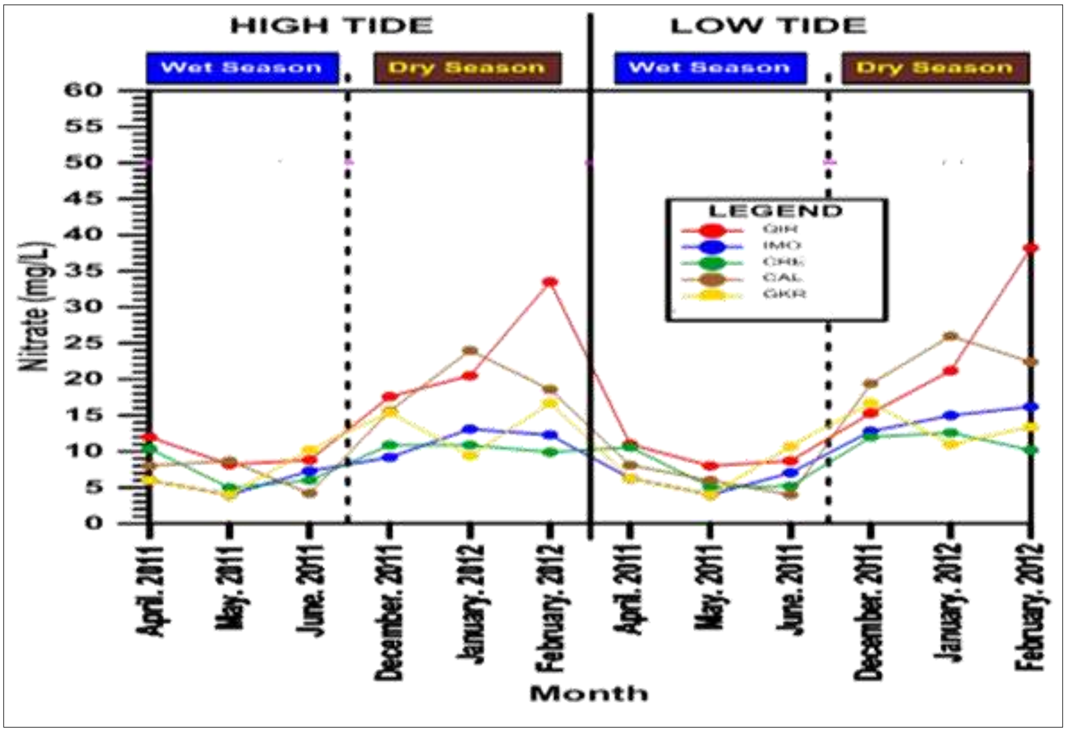

Figure 4 Seasonal and Tidal variations in nitrate of the studied rivers

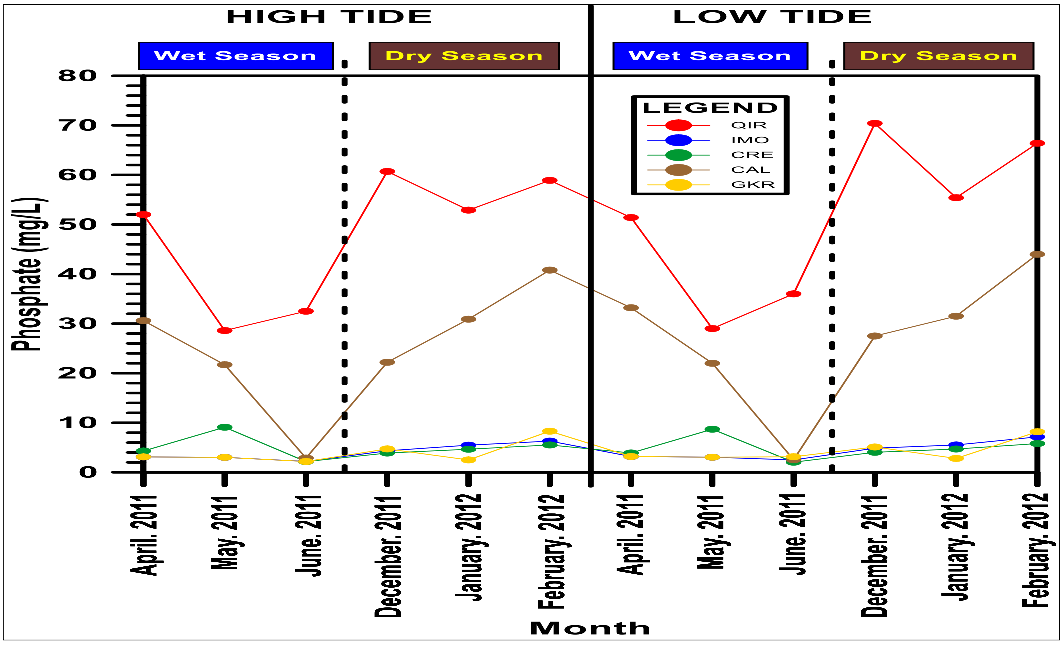

Figure 5 Seasonal and Tidal variations in phosphate of the studied rivers

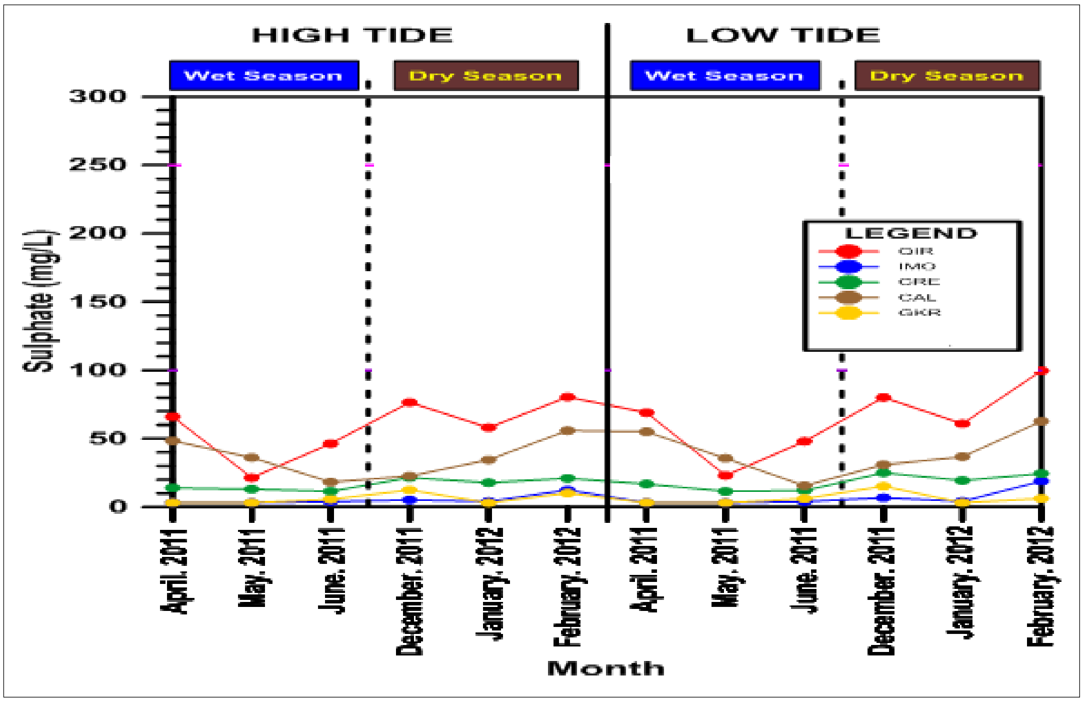

Figure 6 Seasonal and Tidal variations in sulphate of the studied rivers

3. Results and discussion

3.1. Physicochemical Properties of the Studied Rivers

Results for the physicochemical properties of water examined in the studied rivers are shown in Figure 2 - 6.

Dissolved oxygen (DO) is an important parameter that affects life aquatic ecosystem seriously and is used an index to assess the pollution status of a water system [53, 54]. DO of the studied rivers varied between 1.08 and 6.16 mg/L (Figure 2). As shown in Figure 2, the highest level of DO was recorded in samples from Qua Iboe River while lowest was obtained at Cross River. The range of DO obtained in this study is consistent with 3.07 -6.53 mg/L reported in Bomadi Creek, Niger Delta Area of Nigeria by Iwegbue *et al.* [55]. The reported DO range for the studied rivers is however; lower than 7.54 - 9.25 mg/L obtained in Cascade River in Nanning City, China by Zhong *et al.* [56]. The mean value of DO recorded (3.40±1.15 mg/L) is below the 4.0 mg/L standard by NESREA, [57]. The low level of DO reported in the studied rivers may have a negative impact on the aquatic organisms [58, 59]. This could be due to high levels of organic wastes and fertilizers originating from anthropogenic into these water channels [60].

Results for the biochemical oxygen demand (BOD) of the studied river channels are illustrated in Figure 3. BOD of the studied rivers ranged from 0.33 to 3.05 mg/L. The highest value was recorded in sample from Qua Iboe River Estuary while the lowest was obtained in Calabar River. This may be an indication of low biodegradable wastes and nutrients in Calabar River channel [15, 61]. The BOD range obtained is lower than 727.3 - 870.4mg/L reported in River Benue, Nigeria by Aho *et al.* [62]. The overall mean BOD obtained (1.48±0.62mg/L) is below the 6.0 mg/L stipulated for unpolluted water body by NESREA, [57]. However, the studied river is in the moderately polluted class according to Verma and Singh, [63].

The distribution of nitrate (NO_3^-) in the studied water channels is shown in Figure 4. Results obtained indicated a range of 4.00 – 38.20mg/L for NO_3^-. The highest level was obtained in Qua Iboe River Estuary while the lowest was at Imo, Calabar and great Kwa Rivers. The low levels of NO_3^- recorded in these aquatic ecosystems may be attributed to low organic matter contents of these channels [64]. Nitrate is the most stable form of nitrogen available for aquatic organisms however; it could be converted to the unstable nitrite by microorganisms in water [31, 65]. The range of NO_3^- obtained is higher than 0.56 – 9.96 mg/L reported in Nwaja Creek, Port Harcourt, Nigeria by Adesuyi *et al.* [22]. The mean concentration of NO_3^- obtained (11.90±7.01 mg/L) is within the permissible limit of 50.0 mg/l by NESREA, [57]. The concentrations of NO_3^- reported in this study may not have negative effects on the aquatic organisms but when the level is above the recommended limit, negative impacts may be experienced [66]. The flora and other green plants around the studied rivers may have reduced the NO_3^- contents of these water channels [67].

Phosphate (PO_4^{3-}) exists mainly in three forms in water, the metaphosphate (polyphosphate), orthophosphate, and organic phosphate [68]. Orthophosphate is the most stable form while metaphosphate also known as polyphosphate is very unstable in water is easily converted to the orthophosphate form [69]. Concentrations of PO_4^{3-} in the studied river channels varied from 2.04 to 70.40 mg/L (Figure 5). The highest was recorded in samples from Qua Iboe River Estuary whereas; the lowest was obtained at Cross River Estuary. The range is higher than 2.144 – 40.204 reported in water bodies within South Eastern Part of Nigeria by Isiuku and Enyoh, [34]. The elevated level of PO_4^{3-} reported in Qua Iboe River Estuary could be due to agricultural and municipal wastes discharged into water channels [70]. A mean concentration of 17.71±19.98 mg/L was recorded for PO_4^{3-} and is above the recommended limit (3.5 mg/L) by NESREA, [57]. The excess concentrations of in the studied water systems can result in luxuriant algae growth [36, 71].

Concentrations of sulphate (SO_4^{2-}) in the studied rivers are illustrated in Figure 6. SO_4^{2-} varied from 3.01 in Qua Iboe River Estuary to 99.60 mg/L at Great Kwa River. The obtained range is higher than 42.46 to 57.36 mg/L reported in Mouri River, Khulna, Bangladesh by Kamal *et al*. [72]. The range is also higher than 3.33-20.33 mg/L recorded in samples from some rivers in Osun State, Southwestern Nigeria by Titilawo *et al*. [73]. However, the mean concentration of SO_4^{2-} recorded (25.58±24.63mg/L) is lower than 500.0 mg/L limit recommended for unpolluted water body by NESREA, [57]. The low sulphate levels reported in the water channels investigated may affect negatively the growth of algae [74].

3.2. Seasonal and Tidal Variations of the Physicochemical Properties in the Studied Rivers

As indicated in Figure 2–6, the concentrations of DO, BOD, and nutrients in the rivers investigated varied in both seasons and tidal regimes. Concentrations of DO in the studied rivers were higher during the wet than in dry season. The higher wet season concentrations of DO are in agreement with the findings by Kamarudin *et al*. [41] and Ikhile, [75]. BOD in the river channels examined indicated higher concentrations during the wet season than in dry. This is similar to the reports by Akaahan and Azua, [76] and Ojok *et al*. [77]. This could be attributed to the high quantities of biodegradable wastes in water during wet season [78]. Results obtained revealed that higher concentrations of NO_3^- were recorded during the dry than in wet season. This is consistent with the results obtained in their studies by Isiuku and Enyoh, [34] and Edokpayi *et al*. [79]. Concentrations of PO_4^{3-} obtained were higher during the dry season than in wet as reported by Adesakin*et al*. [80] and Lanmandjèkpogni *et al*. [81]. Concentrations of SO_4^{2-} in the studied rivers were relatively higher during the dry than in wet season consistent with reports by Makwe and Chup, [82] and Xie *et al.* [83].

Tidal variations showed that, DO and BOD concentrations were higher during the high tide than in low tide. This is in agreement with the higher concentrations of these parameters during the high tide by Purnaini *et al*. [84] and Ni *et al*. [85].However, concentrations of nutrients (NO_3^-, PO_4^{3-}, and SO_4^{2-}) were higher during the low tide than in high tidal regime. This agrees with the results reported for the studies by Mitra *et al*. [86] and Davies, [87].

3.3. Results of Water Pollution index of the Studied Rivers

Table 2 Water Quality

	DO	BOD	NO_3^-	PO_4^{3-}	SO_4^{2-}
Calabar River	0.73	0.19	0.28	7.38	0.08
Cross River	0.73	0.20	0.18	1.4	0.04
Imo River	0.87	0.27	0.19	1.21	0.012
Great Kwa River	0.95	0.31	0.21	1.17	0.012
Qua Iboe River	0.98	0.26	0.34	14.15	0.12

Results for the evaluation of the studied water channels using a single-factor pollution index (Pi) according to Yan *et al*. [51] and Olawusi-Peters, [52] are indicated in Table 2. Results obtained showed that, DO at all the rivers investigated were in the slightly polluted class. BOD, NO_3^-, and SO_4^{2-} at all the studied rivers were in the non-polluted class. PO_4^{3-} varied from moderately polluted class at Imo River, Cross River Estuary, and Great Kwa River to the severely polluted class in Qua Iboe River Estuary and Calabar River.

3.4. Results of the correlation analysis

Table 3 Correlation among the parameters determined in the Rivers Investigated

	DO	**BOD**	**NO_3^-**	**PO_4^{3-}**	**SO_4^{2-}**
DO	1.000				
BOD	0.859	1.000			
NO_3^-	0.375	-0.103	1.000		
PO_4^{3-}	0.345	-0.163	0.985	1.000	
SO_4^{2-}	0.183	-0.334	0.953	0.981	1.000

Results for the relationship among the parameters determined in the studied river cannels are shown in Table 3. Results obtained revealed strong positive relationship between DO and BOD at $P < 0.20$ in the studied aquatic channels as reported by Madhulekha *et al.* [88]. This shows a direct relationship between the two properties in the studied rivers. DO correlated positively though moderately with NO_3^-, PO_4^{3-}, and SO_4^{2-} at $p < 0.20$ as previously documented [89, 90, 91]. NO_3^- showed a significant positive association with PO_4^{3-} at $p < 0.20$. This is consistent with the results obtained in Tigray, Ethiopia by Isiuku and Enyoh, [34]. BOD showed significant negative relationship with NO_3^- at $p < 0.20$ but insignificantly with PO_4^{3-}, and SO_4^{2-} in the studied rivers [8, 9, 92]. Nitrate also demonstrated a strong positive relationship with SO_4^{2-} at $p < 0.20$ as previously observed by Gebresilasie *et al*. [93]. PO_4^{3-} showed a significant positive association with SO_4^{2-} in the studied rivers. This is similar to the results reported in samples from Litani River, Quaraoun by Hayek *et al*. [94]. The r-values of these relationships exhibited by the properties determined in the studied rivers are shown in Table 3.

3.5. Results of Principal Component analysis of the parameters determined

Table 4 Principal component analysis of the parameters determined

	F1	**F2**
Parameter		
DO	0.376	0.923
BOD	-0.129	0.990
NO_3^-	0.991	0.016
PO_4^{3-}	0.998	-0.034
SO_4^{2-}	0.975	-0.206
% Total Variance	61.7	37.5
Cumulative %	61.7	99.2
Eigen value	3.09	1.88

Results for the principal component analysis (PCA) of the mean values of parameters determined during both seasons and tidal regimes are shown in Table 4. The results obtained revealed two (2) major factors responsible for the buildup of these parameters in the studied aquatic channels. These two factors had Eigen values higher than one (1) with a total variance of 99.2 %. Factor one (F1) has Eigen value of 3.09, donated 61.7 % to the total variance and is strongly influenced by NO_3^-, PO_4^{3-}, and SO_4^{2-} (Table 4). This could be attributed to anthropogenic influence on the quality of the studied river channels [95]. Factor two (F2) has Eigen value of 1.88, contributed 37.5 % of the total variance and has significant loadings on DO and BOD (Table 4). This could be the impacts of both the natural and anthropogenic on the quality of rivers assessed [96, 97].

3.6. Results of Cluster analysis of the parameters determined

Hierarchical clusters analysis (HCA) of the parameters determined during both seasons and tidal regimes are illustrated in Figure 7. The Figure shows three (3) major clusters with the first one joining DO and BOD together similar to what the PCA indicated in Factor 2. The second cluster links nitrate only while cluster three connects phosphate and sulphate together. This shows that, DO and BOD has strong similarities in both source and properties has previously mentioned in by correlation analysis in Table 3 [98]. The HCA exhibited by nitrate could be due to difference in properties and source [99, 100]. Cluster 3 corroborates the findings by PCA in Table 4 concerning the common relationship and properties between phosphate and sulphate [101, 102].

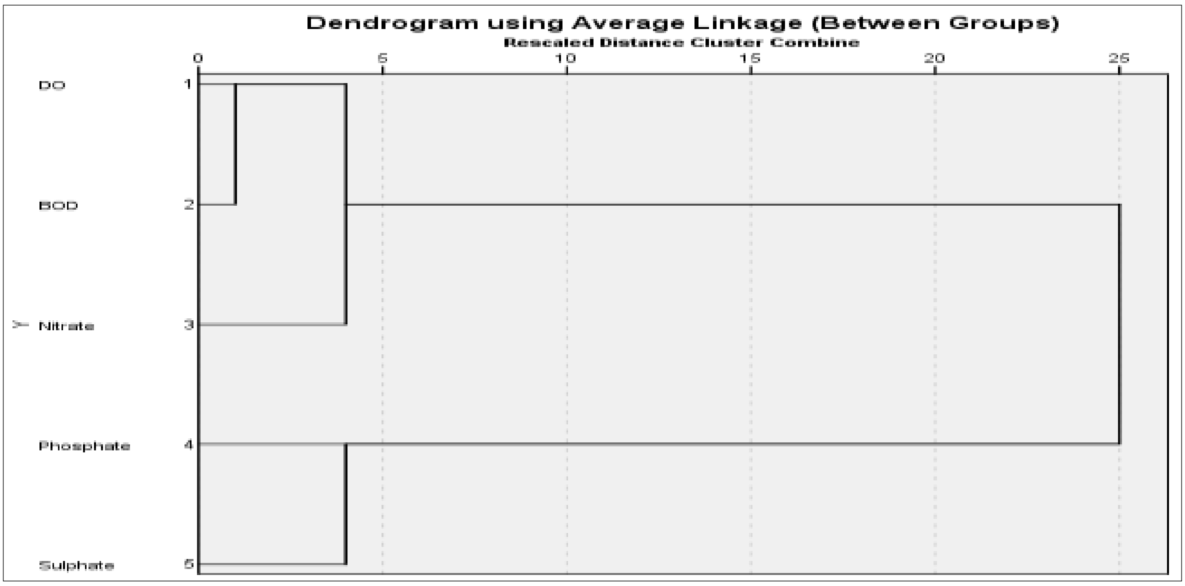

Figure 7 Hierarchical Clusters for the parameters during both seasons and tidal regimes

4. Conclusion

The study showed the variations of DO, BOD, NO_3^-, PO_4^{3-}, and sulphate SO_4^2 in Calabar, Cross River, Imo, Great Kwa, and Qua-Iboe Rivers based on the seasonal variations. It has also shown the relationships among the parameters determined and the effect on the quality of the river channels examined. The negative impacts of anthropogenic activities especially by the Oil Companies within the study area on the health of the studied rivers have been highlighted. The quality of these aquatic ecosystems based on the extent to which each of the parameters affect the rivers investigated has been indicated. The Factor analysis identified the human activities as the major source of nutrients in the studied aquatic ecosystems. The common properties and sources of the parameters determined has been identified by the Hierarchical clusters analysis. The research has shown the significance of assessing the DO, BOD, and nutrients in aquatic environment and how their relationships can affect the aquatic life.

Compliance with ethical standards

Acknowledgments

We the authors of this work acknowledge the contributions made by the Technologists in the Laboratory of Department of Chemistry, University of Uyo, Uyo. We also appreciate the efforts of the Staff of the Ministry of Science & Technology, Akwa Ibom State, Nigeria.

Disclosure of conflict of interest

We wish to indicate undoubtedly that, this work and the article produced has no conflict of interest.

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