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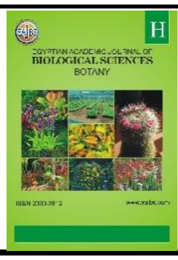

Nutrients Dynamics and Trophic Status in A Tropical Ocean off The Lagos Coast, Nigeria

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ABSTRACT

A preliminary investigation of stoichiometric nutrient ratio and the trophic status in the neritic water off the coast of Lagos, Nigeria was conducted. Monthly water samples collected from May 2015 to April 2017 were analysed using standard methods. The nutrient molar stoichiometric ratio was assayed and analysed for the potentiality of its limitation using factomineR. Physical and chemical variables showed mild variations across bi-annual seasons. Analysis of variance on the physical variables (water temperature and rainfall) and some of the chemical variables (total suspended solids, dissolved oxygen, silica and manganese) showed statistical significance ($p < 0.05$). Whereas salinity, acidity, nitrate, phosphate, zinc, iron and chlorophyll *a* were not statistically different ($p > 0.05$) across the wet and dry seasons of the two-year study. The stoichiometric nutrient limitation transited from nitrate limiting in the wet season with mean N: P (35.23) to silica and phosphate limiting in the dry season with mean N: Si (8.46) and Si: P (6.73) respectively which were not in the criteria threshold. Trophic status in the study area was oligotrophic. This could be evident by the clarity of water measured by the total suspended values and oxygen availability throughout the sampled period due to the continuous mixing of the studied area.

INTRODUCTION

The distribution of phytoplankton in the oceans is governed primarily by the adaptation of communities to characteristic regional conditions. These conditions include nutrients availability in particular bio-limiting elements such as carbon, nitrogen, phosphorus and silicon for diatoms (Cullen *et al.*, 2002; Onyema, 2017) turbulence, temperature and light levels (Tilman *et al.*, 1982; Wu *et al.*, 2014). These essential nutrients are replenished mainly by way of degeneration of dead cells and mixing of nutrient-rich bottom water by upwelling and turbulence, which is governed to a great extent by local climatic conditions and geography of the area.

Nutrient structure and ratios are the main driving force for phytoplankton growth with nutrient transformations and nutrient uptake leading to phytoplankton growth (Galbraith and Martiny, 2015). If the growth proceeds at a high rate, it could suggest the trophic status (oligotrophic, mesotrophic or eutrophic) of an aquatic environment (Suzuki *et al.*, 2002; Giovanardi and Vollenweider, 2004). Wu *et al.* (2014) documented that the nutrient concentration and its ratios play a decisive effect on the species composition of the phytoplankton since different algal species have different nutrient requirements. Any imbalance to this cellular nutrient requirement might lead to an altered ecological facet as well as phytoplankton community restructuring as a result of alteration in ambient nutrient ratios (Justić *et al*., 1995; Wu *et al*., 2014).

Chlorophyll-*a* is a surrogate measure of phytoplankton abundance in the water column and its levels are increased by nutrients (USEPA, 2012). It is also an important pigment in phytoplankton that can provide indications on the trophic status, water clarity and phytoplankton biomass, Boyer *et al*. (2009) and Nincevic-Gladan *et al*. (2015). Therefore, the trophic state generally refers to aspects of aquatic systems associated with the growth of algae, decreasing water transparency and low oxygen levels in the lower water column that can harm fish and other aquatic life (USEPA, 2012).

Nitrate is widely known as the most nutrient limiting factor to primary production in coastal marine waters (Weber and Deutsch, 2010) while phosphate limitation is mostly confined to fresh water (Trommer, *et al*., 2013). Reports of Redfield (1934; 1958) and more recently Klausmeier *et al*. (2008); Galbraith and Martiny (2015) revealed that phytoplankton in marine and freshwaters contain an empirical molar C: N: P quotient in the ratio of 106:16:1 (50:7:1 by weight) and its use as means of assessing nutrient quantification has become predominant in freshwater and marine phytoplankton studies. Nutrient deficiency occurs when there is an anomalous departure from this ratio using the elemental stoichiometric ratio of ambient nutrient.

Monitoring the water quality in the aquatic environment particularly inland and coastal (neritic) areas for its nutrients and chlorophyll-*a* variations should be continuous and accurate. This is because monitoring is an essential tool for determining and controlling pollution prone areas in order to conserve the planet earth (Salem *et al*., 2017). The inland water contains approximately 90% of the global freshwater that supports human activities, Zhou and Zhao (2011) while the open ocean provides the majority of the dissolved organic carbon (DOC), which is a vital link in the global carbon cycle, Mannino *et al*. (2008). Water constituents' concentrations which include chlorophyll-*a*, total suspended solids, total dissolved solids, nutrients and so on (Usali and Ismail, 2010; Schroeder *et al*., 2007) are used as indicators to assess water quality.

Therefore, nutrients (nitrate, phosphate and silica), chlorophyll-*a*, dissolved oxygen and water clarity are the critical four interlinked essential components related to the trophic status of an environment. Consequently, the aim of this study was to investigate the nutrients and chlorophyll-*a* variations on a seasonal and temporal scale in order to assess the trophic status and stoichiometric nutrients limitation of the Atlantic Ocean off the coast of Lagos, Nigeria.

MATERIALS AND METHODS

Description of Study Sites:

The study area was in the Ocean Off the coast of Lagos, Nigeria which lies between Latitude 6°15'52.9"N and Longitude 4°05'49.4"E. Lagos State, the adjacent location on land of the study area, is an African megacity and falls within the barrier lagoon complex (200 km) of the south-western Nigerian morphology units (Nwilo, 2017) on the West Coast of Africa. This city is of great economic, commercial and industrial importance to the country. Besides, the city functions as the home to about 15 million people (Okude and Taiwo, 2006) making it even one of the biggest cities in Africa. A significant percentage of the land in Lagos State has an elevation of fewer than 15 m above sea level (Longhurst *et al*., 2005). The climate of the area as experienced in the Lagos metropolis is influenced by two air masses namely: the tropical maritime and tropical continental air masses. The tropical maritime air mass is wet and originates from the Atlantic Ocean while the tropical continental air mass is a warm, dry and dusty air, originates from the Sahara Desert (Obiefuna *et al.,* 2017). There are two main seasons in the region, namely; the wet (May - October) and the dry (November - April) seasons and they are related to the seasonal migration of Southeast trade wind system (Nwankwo, 2004). Ten stations were randomly selected and fixed with the aid of the Global Positioning System GPS (Magellan, SporTrak PRO MARINE [IEC – 529 IPX7 Model]) kit in the Atlantic ocean off the Lagos coast for present study, viz., Offshore Badagry I (6°15'52.9"N, 2°49'46.2"E), Offshore Badagry II (6°16'11.4"N, 2°58'20.1"E), Offshore Agbaja (6°15'52.9"N, 3°08'51.7"E), Offshore Ilashe (6°16'42.4"N, 3°17'00.8"E), Offshore Lagos Harbour (6°17'07.2"N, 3°23'30.9"E), Offshore Elegushi Beach (6°16'48.6"N, 3°30'19.5"E), Offshore Atican Beach (6°16'23.8"N, 3°35'22.9"E), Offshore Lakowe (6°16'17.6"N, 3°42'05.3"E), Offshore Badore (6°16'54.8"N, 3°51'22.6"E) and Offshore Lekki Beach Golf Resort (6°16'30.0"N, 4°05'49.4"E).

Collection of Water Samples:

Sampling was conducted at ten stations in the Atlantic Ocean off the coast of Lagos for 24 consecutive months (May 2015 to April 2017). Surface water samples were collected just a few centimeters below the water surface at each of the ten stations on each occasion for physical (temperature, rainfall) and chemical (total suspended solids, nutrients, salinity and chlorophyll *a*) analyses using 1000 ml plastic containers with screw caps (APHA, 2012).

Analysis of Physical and Chemical Variables:

Surface water temperatures (°C) were determined *in-situ* with a mercury-in-glass thermometer. Rainfall values were obtained from the Nigerian Meteorological Agency, Lagos (NIMET). Nitrate-nitrogen, reactive silica and reactive phosphorus concentrations were determined on 10 ml aliquot of filtered sample by cadmium reduction method (HACH Method 8039), molybdate-3 reagent solution (HACH Method 8186) and molybdate in an acid medium (PhosVer 3 reagent powder, HACH Method 8048) respectively using HACH DR 3900 spectrophotometer following standard procedures as described by APHA (2012). Whereas for chlorophyll *a* concentration, 200 mL aliquot of the water sample was filtered in a dark room through a glass fiber filter. The pigment is extracted from the filter through maceration and centrifugation in 90% acetone. The extract is then analyzed before and after acidification, using a spectrophotometer. Test results were validated with chlorophyll calibration standards (5 - 20 ug /L). The pigment concentration was calculated as follows:

$$\text{Chlorophyll } a \text{ [corrected; } (\mu g/L)] = \frac{26.7 \text{ x } (\text{A}664b - \text{A}665a) \text{ x Vextract}}{\text{Vfiltered x L}}$$

Where: $V_{extract}$ = volume of extract (mL)

$V_{filtered}$ = volume of sample filtered (L)

L = light path length or width of cuvette, cm

664*b* = corrected absorbance of extract before acidification

665*a* = corrected absorbance of extract after acidification

The value 26.7 is the absorbance correction factor ($A \times K$)

A = absorbance coefficient for chlorophyll *a* at 664 nm = 11.0

K = ratio expressing correction for acidification = 2.43

Analysis of Trophic Status:

Carlson (1977) trophic state index (TSI) classification modified and adopted by Nincevic-Gladan *et al*. (2015) was used in this study. The formula for TSI chlorophyll-*a* calculation was given as and the result was compared in the class boundary:

$$\text{TSI (Chlorophyll } a) = 9.81 \text{ In Chlorophyll } a \text{ (ug/L)}$$

Analysis of Nutrient Stoichiometric Limitation:

Redfield nutrient ratios N: P: Si – 16:16:1 adopted by Sterner (2015) and Galbraith and Martiny (2015) citing Justic *et al*. (1995) was the criterion used for determining the stoichiometric nutrient limitation with the factomineR package. A similar methodology was used by Agboola *et al*. (2013) and Xu *et al*. (2015). Nitrate is limiting when N: P > 16 and N: Si > 1; phosphate limitation occurs when N: P > 16 and Si: P > 16 while silica is limiting when N: Si > 1 and Si: P < 16.

RESULTS

The seasonal variations (minimum, maximum, mean and standard deviation) in the nutrients, chlorophyll-*a* and some environmental variables with the correlation coefficients of the surface water for the two-year study between May 2015 and April 2017 off the coast of Lagos, Nigeria are presented in Table 1 and 2 respectively. Analysis of variance on the physical variables (water temperature and rainfall) and some of the chemical variables (Total suspended solids, dissolved oxygen, silica and manganese) showed statistical significance ($p < 0.05$). Whereas salinity, acidity, nitrate, phosphate, zinc, iron and chlorophyll *a* were not statistically different ($p > 0.05$) across the wet and dry seasons of the two-year study Table 1. However, nutrients (nitrate, phosphate and silica) were found to significantly ($p < 0.01$) correlated with chlorophyll-*a* values for the study period. The mean concentration of nitrate and chlorophyll-*a* across ten sampling stations in both wet and dry seasons of the study is depicted in Fig. 1 and 2a. Nutrients were found to increase chlorophyll-*a* concentration more in the wet than the dry season of the study, Fig. 2b while Fig. 2c revealed that nitrate, rainfall, salinity, dissolved oxygen and temperature affect chlorophyll-*a* concentration.

Table 1: Seasonal Variations in Nutrients, Chlorophyll *a* and some Environmental Variables off the Coast of Lagos, Nigeria (May 2015 - April 2017).

VARIABLES	Wet Season			Dry Season				
	Min.	Max.	Mean ±SD	Min.	Max.	Mean ±SD	P_{value}	Sig. Level
W. Temp. (°C)	25	31	27.69 ±1.22	26	31	29.47 ±1.36	2.20E-16	P < 0.05
Rainfall (mm)	45.9	449.3	203.60 ±103.80	0	164.4	57.43 ±53.12		P < 0.05
TSS (mg/L)	1	12	1.12 ±1.02	1	3	1.2 ±1.06	0.27	P > 0.05
Salinity (‰)	12.11	31.81	26.99 ±3.94	14.4	30.04	27.78 ±3.42	0.1	P > 0.05
Acidity (mg/L)	0.5	12.3	2.82 ±3.12	<0.5	55	1.78 ±6.87	0.2	P > 0.05
DO (mg/L)	5.6	6.84	6.24 ±0.36	5.73	6.88	6.43 ±0.29	7.83E-06	P < 0.05
NO_3 (mg/L)	0.11	18.47	5.00 ±4.81	0.37	16.39	5.89 ±3.16	0.09	P > 0.05
PO_4 (mg/L)	0.01	15.7	1.21 ±2.10	0.01	3.61	0.91 ±0.88	0.12	P > 0.05
Silica (mg/L)	0.37	9.24	1.51 ±1.19	0.1	6.07	1.02 ±1.15	0.001	P < 0.05
Zinc (mg/L)	0.005	0.071	0.0025 ±0.00094	0.005	0.079	0.0019 ±0.00086	0.82	P > 0.05
Iron (mg/L)	0.019	0.19	0.063 ±0.027	0.021	0.227	0.067 ±0.034	0.4	P > 0.05
Mn (mg/L)	0.005	0.073	0.019 ±0.014	0.002	0.042	0.010 ±0.008	2.05E-09	P < 0.05
Chl-*a* (µg/L)	7.2	38.52	13.35 ±6.02	6.4	22	14.10 ±3.99	0.26	P > 0.05

Table 2: Correlation Coefficients of the Nutrients, Chlorophyll a and some Environmental Variables off the Coast of Lagos, Nigeria (May, 2015 - April, 2017) at *P < 0.05, **P < 0.01

VARIABLES		1	2	3	4	5	6	7	8	9	10	11	12	13
W. Temp. (°C)	1	1												
Rainfall (mm)	2	-.172**	1											
TSS (mg/L)	3	0.024	-0.014	1										
Salinity (‰)	4	0.019	-0.008	-.293**	1									
Acidity (mg/L)	5	-0.028	0.02	0.098	-.543**	1								
DO (mg/L)	6	.302**	-.232**	-.297**	-0.078	0.034	1							
NO_3 (mg/L)	7	.502**	-0.124	0.008	-0.009	-0.05	.239**	1						
PO_4 (mg/L)	8	0.017	0.108	.523**	-0.093	-0.13	-.206**	**.306****	1					
Silica (mg/L)	9	-0.067	.138*	.598**	-.769**	.628**	-0.03	**0.007**	**.174****	1				
Zinc (mg/L)	10	.191**	-0.098	.228**	-.404**	.328**	.499**	0.083	-.296**	.244**	1			
Iron (mg/L)	11	0.018	-0.042	.542**	-.395**	.144*	-.132*	-.19**	-.194**	.281**	.258**	1		
Mn (mg/L)	12	-.150*	.326**	.477**	-0.036	-0.02	-.231**	0.078	0.104	0.108	-0.03	.265**	1	
Chl-*a* (µg/L)	13	.308**	**.161***	0.069	0.028	-0.05	-.159*	**.523****	**.190****	**0.15***	-.194**	0.002	.222**	1

Key: W. Temp. - Water Temperature; TSS – Total suspended solids; DO - Dissolved Oxygen; NO_3 – Nitrate; PO_4 – Phosphate; Mn – Manganese; Chl-*a* – Chlorophyll-*a*

Nutrient Fluxes off the Coast of Lagos:

The visualization of nutrients (nitrate, phosphate and silica) variability to chlorophyll *a* concentration in the entire off the coast of Lagos using their r- squared values in regression analysis was shown in Fig. 5. Nitrate was the most abundant of all the nutrient in the ocean off the coast of Lagos in all stations, hence contributed more to chlorophyll-*a* levels across the ten stations. However, (S9) off Badore recorded 49% of nitrate concentration, off Agbaja (S3) has a higher percentage of phosphate 24% while off Ilase (S4) has 7.5% for silica concentration.

Nutrient Limitation and Trophic Status:

The overall mean for N: P ratio was 35.23, N: Si ratio was 8.46, Si: P ratio was 6.73 and Si: N ratio was 0.87 for the two-year study respectively. Ordinarily, this showed that N: P ratio was significantly higher than the rest (35.23) and the lowest was Si: N (0.87). Molar quotients between the concentrations of potentially limiting nutrients are delimited in Fig. 6 for the entire sampling period and Fig. 7 across wet and dry season (Log Si: N vs Log N: P) by the Si: N = 1:1, N: P = 16:1 and Si: P = 16: 1 line. The lines define six different areas characterized by the potentially limiting nutrients in order of priority within the plot. Mean TSI for chlorophyll *a* for the ten sampling stations was 25.68 µg/L (Fig. 8) indicating the trophic status off the coast of Lagos.

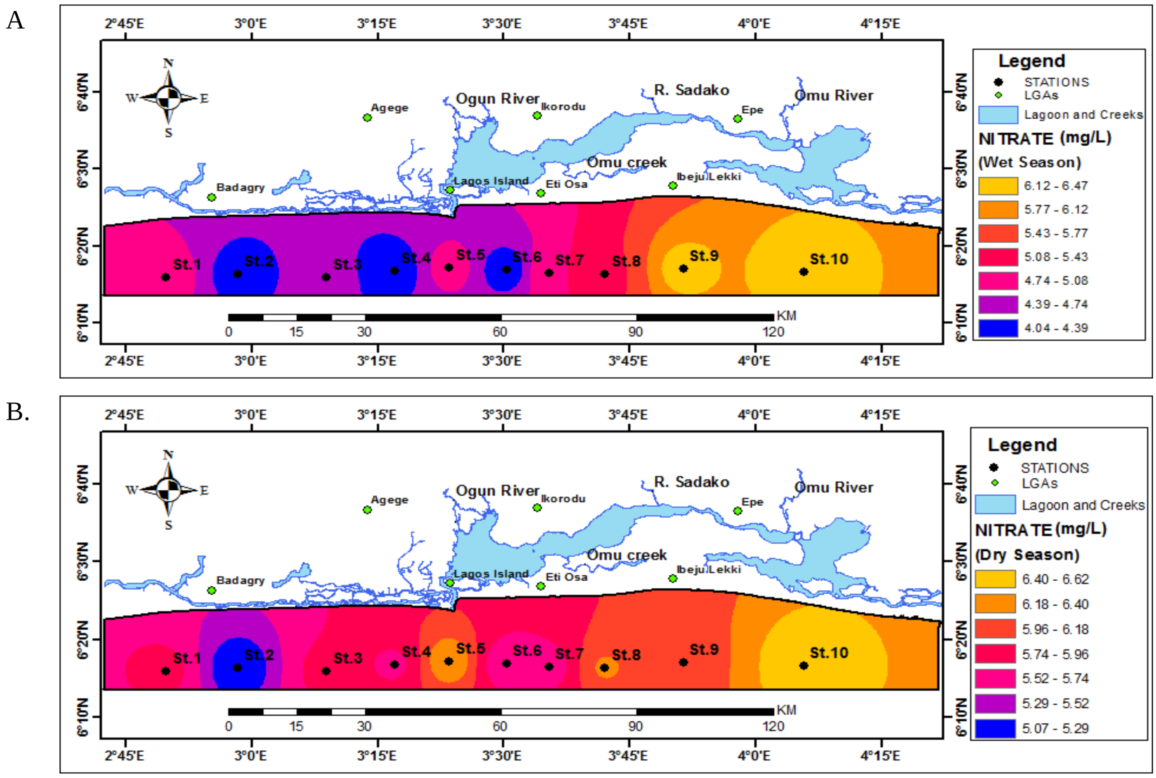

Fig. 1: Seasonal (A. - Wet and B. - Dry) and Spatial Variation in Nitrate levels off the Coast of Lagos, Nigeria (May 2015 - April 2017).

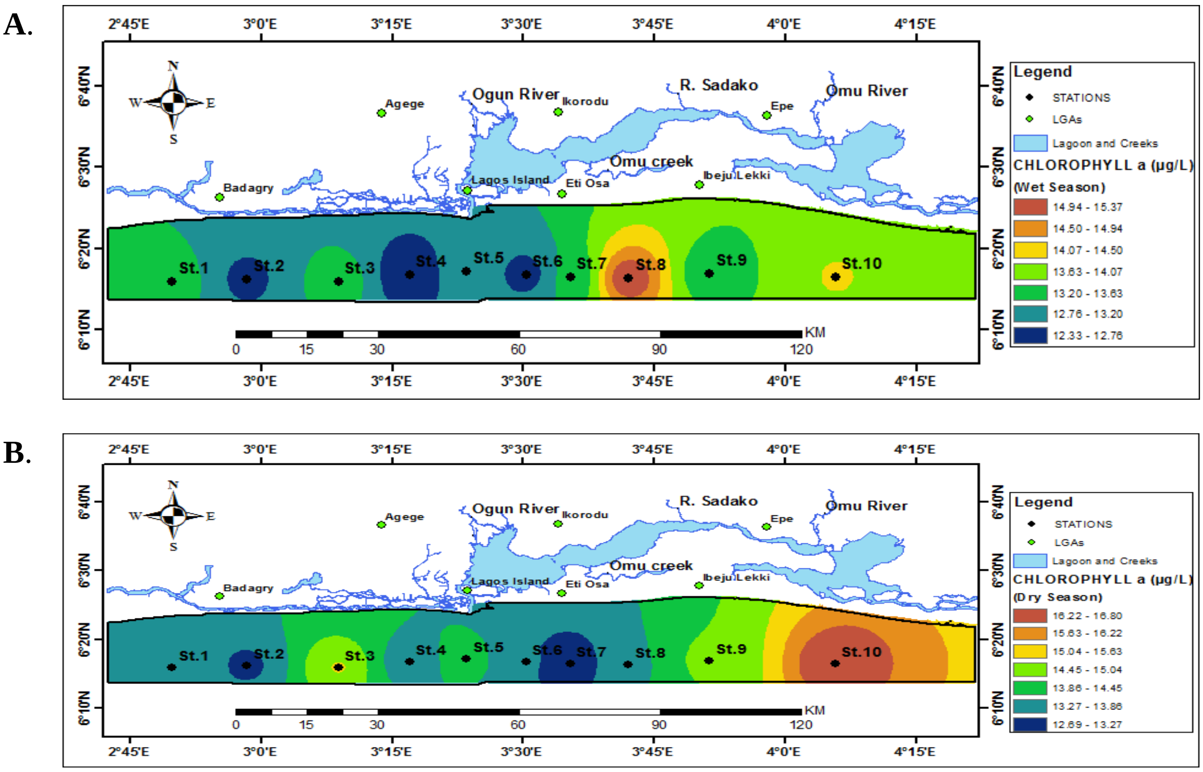

Fig. 2: Seasonal (A. – Wet and B. - Dry) and Spatial Variations in Chlorophyll-*a* levels off the Coast of Lagos, Nigeria (May 2015 – April 2017).

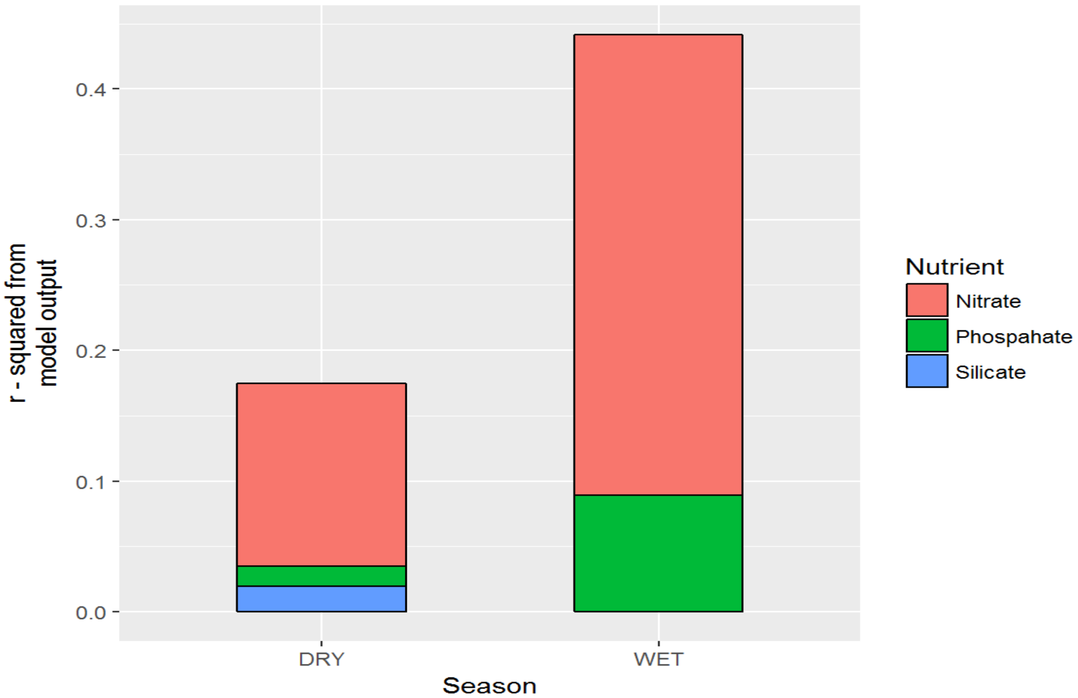

Fig. 3: Seasonal Nutrient variability to Chlorophyll-*a* dynamics off the Coast of Lagos, Nigeria (May 2015 – April 2017).

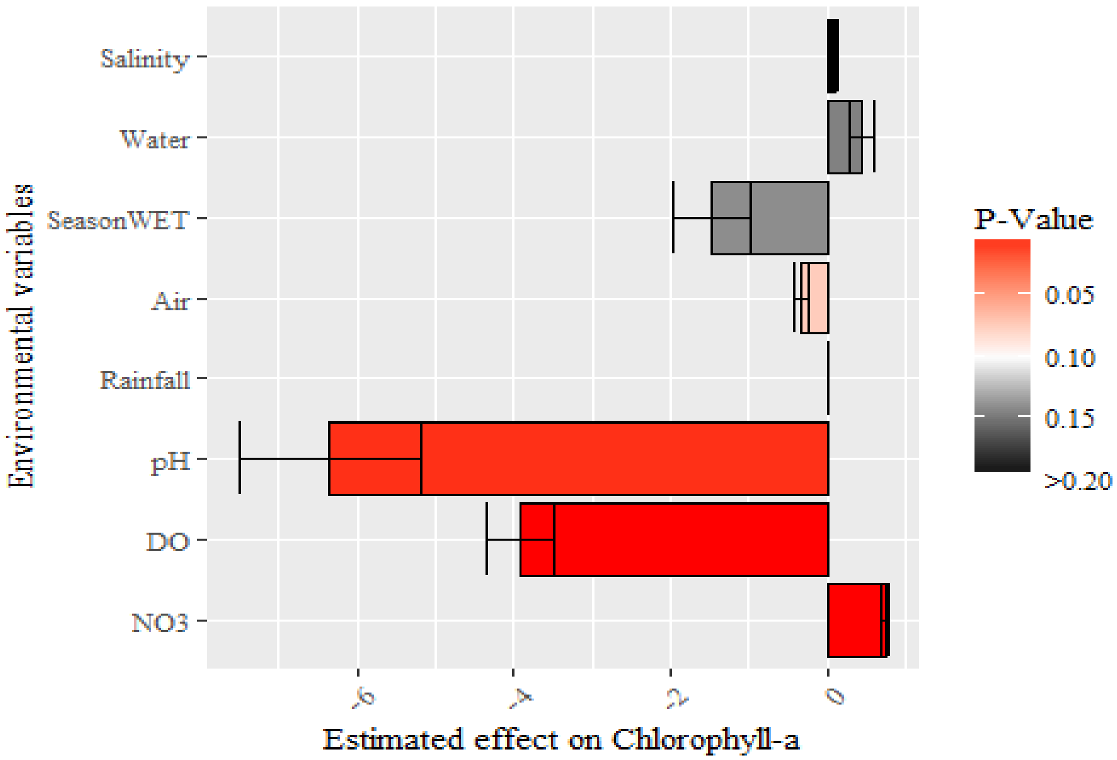

Fig. 4: Estimated Effects of some Environmental Variables on Chlorophyll-*a* off the Coast of Lagos, Nigeria (May 2015 – April 2017).

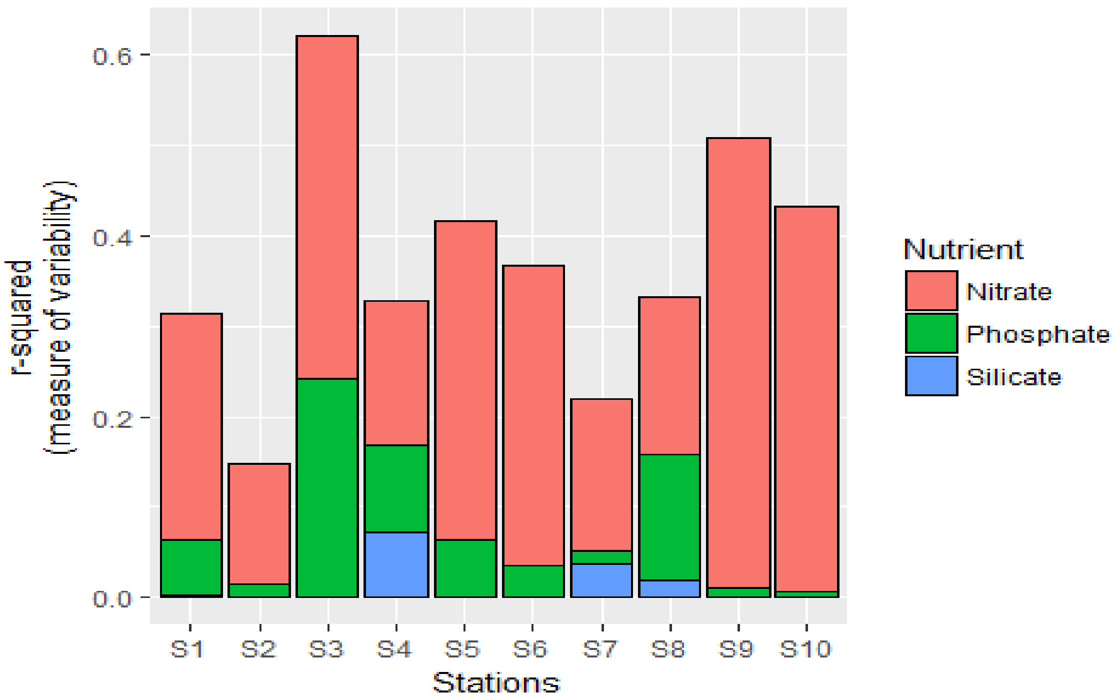

Fig. 5: Average Contribution of Nutrients (Nitrate, Phosphate and Silica) to chlorophyll-*a* Concentrations off the Coast of Lagos, Nigeria (May 2015 – April 2017).
S9 = 49% for Nitrate, S3 = 24% for Phosphate and S4 = 7.5% for Silica

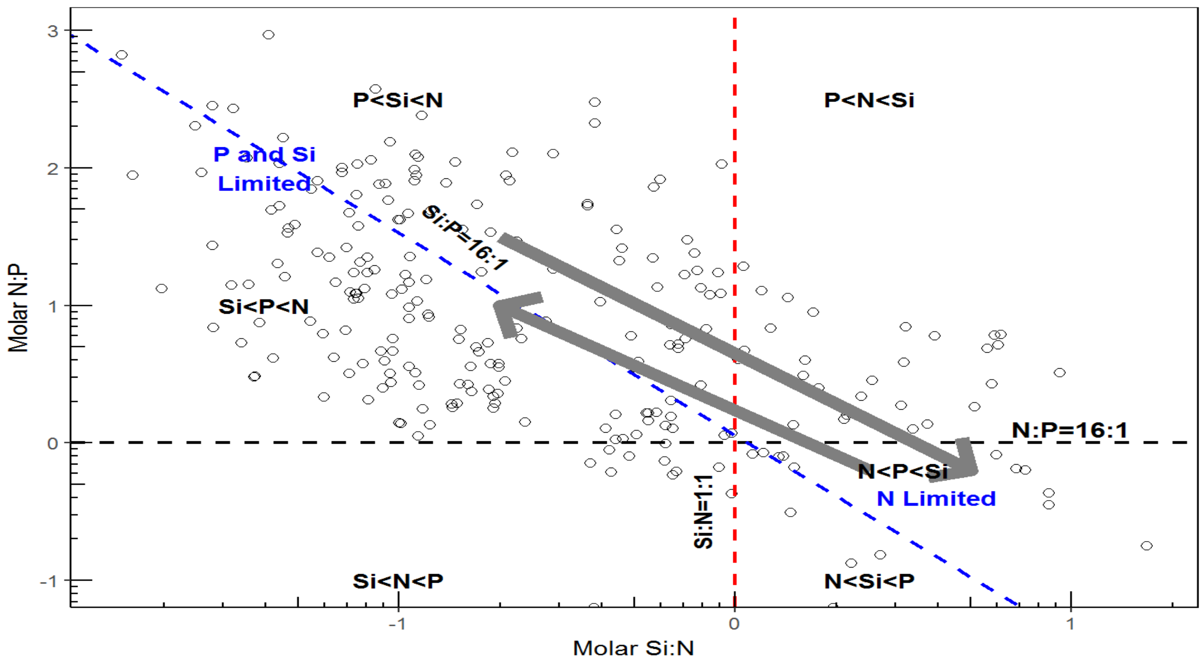

Fig. 6: Scatter plot of the N: P: Si Atomic Nutrient ratios off the Coast of Lagos, Nigeria (May 2015 – April 2017).

Note: The data points were largely around the second quadrant (upper left) where either silica (highly likely) or phosphate is limited. Although, Nitrate is limited in some data point but its effect is marginally small compared to the other.

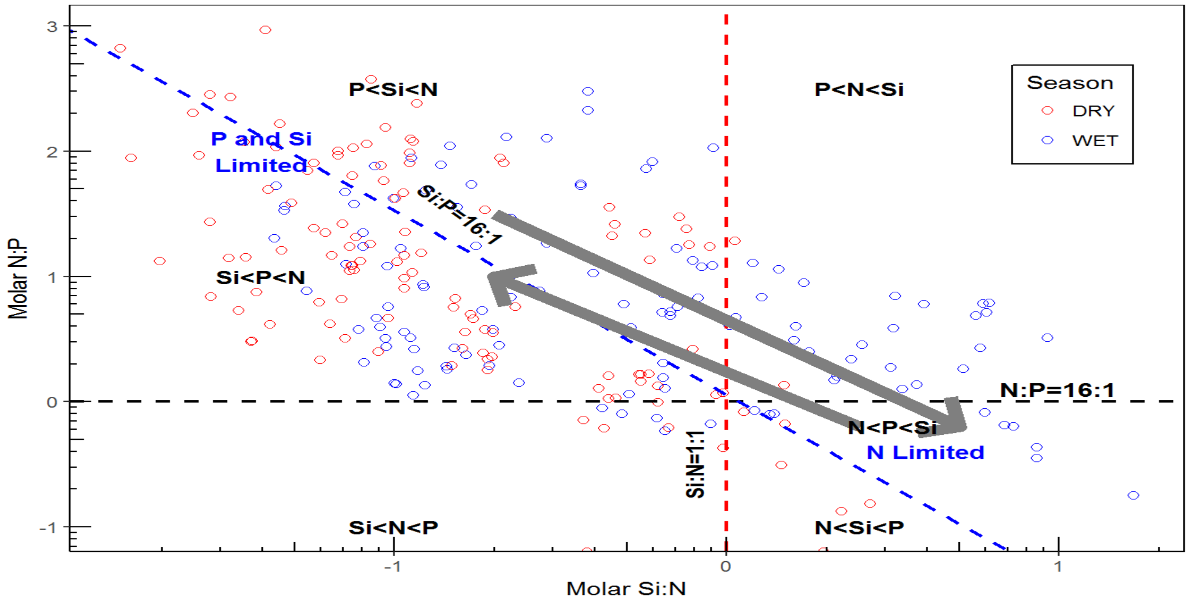

Fig. 7: Seasonal N: P: Si Atomic Nutrient ratios (Redfield) of the Surface Water off the Coast of Lagos, Nigeria (May 2015 - April 2017).

Note: A seasonal plot of molar N: P and Si: N ratios indicated that the limiting factor transited from Nitrate limiting in wet season to Silica and Phosphate limiting in the dry season.

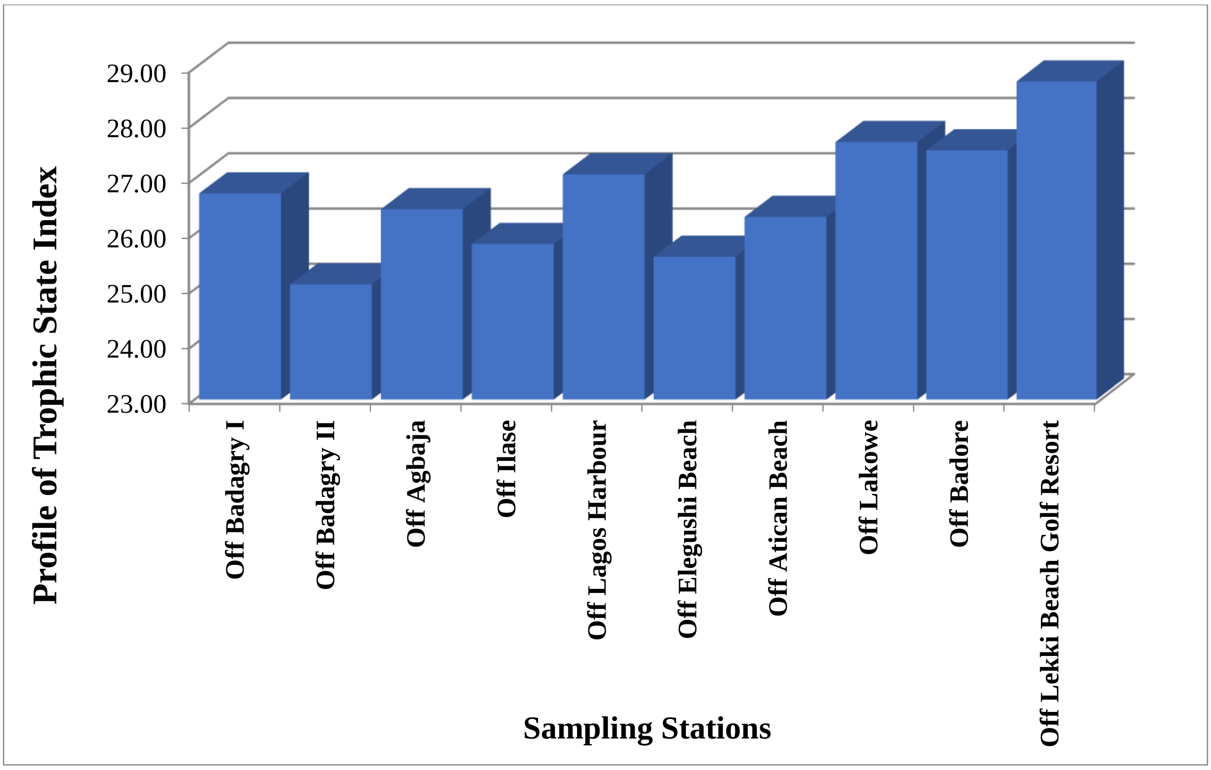

Fig. 8: Profile of Trophic State Index off the Coast of Lagos, Nigeria (May 2015 – April 2017).

DISCUSSION

The physical and chemical variables reflected tropical neritic water quality while nutrients were related to the biomass across wet and dry seasons. Nutrients levels especially nitrate are higher in the wet than dry season. This may be attributed to the fact that nutrients (nitrate, phosphate and silica) in the marine environment would exhibit substantial seasonal variations depending on the rainfall, freshwater input and consumption of nutrients by autotrophs such as phytoplankton. Possible reasons for high nitrate levels in Tropical Ocean have been explained by a number of authors. For instance, new nitrogen can be introduced to the Atlantic Ocean through wet and dry atmospheric deposition (Baker *et al*., 2003). Additionally, material emitted from equatorial Africa to the atmosphere and transported to the low latitudes of the Atlantic could also be a source of nitrate introduction (Galloway *et al*., 2004) and natural one occurs due to substrate re-mineralization, upwelling and increase of rivers inflow (Bužančić *et al*., 2016). Moreover, silica in seawater is mainly transported through rivers (Vajrevelu *et al*., 2017). It is suggested that the source of silica for the study area are through Lagos harbour from Lagos lagoon system and from Cotonou harbour through Lake Nokue and Lake Porto-Novo. Anyanwu and Ezenwa (1988) have reported inputs from surface run-offs. Other land-based sources are also additional or supplementary sources of nitrates to the region. Phosphate on the other hand, has been known to mineralize in the seabed and soil layers (Ekholm, 2008; Klausmeier *et al*., 2008; Wu *et al*., 2014) as it can originate from sediments and re-suspension. In all these instances nutrients are higher in the wet than dry seasons.

The concentration of chlorophyll-*a* during the wet season as well as significant positive correlation with rainfall might be due to the availability of sufficient amount of pristine water condition due to rainfall, consumption of silica and phosphate by primary producers. This agrees with works of Sardessai *et al*. (2007) in the Bay of Bengal, Prabhahar *et al*. (2011) in the Nagapattinam Coastal area Tamilnadu in India, Vajravelu *et al*. (2017) in the Parangipettai coastal waters recording high levels of chlorophyll-*a* in the monsoon period. Also, Carvalho *et al*. (2016) reported that the biggest determinant for the concentrations of chlorophyll-*a* is the rain because it can contribute to the enrichment of nutrient salts which can lead to an increase of biomass.

The relationship between chlorophyll-*a* and nutrients, water temperature and rainfall is highly dynamic and has always been the major focus among researchers to explain the experimental ecology (Chattopadhyay *et al.*, 2003). Recently, various anthropogenic activities have increased, which in turn enhance the nutrient concentration. Thus, this leads to high productivity in the coastal environment and neritic waters (Rakhesh *et al.*, 2013). Similarly, in a report by Smayda (1980), the availability of nutrient plays an important role in phytoplankton diversity that reflects the environmental condition of an ecosystem. Nitrate, phosphate and silica were the key nutrients in phytoplankton production in the sea off the coast of Lagos especially with regards to primary pigment concentration. This was reflected in significant positive correlation of chlorophyll *a* with nitrate (r = 0.590; $p < 0.01$), phosphate (r = 0.190; $p < 0.01$) silica (0.156; $p < 0.05$), water temperature (r = 0.308; $p < 0.01$) as well as rainfall (r = 0.161; $p < 0.05$).

The stoichiometric nutrient limitation revealed mean N: P (35.23), N: Si (8.46) and Si: P (6.73) respectively which were not in the criteria threshold reported by Galbraith and Martiny (2015), Agboola *et al*. (2013) and Xu *et al*. (2015). Recent analyses of global nutrient and particulate observations have shown that N: P, the most commonly discussed ratio, varies regionally, including low N: P in the high-latitude Southern Ocean and high N: P in the low-latitude oligotrophic regions (Martiny *et al*., 2013). This high N: P in oligotrophic waters have often invoked an enhanced reliance on N-rich proteins for gathering scarce resources (Deutsch and Weber, 2012) while low N: P in the Southern Ocean has been variously attributed to the abundance of P-rich molecules in cold, fast-growing plankton (*Toseland et al., 2013*) or to the availability of Si, which supports P-rich diatom communities. Also, the nutrient limitation (N: P: Si) could be related to the concentration present in the water column as well as their assimilation within the cell of the phytoplankton (Redfield, 1958; Sterner, 2015; Hecky *et al*., 1993; Agboola *et al*., 2013). The nutrient limitation transited from nitrate limiting in the wet season to silica and phosphate limitation in the dry season for the study.

Chlorophyll-*a* was the primary index for trophic status index classification and was the most accurate of the three variables used in predicting algal biomass according to Boyer *et al*. (2009) and Nincevic-Gladan *et al*. (2015). In view of this assertion, trophic status in the study area was oligotrophic as revealed by the mean TSI of 25.68 µg/L for chlorophyll-*a* which falls within the upper boundary of classical oligotrophy. This is additionally evident in the clarity of the water and dissolved oxygen availability throughout the sampled period.

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