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Photosynthetic pigments and nutrients in a freshwater swamp Lagos State, Nigeria

***Onyema, I. C., Akanmu, R. T. and Plumptre, A. O.**

Department of Marine Sciences, University of Lagos, Akoka, Lagos, Nigeria

Corresponding author email address < ionyema@unilag.edu.ng >

Abstract

The concentrations of chloroplast-based pigments molecules found in plants, algae and cyanobacteria which photosynthesize in a freshwater swamp in Lagos State, Nigeria were monitored bi-monthly from October, 2017 to March, 2018 in relation to water chemistry changes. The physico-chemical parameters recorded for this study were temperature (27 - 32 °C), rainfall (0 – 154.50 mm), salinity (0.10 – 0.70 ‰), total suspended solids (5 - 69 mg/L), nitrate (0.61 – 8.11 mg/L), silica (1.07 – 16.20 mg/L), phosphate (1.32 – 6.58 mg/L), nickel (0.0002 – 0.0015 mg/L), manganese (0.01 – 0.07 mg/L), iron (0.08 – 0.19 mg/L), chlorophyll *a* (1.00 – 12.00 µg/L), chlorophyll *b* (0.10 - 0.50 µg/L) and phaeophytin *a* (0.10 - 0.30 µg/L). Photosynthetic pigments were significantly positively correlated ($p < 0.05$) with nitrogen-based nutrients and heavy metals. Significant negative correlation ($p > 0.05$) on the other hand were recorded between the photosynthetic pigments and salinity, phosphate, sulphate, total suspended solids and potassium. The water chemistry parameters showed variations linked with rain induced floodwater inflow from the surrounding wetland areas. Increasing salinity was a limiting factor to the increase in photosynthetic pigments concentration in this environment.

Keywords: Algal pigments, Chlorophyll, Wetland, Water Chemistry, Heavy Metals

Introduction

Swamps are unique aquatic ecosystems situated in shallow depressions usually connected to a river, creek, estuary and the like by narrow channels (Amaeze and Onyema, 2014). In coastal environments, both freshwater and mangrove (brackish water) swamps may exist in close proximity (Roy et al., 2006). Freshwater swamps are usually formed by the flooding action of rivers or the inflow of floodwaters associated with precipitation (rain) in a particular adjacent lowland area (Varadharajan and Soundarapandian, 2014). Swamp areas especially in coastal zones of the world are under increasing stress due to development of industries, trade, commerce, tourism and their resultant human population growth leading to deteriorating water quality and hydrological conditions (Wu et al., 2014). Domestic and industrial waste waters contain large quantities of chemical substances that drain into rivers and swamp/wetland areas without treatment causing serious water pollution from the introduction of chemicals, pesticides and heavy metals enriched wastes (Otitoloju, 2018). Several researchers have reported that pollution exert profound effects on the number, abundance and distribution of the biodiversity in any aquatic ecosystem. Consequently, this results in deteriorating changes in the total number of species or organisms present as well as its suitability for both domestic and industrial uses (Chukwu, 2010; Otitoloju, 2018).

The phytoplankton are important microscopic aquatic single celled plants that play key roles in the ecosystem as primary producers through oxygenic photosynthesis (Wu et al., 2014). The key groups of phytoplankton in freshwater ecosystems would include diatoms, blue-green algae, green algae (chlorophlytes), chrysophytes and dinoflagellates (Agribas et al., 2017). Traditionally, the phytoplankton composition and abundance are determined by microscopic examination and identification and therefore requires much time and specific/highly skilled experts to achieve good results (Onyema, 2010).

Photosynthetic pigments, phytochemicals and algal pigment are molecules found in the plants algae and phytoplankton that are very important in the oxygenic photosynthesis process. Photosynthetic pigments are usually chloroplast-based pigment molecules found in plants, algae and cyanobacteria which can photosynthesize. They include chlorophylls *a*, *b* and phaeophtin *a* which is a degradation product of chlorophyll *a*. Among the photosynthetic pigments, chlorophyll is used as a photoreceptor that absorbs light energy. There are six different forms of chlorophylls (a – f) and each reflect slightly different ranges of green wavelength. Importantly, chlorophyll *a* is the primary molecule responsible for photosynthesis. Chlorophyll is not the only photosynthetic pigment that is found in the phytoplankton. There are also carotenoids and phycobilins (biliproteins) which are similar in function to chlorophyll *b*, *c*, *d*, *e* and *f* molecules in improving light energy absorption but are not a primary part of photosynthesis (Gibb et al, 2000).

The measurement of phytopigment content could also be a useful tool in the establishment of eutrophic levels (Kowalewska et al., 2004). Several studies have shown that photosynthetic pigments are an excellent tool for the study of algal communities (Jeffrey and Vesk, 1997; Onyema, 2013a). Before now, most studies on algal pigment concentration especially with chlorophyll have been carried out in the marine environment (Onyema, 2013; Onyema and Akanmu, 2017; 2018). These reports and more have been in Nigeria on investigating phytoplankton class-specific pigment markers and to know the algal pigments concentrations in a bid to quantifying phytoplankton biomass and qualifying water quality and the status of aquatic ecosystems. These studies generally have shown that the phytoplankton depends on specific conditions for growth and are a first indicator of a change in the aquatic environment (Nwankwo, 2004; Wu et al., 2014).

Over the years, indiscriminate dumping of waste around swamps especially in coastal cities have become a huge problem. These wastes impact on the health and productivity of these delicate aquatic ecosystems. The deleterious effects of excessive nutrients from domestic and industrial concerns, as well as heavy metal enrichment from small and medium scale industries that are poorly monitored with regards to their waste discharges have now risen to levels of high ecological concerns (Ajao et al., 1996; Chukwu, 2010; Otitoloju, 2018). The concentration of algal pigments (chlorophyll *a*, *b* and phaeophytin *a*) in any aquatic ecosystem is crucial in determining the algal biomass and could be impacted by anthropogenic activities such as domestic (sewage disposal), agricultural (runoff manure and fertilizers) and industrial wastes. Detailed analyses of pigment patterns are virtually non-existent for the vast majority of the freshwater swamp areas around the world. Therefore, the aim of this study was to investigate the bi-monthly water chemistry (nutrient) and photosynthetic pigment concentration changes at a freshwater swamp around the University of Lagos, Nigeria. This study will provide more information in a bid to further understand the implications of water associated nutrients on the phytoplankton assemblage as represented by photosynthetic pigment concentrations.

Materials and method

Description of study site

The freshwater swamp for this study is located at the University of Lagos and has a G. P. S. coordinate of 6°30'49.3"N and 3°23'42.5"E (Fig. 1). It is connected to a forested area consisting of a variety of shrubs, bamboos, ferns and other plants. Around the vegetated freshwater swamp are landfills of solid waste materials from domestic concerns located largely to the east and west of the swamp. Additionally, is the existence of a hospital in the area with its possible attendant waste inputs. During the wet season, floodwaters from different parts of the university environment flow into the swamp area raising water levels and flooding the swamp. In the dry season, water levels are much lower and much more stagnant.

Collection of samples

The freshwater swamp was sampled bi-monthly for six months (October, 2017 - March 2018). Water samples were collected on each occasion for photosynthetic pigments, nutrients and physicochemical analyses. Sample for dissolved oxygen was fixed *in situ* with Winkler's reagents (APHA, 2012). Water samples were collected using 75cl plastic containers with each container indicating the sample area and period of collection. Sampling was carried out between 09:00 and 11.00 hrs.

Determination of physicochemical parameters of the surface water samples

Surface water temperature was measured using a mercury thermometer. Rainfall values were obtained from the Nigerian Meteorological Agency, Lagos (NIMET). pH was determined by Electrometric/Cole Parmer Testr3. Total suspended solids, salinity, dissolved oxygen, nitrate, dissolved inorganic nitrogen, dissolved organic nitrogen, phosphate, dissolved inorganic phosphate, sulphate and silica were measured using methods according to American Public Health Association (2012) for water analysis. Calcium, magnesium, copper, iron, zinc, manganese and nickel were estimated using Inductively Coupled Plasma Optical Emission Spectrometer (Agilent ICP-OES 710 Axial).

Determination of photosynthetic pigments (Chlorophyll *a*, *b* and Pheophytin *a*) (µg/L)

Photosynthetic pigments were analyzed using spectrophotometric determination of chlorophylls in water samples. A 200 mL aliquot of the water sample was filtered in a dark room through a membrane or glass fiber filter. The pigment is extracted from the filter through maceration and centrifugation in 90 % acetone. The extract was then analyzed before and after acidification, using a spectrophotometer with a 2 nm spectral bandwidth and detection limit of 5µg/L (Arar and Collins, 1997). Test results were validated with chlorophyll calibration standards (0.5 – 20 ug/L). The photosynthetic pigments were determined using the following computational formulae as reported in Onyema and Akanmu (2017).

$$\text{Chlorophyll } a \text{ [corrected; (µg/L)]} = \frac{26.7 \text{ x } (\text{A664}b - \text{A665}a) \text{ x Vextract}}{\text{Vfiltered x L}}$$

$$\text{Phaeophytin } a \text{ (µg/L)} = \frac{26.7 * [1.7(\text{A665}a) - \text{A664}b] \text{ x Vextract}}{\text{Vfiltered x L}}$$

$$\text{Chlorophyll } b \text{ (µg/L)]} = \frac{21.03(\text{A647}b) - 5.43(\text{A664}b) - 2.66(\text{A630}b) \text{ x Vextract}}{\text{Vfiltered x L}}$$

$$* \text{ Chlorophyll } a \text{ (µg/L)} = \frac{[11.85(\text{A664}) - 1.54(\text{A647}) - 0.08(\text{A630})] \text{ x Vextract}}{\text{L x Vfiltered}}$$

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*, 647*b*, 630*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 × K)
A = absorbance coefficient for chlorophyll *a* at 664 nm = 11.0
K = ratio expressing correction for acidification = 2.43

Fig. 1: University of Lagos showing the location of the study area, A Freshwater Swamp in Lagos, Nigeria

Statistical analysis

Standard deviation on a normally distributed data was used to treat the water chemistry and other data. Pearson rank correlation was used on normally distributed data set of nutrient parameters, photosynthetic pigments and other physicochemical data from the freshwater swamp site.

Results

Water chemistry

Water temperature ranged between 27 and 32 °C. The mean water temperature was 29.5 °C and the standard deviation was 1.19. Total Suspended Solid varied between 5 and 69 mg/L. Rainfall during the study period was between 0 and 154.50 mm. The highest rainfall volume was in October, 2017 and the lowest was in January and February, 2018. The pH ranged between 6.50 and 7.48, while the estimate for salinity was between 0.10 and 0.70 ‰. The highest Salinity value was in February at 0.70 ‰. Dissolved oxygen varied between 4.16 and 5.43 mg/L. With the highest value recorded in January. Potassium value ranged between 0.91 and 5.53 mg/L with an average of 2.52 mg/L while sodium was between 28.10 and 205.88 mg/L.

Nutrients

The nitrate concentration varied between 0.61 and 8.11 mg/L. Whereas, Dissolved Inorganic Nitrogen (DIN) varied between 0.14 and 6.83 mg/L, Dissolved Organic Nitrogen (DON) was between 0.03 and 0.4 mg/L. On the other hand, Phosphate concentration was lowest in October with a value of 1.32 mg/L and peaked in February (6.58 mg/L). Dissolved Inorganic Phosphate (DIP) varied between 0.44 and 2.19 mg/L but with a mean value of 1.22 mg/L. The concentration of Sulphate ranged between 6.1 and 40.6 mg/L, with the minimum concentration recorded in October. Silica values were between 1.07 and 16.20 mg/L.

Heavy metals

Values for Copper ranged between 0.002 and 0.007 mg/L. For Iron, the highest value (0.081 mg/L) was recorded in November while the lowest value (0.191 mg/L) was recorded in October. The mean value was 0.12 and the standard deviation was 0.033. For Zinc, the lowest value (0.009 mg/L) was recorded in November while the highest value (0.077 mg/L) was recorded in October and a mean value of 0.022. Manganese values ranged from 0.008 to 0.066 mg/L. Nickel values ranged between 0.0002 and 0.0015 mg/L. The highest value recorded was in November whereas the lowest value was in October. Fig. 2 shows variation in Nitrate, Phosphate, Sodium, Silica and Potassium at the freshwater swamp.

Photosynthetic pigments (Chlorophyll *a*, *b* and Phaeophytin *a*, µg/L)

The chlorophyll *a* values ranged between 1 and 12 µg/L. The mean value during the study was 2.9 µg/L. The chlorophyll *b* values ranged between 0.1 and 0.5 µg/L and a mean of 0.22 µg/L was estimated. The phaeophytin *a* values ranged between 0.1 and 0.3 µg/L with a mean value of 0.12 µg/L. Chlorophyll *a* correlated strongly with chlorophyll b (r = 0.84) and Phaeophytin *a* (r = 0.82). Similarly chlorophyll *b* correlated strongly and positively with Phaeophytin *a* (r = 0.87).

Correlation of physicochemical parameters with nutrients and heavy metals

Salinity with nutrients

Nitrate, DON and DIN correlated negatively with salinity at r = -0.76, - 0.76 and 0.22 respectively. Conversely with regard to Phosphate and Silica (r = 0.77 and 0.66), correlation values with Salinity were strongly positive.

Rainfall with nutrients

Rainfall was positively correlated with Nitrate (r = 0.31), DIN (r = 3.31), DON (r = 0.10) and negatively correlated with Phosphate (r = -0.21), DIP (r = 0.21) and Silica (r = -0.79).

pH and nutrients

pH was negatively correlated with nitrate (r = -0.73) and DON (r = -0.31). Positive correlation was recorded between pH and sulphate (r = 0.17), phosphate (r = 0.51), DIP (r = 0.51) and silica (r = -0.69).

Nutrients and heavy metals

Nutrients (nitrate, phosphate and silica) were generally positively correlated. For instance, Nitrate was positively correlated with Ni (r = 0.49), Mn (r = 0.19), Zn (r = 0.36), Fe (0.09). Silica was also positively correlated with Ni (r = 0.20), Mn (r = 0.46), Fe (r = 0.42), Cu (r = 0.18) but strongly negatively correlated with Zn (r = 0.92). Fig. 2 shows variation in Salinity and the three photosynthetic pigments as well as Manganese and Iron.

Photosynthesis pigments, physicochemical parameters and heavy metals

The photosynthetic pigments – chlorophyll *a*, chlorophyll *b* and phaeophytin *a* were positively correlated with nitrate as well as DIN in the same values (r = 0.69, 0.37 and 0.31) and DON (r = 0.82, 0.79 and 0.61). Negative correlation was recorded between phosphate as well as DIP (r = 0.46, -0.26 and-0.12) and sulphate (r = -0.23, -0.006 and -0.29) with chlorophyll *a*, *b* and phaeophytin *a* respectively. Silica recorded r = -0.15, 0.23 and 0.23 while Dissolved Oxygen (DO) recorded r = -0.12, 0.29 and 0.10 for the photosynthetic pigments. TSS recorded r = -0.07, 0.44 and -0.11, pH recorded r = 0.21,-0.10, and -0.16. Salinity was negatively correlated with all three photosynthetic pigments. Increases in salinity resulted in decrease in three photosynthetic pigments. A negative correlation was recorded as r = -0.56, -0.18 and -0.20 respectively for salinity. Similarly, potassium (r = -0.51, -0.14 and -0.17) and sodium (r = -0.51, -0.14 and -0.17) also record a negative correlation (Fig. 3) with the three photosynthetic pigments. Fig. 4 shows chlorophyll *a*, *b* and phaeophytin *a* variation in relation to nitrate, silica and phosphate

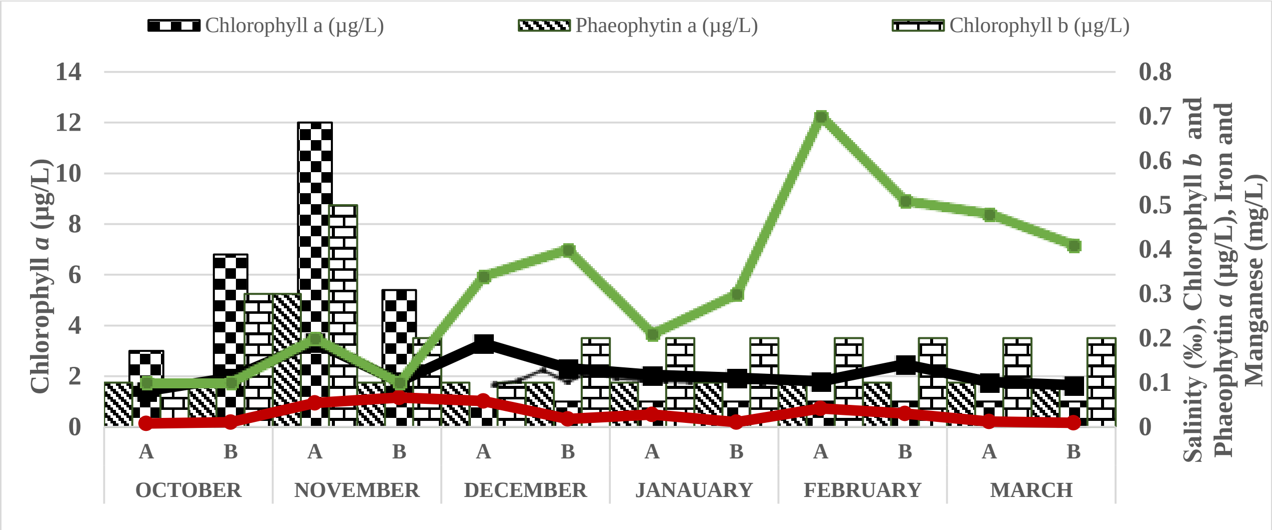

Fig. 2: Chlorophyll *a*, Salinity, Chlorophyll *b* and Phaeophytin *a*, Iron and Manganese in a Freshwater Swamp Lagos State, Nigeria (October, 2017 - March 2018).

PARAMETERS	Minimum	Maximum	Mean	Std. Error	Std. Dev. (±)
Water temperature (°C)	27.00	32.00	29.50	0.36	1.24
Rainfall (mm)	0.00	154.50	49.20	15.07	52.20
pH @ 25°C	6.50	7.48	7.03	0.07	0.24
Total Suspended Solids, (TSS) (mg/L)	5.00	69.00	16.92	5.11	17.70
Salinity (‰)	0.10	0.70	0.32	0.05	0.19
Dissolved Oxygen (DO) (mg/L)	4.15	5.43	4.82	0.11	0.39
Nitrate (mg/L)	0.61	8.11	3.45	0.80	2.78
Dissolved inorganic nitrogen (DIN) (mg/L)	0.14	1.83	0.78	0.18	0.63
Dissolved organic nitrogen (DON) (mg/L)	0.03	0.40	0.16	0.04	0.12
Sulphate (mg/L)	6.10	40.6	21.95	2.65	9.18
Phosphate (mg/L)	1.32	6.58	3.66	0.51	1.77
Dissolved inorganic phosphate (DIP) (mg/L)	0.44	2.19	1.22	0.17	0.59
Silica (mg/L)	1.07	16.20	11.96	1.40	4.85
Sodium (mg/L)	28.10	205.88	92.98	16.02	55.50
Potassium (mg/L)	0.91	5.53	2.52	0.40	1.38
Zinc (mg/L)	0.01	0.08	0.0220	0.0062	0.0215
Iron (mg/L)	0.08	0.19	0.1227	0.0101	0.0350
Copper (mg/L)	0.0002	0.0007	0.00048	0.00005	0.00017
Nickel (mg/L)	0.0002	0.0015	0.00055	0.00011	0.00037
Manganese (mg/L)	0.01	0.07	0.029	0.006	0.021
Chlorophyll *a* (µg/L)	1.00	12.00	2.933	1.004	3.479
Chlorophyll *b* (µg/L)	0.10	0.50	0.217	0.030	0.103
Phaeophytin *a* (µg/L)	0.10	0.30	0.117	0.017	0.058

Table 1: Summary data on physcicochemical parameters in a Freshwater Swamp Lagos State, Nigeria (October 2017 - March 2018).

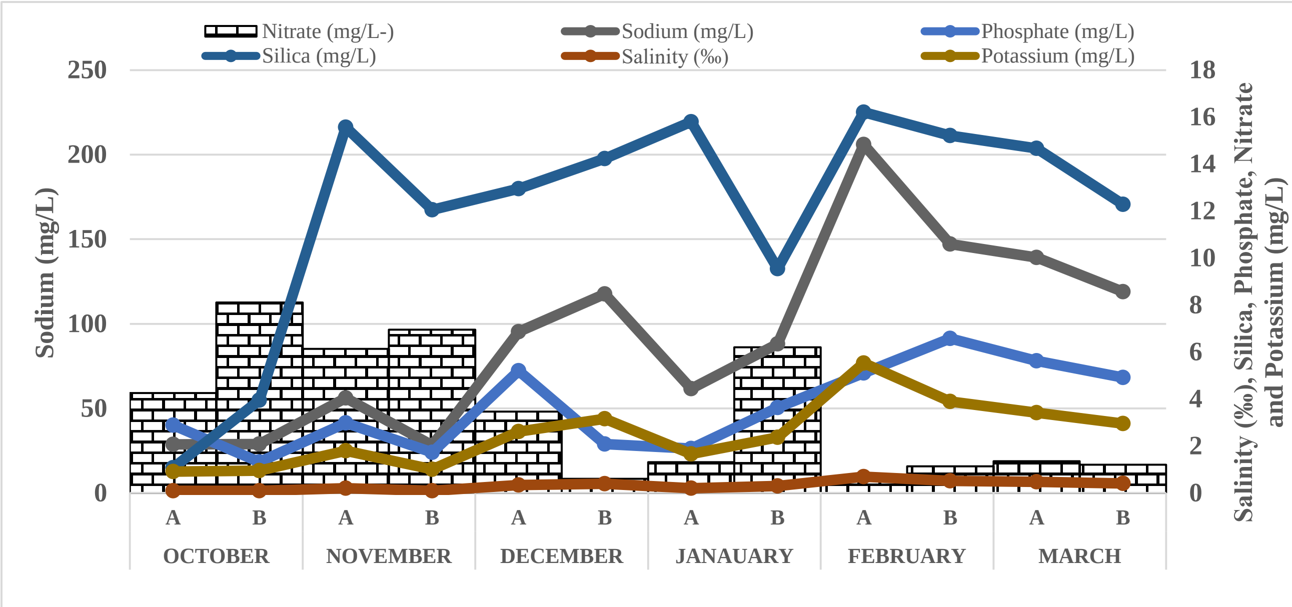

Fig. 3: Variation in Nitrate, Phosphate, Sodium, Salinity, Silica and Potassium in a Freshwater Swamp Lagos State, Nigeria (October, 2017 - March 2018).

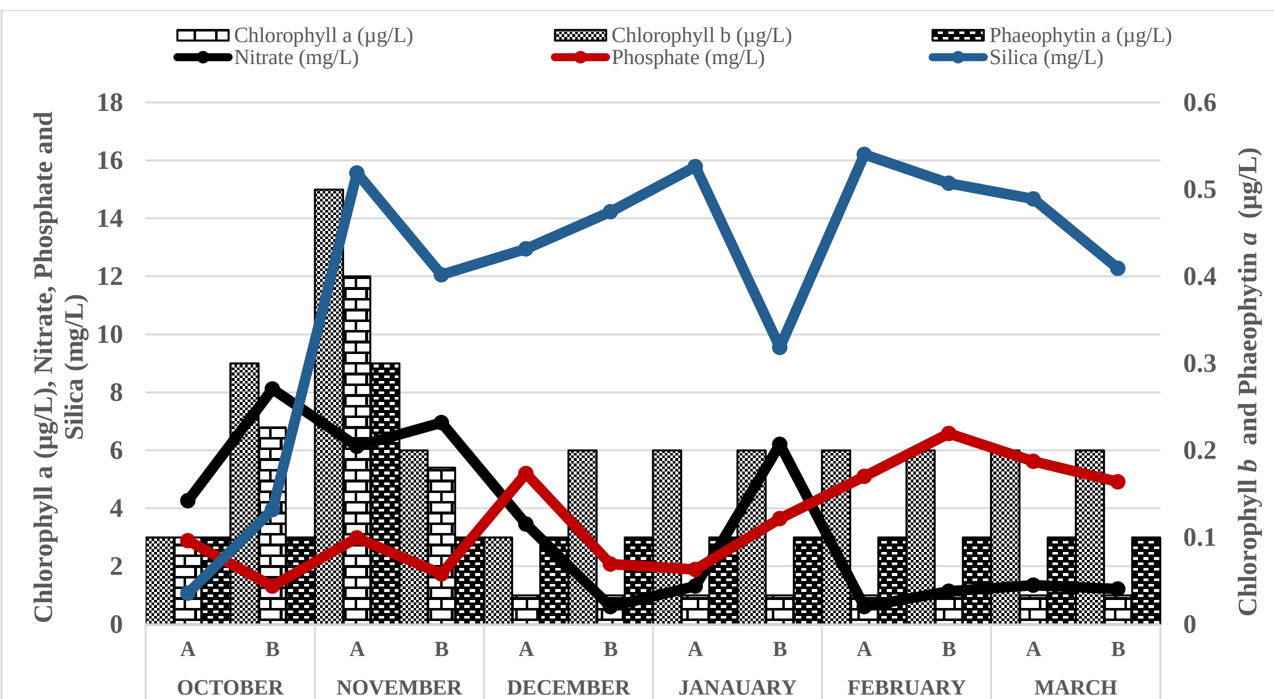

Fig. 4: Chlorophyll *a*, Nitrate, Phosphate and Silica, Chlorophyll *b* and Phaeophytin *a* in a Freshwater Swamp Lagos State, Nigeria (October, 2017 - March 2018).

Discussion

Water temperature and rainfall volume estimates confirmed the region falls within the tropical rainforest belt. Results from the study showed a good positive correlation between the introduction of nutrients and heavy metal levels. It is evident that both domestic and medical waste inputs are largely from the same source which is the immediate environment. The acidic nature for most of the study period is typical of freshwater environments (Onyema and Emmanuel, 2009). The swamp water conditions were acidic until the dry season set in and it became slightly alkaline. Alkaline pH recorded in the dry season is probably connected to the cessassion of floodwaters and high seepage inputs from the surrounding wetland and dump site areas. The freshwater swamp is flooded periodically or semi-periodically resulting in waterlogged soils that are anaerobic and unstable. These factors allow for the sustenance of a unique habitat that supports some diversity of flora and fauna that are adapted to the prevailing conditions.

The hydrological stability and gradual increase in salinity, potassium, sodium, silica, phosphate and sulphate especially during the dry season would be as a result of increased evaporation and reduced flood water inflow. Onyema and Akanmu (2018) is of the view that during the raining seasons coastal wetlands, lagoons and creeks are diluted considerably by freshwater from rain and river systems while in the dry season, evaporation becomes more prominent. According to Nwankwo (1993), owing to the seasonal distribution of rainfall, the Lagos lagoon system experiences seasonal flooding which also introduces a lot of detritus, nutrients and dilutes the salinity of the water considerably. Similarly, with regards to waste discharges in coastal wetland ecosystems, Onyema and Nwankwo (2006) are of the view that apart from enriching the water with high amounts of biodegradable matter, flood water associated waste discharges introduces nutrients, toxic and other land based substances that consequently signal epidemiological problems and an increase in human induced stressors which impairs the quality of aquatic biodiversity.

The significant correlation ($p < 0.05$) among the three photosynthetic pigments adduce to their likely control by the same set of factors whether directly or indirectly. Reports from studies on algal pigments concentration for the western parts of the Lagos lagoon (Onyema et al., 2016), Atlantic Ocean off the coast of Badagry in Lagos (Onyema and Akanmu, 2017), Onyema and Akanmu (2018) in a mangrove swamp and tidal pond and Onyema (2018) for mid-lagoon, Lagos when tested with one sample t-test ($p < 0.05$) were significantly low compared to recorded values of chlorophyll *a*, chlorophyll *b* and phaeophytin *a* for this study. The low levels reported for this study could be due to the depressing effect of pollution from the surrounding solid waste site and its impact on aquatic life.

Increasing salinity, sodium and potassium levels were strongly negative in relationship to the photosynthetic pigment in the freshwater swamp. It is important to note that salinity nay, increasing salinity is an important limiting factor to freshwater species in freshwater ecosystems. For this study, increasing salinity was directly related to reduced values for the photosynthetic algal pigments. According to Onyema (2010), it is worthy of note that salinity acts as a limiting factor to algal production in the Lagos lagoon especially in the wet season and this may be as a results of the fact that most phytoplankton forms at this time are freshwater species and may have drifted downstream from freshwater creeks and rivers into the Lagos lagoon.

Photosynthetic pigments were also positively related with nitrate, DIN and DON. A similarly direct relationship was also recorded with heavy metals for this study. Nitrogen based nutrients (Nitrate, DIN, DON) are quite essential for primary production by the phytoplankton and in the photosynthetic process. Rainfall also dissolves the nitrogen based nutrients and transports these nutrients along with heavy metals in floodwaters from the surrounding area to the freshwater swamp. These parameters are directly related. Floodwaters are known to be a main source of introduction of nutrients to aquatic ecosystems. A similar situation was reported by Onyema *et al*. (2016) for the wet season in the Lagos lagoon. In that study, the positive relationship (correlation) between iron, nitrate, phosphate and total suspended solids was noteworthy. Increase in the level of nutrients notably nitrate, DIN and DON led to corresponding increases in all algal pigments within the aquatic systems. Varadharajan and Soundarapandian (2014) are of the view that phytoplankton species diversity responds rapidly to changes in the aquatic environment particularly in relation to nutrients.

Nutrient levels were comparatively lower during the rains and higher in the dry periods of the study. This is explainable by the effect of dilution linked to the introduction of floodwaters during the rains or wet season. Conversely, higher evaporation rates and reduced introduction of floodwaters increased the concentration of the nutrients for instance silica, sulphate and phosphate in the dry season. This may be attributed additionally to evaporative concentration, high light intensity (insolation), reduced cloud cover and more stagnant water conditions (Onyema and Emmanuel, 2009) as similarly reported for the Lekki lagoon in Lagos. Adequate insolation, nutrients and hydrological stability are essential for optimum aquatic primary production (Onyema, 2018).

Conclusion

The photosynthetic pigment concentrations were significantly affected by nutrient distribution particularly nitrogen-based nutrients (nitrate, dissolved inorganic nitrogen and dissolved organic nitrogen) and heavy metals (nickel, magnesium and iron) at the freshwater swamp.

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