Seasonal Variation of the Nutrients Distribution in the Sediments of Great Kwa River, Calabar South-South Nigeria.

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Abstract
The nutrients (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, TN and TP) distributions in the surface sediment samples from the Great Kwa River were investigated during wet and dry season to establish the health of the ecosystem and monitor its seasonal variations. The Kjedahl and the spectrophotometric methods were adopted and the results obtained showed the following increasing order of the concentrations of such nutrients. PO_4^{3-} (0.570±0.194) < NO_2^- (1.768±0.399) < TP (2.0±0.289) < NH_4^+ (6.170±0.428) < NO_3^- (34.52±3.291) < TN (57.66±3.633)µM during wet season and same trend with varying concentrations PO_4^{3-} (0.36±0.082) < NO_2^- (1.416±0.35) < TP (2.144±0.313) < NH_4^+ (4.212±0.64) < NO_3^- (29.40±2.409) < TN (42.80±1.97)µM during dry season. All the nutrients except TP that is almost constant, varied with the wet season showing higher concentration than the dry season. Also the Redfeld ratio of N: P or NO_3: PO_4^{3-} of 16:1 would vary showing higher value during the dry season. This indicated that despite the lower nutrient of the dry season, the rate of reduction of PO_4^{3-} was faster. Which implies that some biological activities that use up PO_4^{3-} faster during this season may be occurring. This could lead to severe phosphorus deficiency or limitation in such season. However there is clear indication of phosphate limitations and excess nitrate in both seasons of the location.

Keywords: *seasonal variations, Nutrients, Distribution sediment, Great Kwa River*

Introduction

The Great kwa rivers also called kwa Ibo rivers is economically important to the coastal dwellers of Calabar and its environs, as it flows through Cross Rivers state, Nigeria draining the east side of the city of Calabar. The human activities in this basin remains small scale farming, fishing and aqua cultural activities. However the introduction of Calabar free trade zone in recent years has encourage migration of individuals and industries, thus increasing houses and factories around the fresh water and mangrove swamp of the location. The university of Calabar including the university teaching hospital covers a large part of the bank of the downstream of the river creating impact on the activities of the river due to their waste discharge (Ama-Abasi *et al.*, 2017) the rivers takes it's rise from the Oban hills in northern Cross Rivers state, and meander southwards through mainly the rain forest belt, before discharging into the Cross River estuary covering a distant of approximately 56km with an average width of 28km.

Nutrients are element or compound that is important for animal or plant growth and well-being. Common among which are Nitrogen (N), Phosphorus (P), and Potassium (K). However phosphorus is most often considered controller of algae production in water bodies (schidler1997). They enter the aquatic ecosystem through surface area, air or ground water (Selman *et al.*, 2008). Excess nutrient in the Ecosystem can be highly damaging, leading to effects such as anoxia and hypoxia from eutrophication, nuisance algae blooms, dieback of sea grasses and corals and reduced population of fish and shell fish (Price *et al.,* 1985; Abu-Talib *et al.,* 2018), while insufficient nutrient cannot sustain life (Abu-Talib *et al.,* 2018) as malnutrition or insufficient nutrients will lead to stagnation, poor growth and eventually death.

The sediment is an important part of an aquatic ecosystem providing both a sink and a source for nutrient. Sediment refers to the conglomeration of materials, organic and inorganic, that can be carried away by water, wind or ice (Gerringa, 1990). While the term is often used to indicate soil-based, mineral matter (e.g clay, silk, and sand), decomposing organic substances and inorganic biogenic material are also considered sediments. (Daniellsson et al., 1978). Most mineral sediments comes from erosion and weathering, while organic sediment is typically detrinus and decomposing materials such as algae (Gobeil et al., 1987).

According to wokoma, (2014) the major and cheapest source of protein available and accessible to coastal dwellers such as Calabar, Itu, Kalabary etc. in the Niger Delta region of Nigeria is fish and other seafoods like Shrimps, Crabs, Oyster, Periwinkle etc, all obtained from their rivers and estuaries therefore the constant monitoring and maintenance of the health of such rivers are very important and should be given out most attention.

To study the growth, reproductivity or any activity in an ecosystem, the ecologist must understand which factors limit the ecosystem activity. Availability of resources such as light, water and nutrient is the key control on growth and reproduction. Some nutrients are used in specific ratios. The ratio of nitrogen to phosphorus in the organic tissues of algae is about 16:1. Therefore, if the available nitrogen concentration is Greater than 16 times the phosphorus, then the phosphorus will be the growth limiting factor (Levner *et al*., 2005) or vice versa.

These resources influence ecosystem activities differently, depending on whether they are essential, substitutable or complementary. Essential resources limit growth independently of other levels. Meaning, if the minimum level required for a particular activity is not available, such activity will not occur. While for substitutability the activity will be limited by an appropriately weighted sum of the two resources in the environment. When they are supplementary a small amount of one resource can substitute for a relatively large amount of another (Movstakas and Karakassis 2005).

Resources availability serves as a “bottom-up” control on an ecosystem as the supply of energy and nutrients influences ecosystem activities at higher trophic levels by affecting the amount of energy that moves up the food chain. It can also be influenced by “top-down” control, resulting from the abundance of organisms at high trophic levels in the ecosystem. However both types of effect can be at work in an ecosystem at the same time. The understanding or knowledge of whether bottom-up or top-down control is effective in an ecosystem is important as it can influence conservation and environmental protection strategies (Boyd *et al*., 2006).

Materials and Metals:

Sample collection

A total of 10 cluster sediments were collected during wet and dry season (July 2016 and February 2017 respectively) along the Great Kwa River (GK). (5 samples per season) using sediment grab sampler. Each sample was stored in a dark polyethylene bag and poison with HCl to stop biological activities. The sampling container were preconditioned with 5% nitric acid and later rinsed thoroughly with distilled water before sampling was done. Collected samples were then placed in a cooler containing ice and transported to the laboratory prior to chemical investigations.

Sample preparation

Briefly, sediment samples were oven-dried at 60°C to constant mass for approximately 48 hours, and then the coarse debris and gravel were removed by passing the dried sample through a 2 mm sieve. The sieved samples were ground to powder with a mortar and pestle, then sieved using a 63 μm mesh, and homogenized prior to laboratory analyses.

Analytical process

Nutrient analysis was performed according to Hou et al. (2013). Sediment's total nitrogen (TN) was determined by the Kjeldahl Nitrogen method. Total phosphorus (TP) was determined by spectrophotometric method after digesting with aqua regia, HNO_3: HCl (3: 1, V/V) at 200°C. The overall analytical precision was determined at ±5% for TN and ±3% for TP, using standard reference material solutions and blanks. For the determination of NH_4^+, NO_2^- and NO_3^- in sediments; 0.5 g dried sediment samples were added into 100 mL acid-washed screw-cap polyethylene centrifuge tubes with 2 mol/L KCl solution. The tubes were capped and incubated at 25 ± 1°C in an orbital shaker at 200 rpm for 2 h. After homogenization, the sample solution was immediately centrifuged at 3000rpm for 15 min and then filtered through 0.45 μm GF/C filter membrane. The filtrate was extracted and the extracts were analysed for the concentrations of nitrite-N, nitrate-N, ammonia-N, and ortho-P. Ammonia-N was determined by indophenol-blue method, while nitrite-N and nitrate-N by cadmium reduction.

Results:

The results of the nutrients concentrations in the surface sediment of Great Kwa River (GK) during wet and dry seasons are presented in Tables 1-3 and Figures 1-3 below

Table 1: Concentration of nutrients in the surface sediments of Great Kwa River (coordinates, N 4.953135^0, E 8.363356^0) during wet season.

Sample ID	Nutrients	NO_3^-	NO_2^-	NH_4^+	PO_4^{3+}	TN	TP
GK1		45.3	2.11	6.02	0.32	62.1	1.54
GK2		31.2	3.02	6.44	0.29	47.8	3.04
GK3		28.2	1.27	7.26	0.64	44.1	2.01
GK4		28.2	1.12	6.24	0.58	56	1.92
GK5		32.3	1.32	4.89	0.72	48.3	1.77

Table 2: Concentration of nutrients in the sediment of Great Kwa River during dry season.

Sample ID	Nutrients	NO_3^-	NO_2^-	NH_4^+	PO_4^{3+}	TN	TP
GK1		28.3	0.95	3.93	0.23	44.7	2.12
GK2		33.4	2.13	3.34	0.42	42.8	1.99
GK3		21.5	1.32	4.32	0.11	38.6	3.16
GK4		31.6	0.56	3.13	0.53	41.8	2.01
GK5		32.3	2.12	6.34	0.29	49.1	1.44

Table 3: Range, Mean and Standard deviation of Nutrients in sediments from CE, KR and GK during wet season.

Element		wet season	Dry season
NO_3^-	Range	28.2 – 45.3	21.5 – 33.4
	Mean	34.52 ± 3.291	29.4 ± 2.409
NO_2^-	Range	1.12 – 3.02	0.56 – 2.13
	Mean	1.768 ± 0.399	1.416 ± 0.35
NH_4^+	Range	4.89 – 7.26	3.13 – 6.34
	Mean	6.170 ± 0.428	4.212 ± 0.64
PO_4^{3-}	Range	0.29-0.72	0.11 – 0.53
	Mean	0.510 ±0.194	0.316 ± 0.082
TN	Range	44.10 – 62.10	38.6 – 49.1
	Mean	51.66 ± 3.633	42.80 ± 1.97
TP	Range	1.54 – 3.04	1.44 – 3.16
	Mean	2.06 ± 0.289	2.144 ± 0.313

Mean ± SD obtained from values of all five (5) stations of the 3 sampling sites

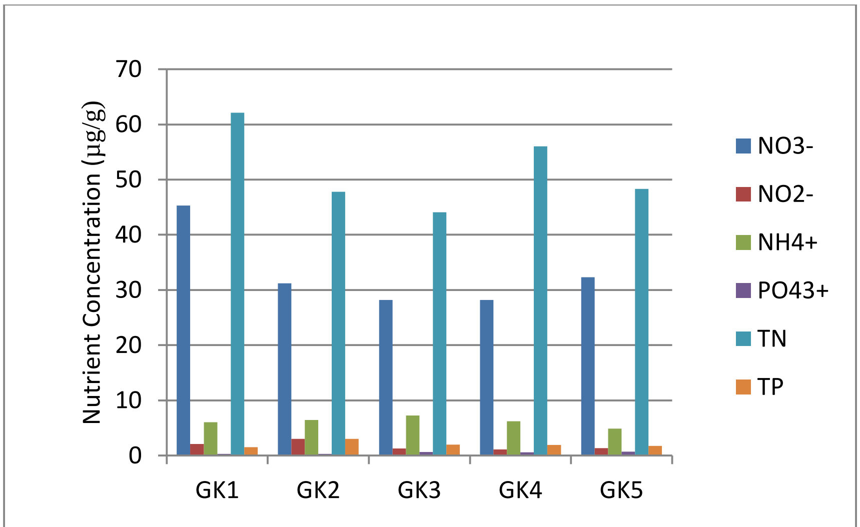

Figure 1: Concentration of Nutrients in the sediments of the Great Kwa River during wet season.

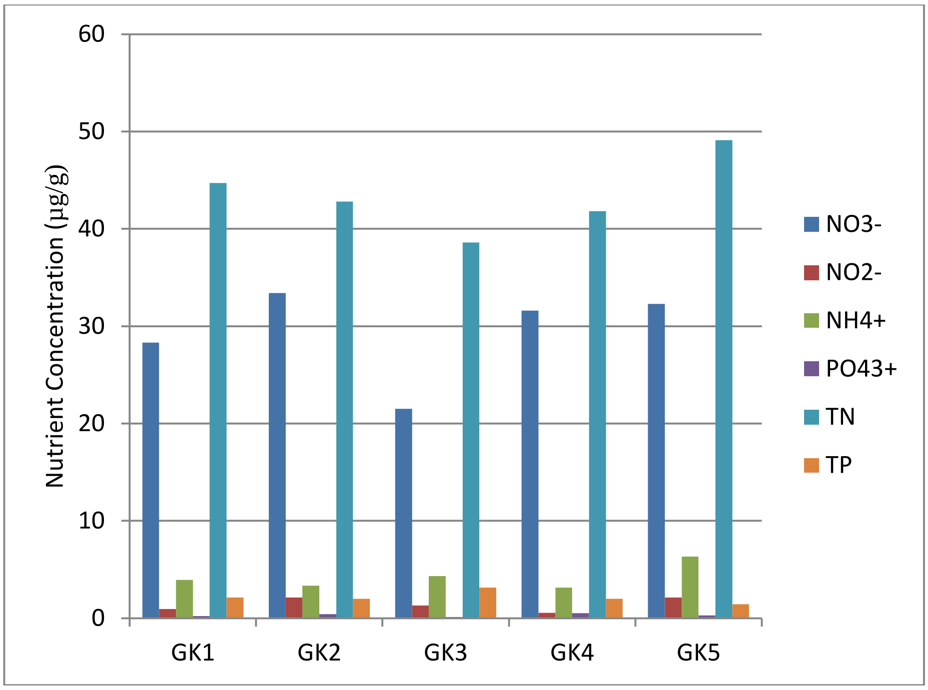

Figure 2: Concentration of Nutrients in sediments of the Great Kwa River during Dry season.

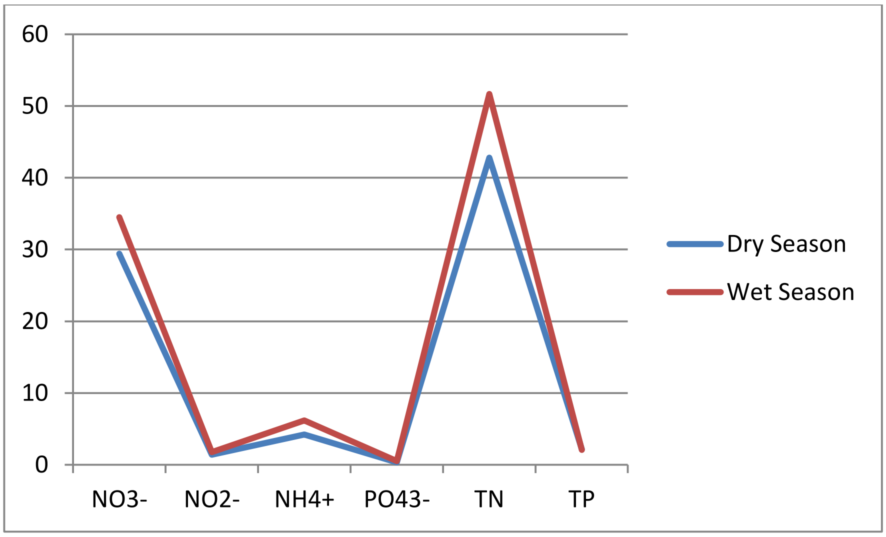

Figure 3: Mean concentration of nutrients in the sediments of the Great Kwa River during wet and dry season.

Discussion:

The results revealed the presence of all the analyzed nutrients in the sediments of the Great Kwa River for both wet and dry seasons.

Total Nitrogen (TN):

The total Nitrogen (TN) is the most abundant of all the nutrients recorded in this location. Its concentration ranged from 44.1-62.1 with an average of 59.66 ± 3.633 µM during the wet season and 38.6-49.1 with a mean of 42.80 ± 0.1.97 µM during the dry season showing a higher TN in the wet season than the dry season. The values obtained in this research were higher than all the range of values 0.29 – 0.59 (0.38) mg/g for Achaloos river estuaries Greece, 0.39-0.53 (0.47) mg/g for Alannssor highland Greece, 1.31 – 4.89 (3.08) mg/g for Anovissors surface sediment Greece and 0.84 – 1.63 (1.23) mg/g for Rafina surface sediment Greece as reported by Ladakis *et al*, (2005). These values are also higher than the value 1.6mg.g recorded for missisipi estuary gulf of Mexico (Ruttenberg and Goni, 1997) and 125mg/g reported by Sfriso *et al* for sediments of Vince Lagoon. They are at variance with the values 2.95, 1.74, 0.79 and 0.46g/kg recorded for sediments in several aquatic environment types of the Mediterranean coast wet lands (Gascon *et al.*, 2006). Finally, these values are higher than the range of values 0.34 – 7.68 (2.7) mg/g recorded for surface sediment of Nansi lake in China (Wang *et al.*, 2017).

Nitrate (NO_3^-):

The next most abundant of the nutrients was nitrate where the highest concentration during the wet season was 45.30 µM and the highest concentration during dry season was 33.4 µM. the mean concentrations obtained were 34.52 ± 3.291 and 29.40 ± 2.409 µM for wet and dry seasons respectively. In the same vane the wet season concentration is higher than that of the dry season. The values obtained here were higher than the range of values of the sediment of great kwa river such as 1.824 mg/g (Atimbo), 0.161mg/g (Esuk Atu) and 6.696mg/g (Obufa Esuk) reported by Ama-Abasi *et al* (2017). Ladakis *et al* (2005) recorded range of 8.86-31.8 (17.8) mg/l for coves water, 8.12 – 34.2 (17.8) for Anavissor outer water and 7.14-36.4 (16.0) mg/l for Rafina outer water all in Greece. It was observed that the higher the nitrate, the lower the productivity of phytoplankton therefore, the level of NO_3^- in this research may not favour phytoplankton (Ama-Abasi *et al.*, 2017).

Ammonium (NH_4^+):

NH_4^+ is the next abundant Nutrient in this location with a range concentration of 4.89-7.26 and a mean concentration of 6.170 ± 0.428 and 3.13 - 6.34 with mean of 4.212 ± 0.64 µM for wet and dry seasons respectively also indicating higher concentration during the wet season than the dry season. The Ammonium concentrations recorded in this research were found to be higher than the range 1.96 – 24.5 (10.6) mg/l, 0.28- 31.8 (10.8) mg/l and 2.52 – 16.4 (9.66) mg/l recorded for cove water, anavissors outer ware and outer rafina water respectively (Ladakis *et al.*, 2005). Also higher than the values recorded for different sediments of different areas of the great kwa river, 0.348 mg/g (Esukatu), 1.611 mg/g Atimbo and 1.67 mg/g Obufa Esuk (Ama- Abasi *et al.*, 2017). This high level of Ammonium as compared to other result may be an indication of high biological transformation processes such as bacteria and achaeal nitrification. This may on the other hand contribute to the high nitrate content observed in these locations.

Total Phosphorus (TP):

The range TP concentrations observed in this locations were 1.54-3.04 and 1.44-3.16 µM and the mean concentrations were 2.06 ± 0.289 and 2.144 ± 0.313 µM for wet and dry seasons respectively. Showing slightly higher dry season concentration than wet season. These concentrations were high when compared to the levels recorded for global lakes 0.014±3.7 (0.0136 – 0.0144) mg/l, deep lake 0.017 ± 3.544 (0.0153 – 0.0197) mg/l, shallow lakes 0.034 ± 3.3 (0.0318 – 0.0364) mg/l, North frigid zone of the lakes 0.00797±3.8 (0.0070 – 0.0090) mg/l, South temperate zone 0.033 ± 7.0 (0.0248 – 0.0435) mg/l, the North temperate zone 0.014 ± 3.5 (0.0136 – 0.0145) mg/l and total storage of the global lake of 25 mg/l. (Cheng *et al.*, 2015). Gascon *et al*, (2006) though reported nitrogen limitations for both sediments and water but recorded more phosphorus in sediment than in water with TP values 0.74, 0.76, 0.42 and 0.26 mg/kg in several aquatic environment of the Mediteranean coast wet land. Results in this research were also higher than 0.733mg/kg mean value recorded for 10 basins of China. (Yang, *et al.*, 2017) and 0.39 – 1.37 (0.68) for surface sediment of Nansi lake, China (Wang *et al*., 2017). However, Huang *et al*, (2016) presented very high values between 582.48 ± 42.47 – 754.24 ± 42.47 for five sediments of Dongting Lake.

Nitrite (NO_2^-):

The range and mean concentarion NO_2^- were 1.12 – 3.02(1.1768±0.399) and 0.56 – 2.13(1.416 ± 0.35)µM for wet and dry seasons respectively, indicating higher wet season concentration than dry season. These values are at variance with the range and mean values 0.56- 1.82 (0.84), 0.14-0.98 (0.56) and 0.14- 02.52 (0.98)mg/g recorded for Coves water, Anavissors outer water and Rafina water (Ladakis *et al*., 2005)

Phosphate PO_4^{3-}:

This is the least abundant of all the nutrients, the range and mean concentrations showed 0.32 – 0.72 (0.510 ± 0.194) and 0.11 – 0.53(0.316 ± 0.082) µM for the wet and dry seasons respectively. . The wet season showed higher concentration of PO_4^{3-} than the dry season. Ama-Abasi *et al*., (2017) reported lower levels 0.034 mg/g 0.01 mg/g and 0.028 mg/g for sediments of Atimbo, Esuk-Atu and Obufa Esuk respectively of the great Kwa river. They also reported the population buildup of certain plankton where phosphate is higher than where it is lower. The phosphate concentration recorded at the Greece river 0.93 – 14.2 (4.34) mg/l, 0.62 –8.05 (4.03) mg/l and 2.17 – 3.7 (2.7) mg/l for coves water, Anavissors cover water and outer rafina water (Ladakis *et al.*, 2005) are similar to the results obtained in the present study. This level of phosphate may also enhance the continuous growth of phytoplankton.

Urban waste water contain high concentration of nutrient and as such contribute significantly to the mass loading of Nitrogen and Phosphorus to coastal water. The various inorganic forms of nitrogen and phosphorus stimulate aquatic plant growth and since they are relatively hydrophilic, their removal from the water column is more biologically mediated than for trace metals or hydrophobic organics (Hanson and Rudstam 1990).

Conclusion:

In conclusion therefore, in spite of the claims that phytoplankton production in most coastal marine ecosystems and estuaries is nutrient limited and that increase nutrient input leads to higher production and Eutrophication, this research results showing very high nutrients levels has not cost eutrophication to this location, the ratio of nitrogen; phosphorus or nitrate; phosphate as observed in this research were far higher than 16;1. Expected Redfieid ratio. Therefore this location must be carefully monitored to avoid problems of excess nitrogen\nitrate or limitations of phosphorus/phosphate that may be common with dead ecosystem.

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