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Article

Studies on Tidal Changes, Physicochemical Parameters, Suspended Particulate Matter and Nutrient Concentration in the Great Kwa River, Nigeria

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Abstract: Studies on the variation of nutrient concentration, suspended particulate matter and physicochemical parameters due to tidal oscillation in the Great Kwa River estuary was carried out in May to September, 2019 using standard analytical methods. The result of the variations in the nutrient concentrations, suspended particulate matter and the physico-chemical parameters were shown to have the following range of values; ammonium (0.002-0.017)mg/L, phosphate (0.001-0.009)mg/L, nitrate (0.001-0.0019)mg/L. The influence of tidal changes on physico-chemical parameters such as temperature, conductivity, pH, salinity, turbidity, total dissolved solid, total suspended solid were found to be; 4.0-8.9mg/L for turbidity, 0.0001-0.002FTU for salinity, 6.20-8.10 for pH, 27-29.9ºC for temperature, 0.0006-0.001μs/cm for conductivity 0.001-0-0035mg/L for total dissolved solid (TDS) and 0.0035-0.005mg/L for total suspended solid (TSS). The variation in nutrient is mainly attributed to the re-suspension of sediment, tidal mixing, river discharge, sea water intrusion, displacement of intertidal flats and mangroves swamps caused by tidal activities.

Keywords: Tidal changes, physicochemical parameters, particulate matter, estuary, Nigeria

1. Introduction

The Great Kwa River estuary is an Urbanized tidal tributary of the Cross River estuary, Nigeria the Cross River estuary is one of the most important inland water way, east of the Niger and is the sea route to the eastern port of Calabar the city of Calabar, the capital of Cross River State is located within the proximity of Great Kwa River and discharge waste directly or indirectly into the river and associated swamps. Currently, the city of Calabar and associated water ways is being developed as export processing zone (EPZ). This development will definitely lead to increase in industrial activities and human population, majority of which will concentrate along the estuaries of the Calabar and Great Kwa Rivers. The associated increased in waste loads on these rivers will results in effects which may only be grasped from well-articulated monitoring programmes.

The importance of estuaries cannot be over emphasized. They include, provision of rich fisheries, sheltered anchored and navigation access (De.Vries etal; 1983). The natural load of land-derived nutrients carried by the estuaries result in highly productive water crabs and clams (Mc Conick, etal; 1981).

The movement and distribution of materials in a well mixed estuary with depth during the low-tide and high tides should affect the suspended particulate matter and physico-chemical parameters of an estuary.

It is on the above premise that this study was aim at studying the changes in nutrient distribution and concentration with tides, the influence of the tides as well as hourly variation of physico-chemical properties, influence of water current in suspended particulate matter in estuary and nutrient of the data obtained from the estuary during low tide and high tide.

2. **Materials and Methods**

2.1. Sample Collection

Surface water samples were collected in a boat anchored at one location in the middle of the estuary at an hourly interval covering both low tide and high tide (both ebb tide and flood tide phases) this station was chosen so that homogenous water samples can be obtained due to turbulent mixing.

2.2. The Study Area

The Calabar River is the tributaries of Cross River which originated from the Cameron along the Mamfe Embayment towards the east and follows the Afikpo syncline and finally reaches the height of bonny south of Calabar.

It originates from the hilly region of the northern Cross River State and flows through different places before emptying into the Cross River estuary. It lies between latitude 4^0 54’N and 5^0 50’W and longitude 80^0 0’E and 8^0 20’E.

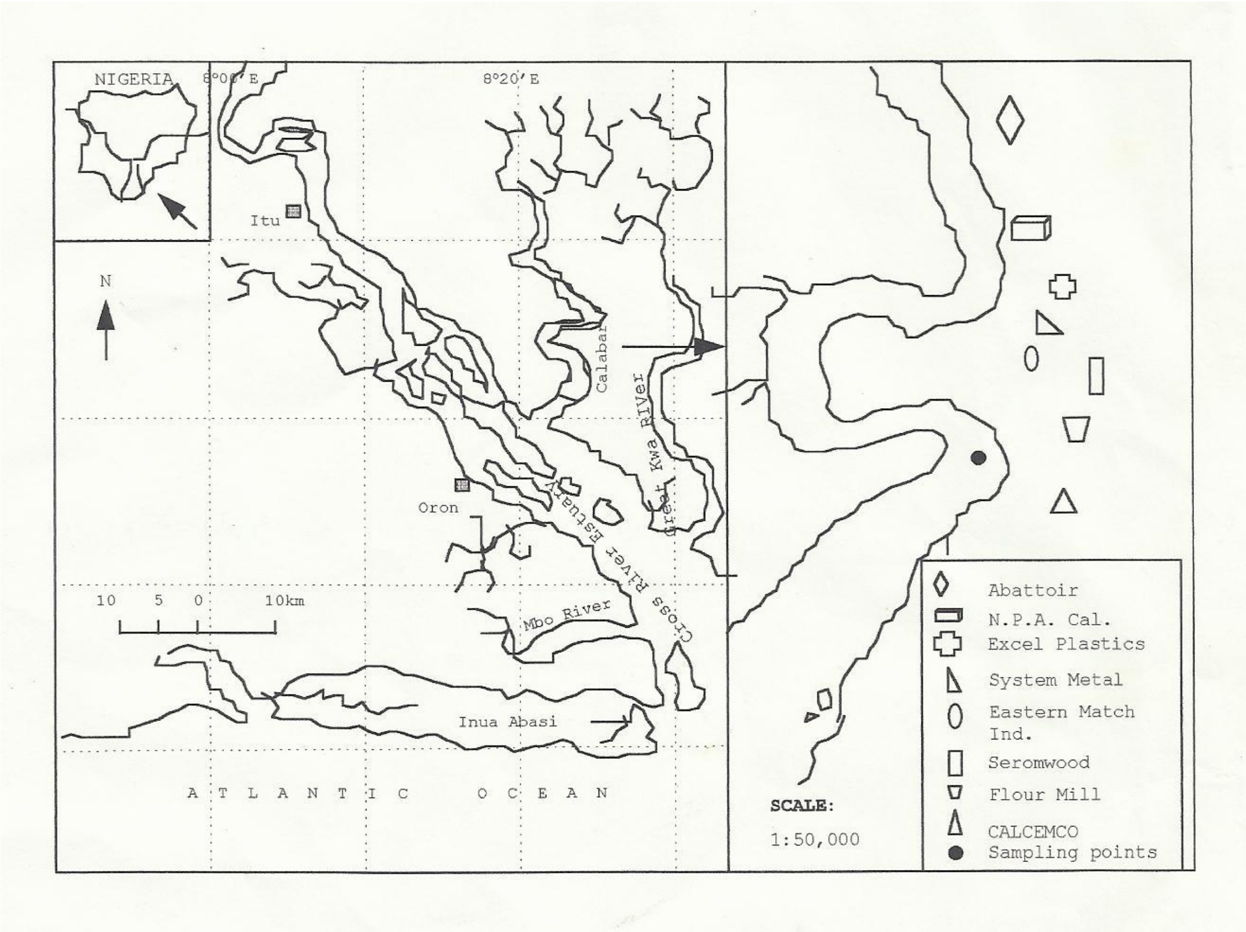

Fig 1: Map of GREAT KWA River Estuary showing sampling station (●)

2.3. Determination of Physico-chemical Parameters

2.3.1. Temperature

The temperature was measured *insitu* using a thermometer immediately after each sampling (model-0-60 ºC calibration).

2.3.2. Hydrogen ion concentration (pH)

The pH was measured *insitu* suing a pH mater after each sampling.

2.3.4. Conductivity

The conductivity was determine using the conductivity meter (Model W.T.L .F 90). After calibration in air (0.00) the probes was rinsed with distilled water and immersed into the water sample. The conductivity button was pressed and the value that displayed on the screen taken.

2.3.5. Turbidity

Turbidity of the sample was conducted using an electronic turbidity meter. The turbidity meter was calibrated with a turbid solution and nitrate solution.

2.3.6. Total Suspended Solid (TSS)

2 litres of water sample was measured for both low tide and high tide, and was filtered. The residue on the filter paper was dried in an ovum to determine the suspended particulate matter.

2.3.7. Total dissolved solid (TDS)

2 litres of the water sample was measured and filtered. The filtrate was evaporated in an ovum to determine the total dissolved solid.

2.3.8. Salinity

100 ml of sample was filtered into a conical flask and 3 drops of 10% potassium chromate solution was added and titrated with 10% silver nitrate. The appearance of a reddish tint which persisted for 1-3 minutes was recorded as the end point.

$$\% \text{ salinity} = \frac{1.86655 \text{xvx} 10 \text{x} 3.55}{100}$$

3. **Nutrient Determination**

Ammonium, nitrate, nitrite and phosphate were determined using different analytical methods.

3.1. Ammonium ($NH4^+$) (Direct nesselerization using spectrophotometer)

1.0ml of a solution of Rochelle salt and 0.5ml of Nessler's reagent were added to 20ml of water sample and clouding was observed after 30miniutes and was measured at 435nm against distilled water in the photometer. The evaluation was done by means of the calibrating curve established with a solution of NH4Cl.

3.2. Nitrite ($N0_2^-$) (Diazotization method using spectrophotometer 540nm)

50ml of filtered water sample was measured and 2ml of sulphonic acid added, mixed thoroughly and allowed to stand for 20minutes. 1ml of NED [(1-napthyl)ethylene diamine] was added, mixed and the concentration measured after 20 minutes in the at 340nm against a blank reagent in the spectrophotometer.

3.3. Nitrate ($N0_3^-$) (cadmium reduction) [column, spectrophotometer 540nm]

10g each of copper sulphide pentahydrate ($CUSO4.5H_2O$) and NH_4Cl was dissolved in1000ml of distilled water. The column was filled with graduated Cadmium (40-60 mesh). The Cadmium was shaken several times with CUSO4 solution and the slorry was washed with NH_4Cl and the sample was then run through the column. The remaining sample in the column was used for analysis as described for nitrate-nitrogen.

3.4. Phosphate ($PO4^{3-}$) (Molybdenum Blue Method)

1ml of ammonium molybdate and 0.4ml of bhydrazine sulphate were added to aliquots of stock standard solution and the solution was made up to 10ml with double distilled water in a standard measuring flask. The standard measuring flasks were kept in a water bath for heating for 30 minutes. The temperature of the water bath was set to 60^0C while heating, a blue colour develops due to the formation of ammonium phosphomolybdate complex. After heating for 30 minutes, the solution was cooled and its absorbance was measured at wave length 830nm. An experimental blank solution was used for carrying out correction for the baseline. The water sample was filtered through Whatman filter paper and collected. Aliquots of the sample were used for its phosphate analysis.

4. Results and Discussion

Variation in the concentration of ammonium, phosphate, nitrate and nitrite in relation to tides in May, June, July, and August is shown in fig. 2, 3, 4 and 5 respectively.

Ammonium

From fig. 2 the values of ammonium ranges from 0.001-0.006mg/L and 0.003-0.0017mg/L respectively. This is closely related to the values given by (Fatema, et al; 2015). Ammonium was high during low order. The high concentration of ammonium at low tide is due to antropogenic activities in the vicinity.

High Concentration of ammonium in estuary might be caused by land activities such as sewage effluent and agricultural run-off (karikari, et al; 2006). Ammonia is one of the nutrients required by phytoplakton for primary productivity (Davis, et al; 2013). Others are nitrate and phosphate (yamamuro, et al; 1993). More so, ammonia is a source of nitrogen and contributes to the fertility of water since nitrogen is an essentials plant nutrient. However it can constitute hazard to aquatic environment (Thurston, et al; 1981).

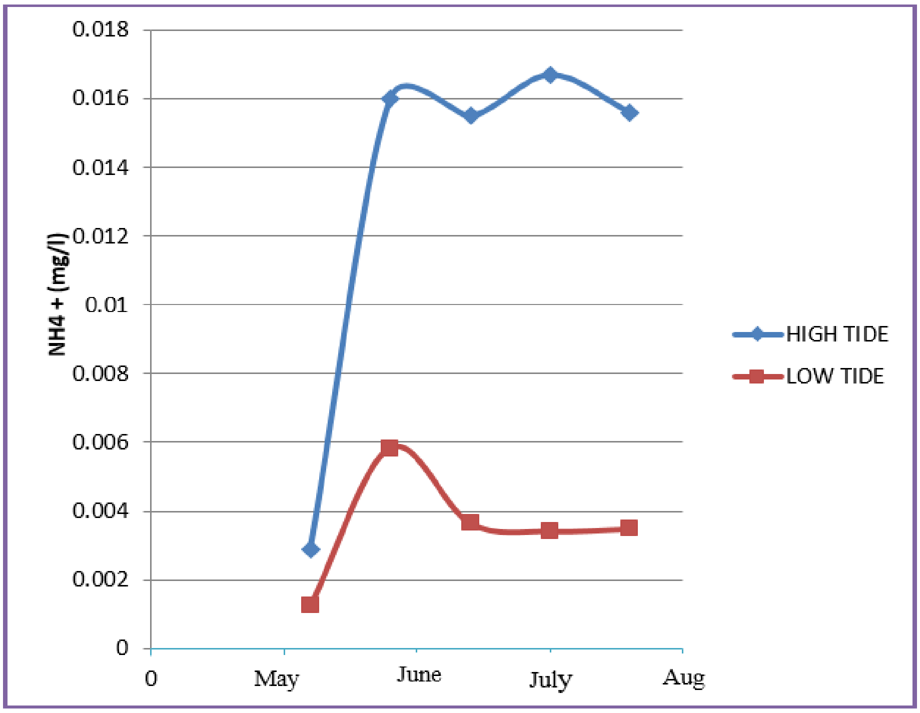

Fig. 2: Variation of ammonium concentration with tides in Great Kwa River Estuary in April, May, June, July and August

Phosphate

From fig. 3, the values of phosphate ranges from 0.001-0-003 respectively. In May-August, phosphate level dropped to minimum value of 0.01mg/L at ebb tide and increased to a maximum of 0.04mg/L at flood tide.

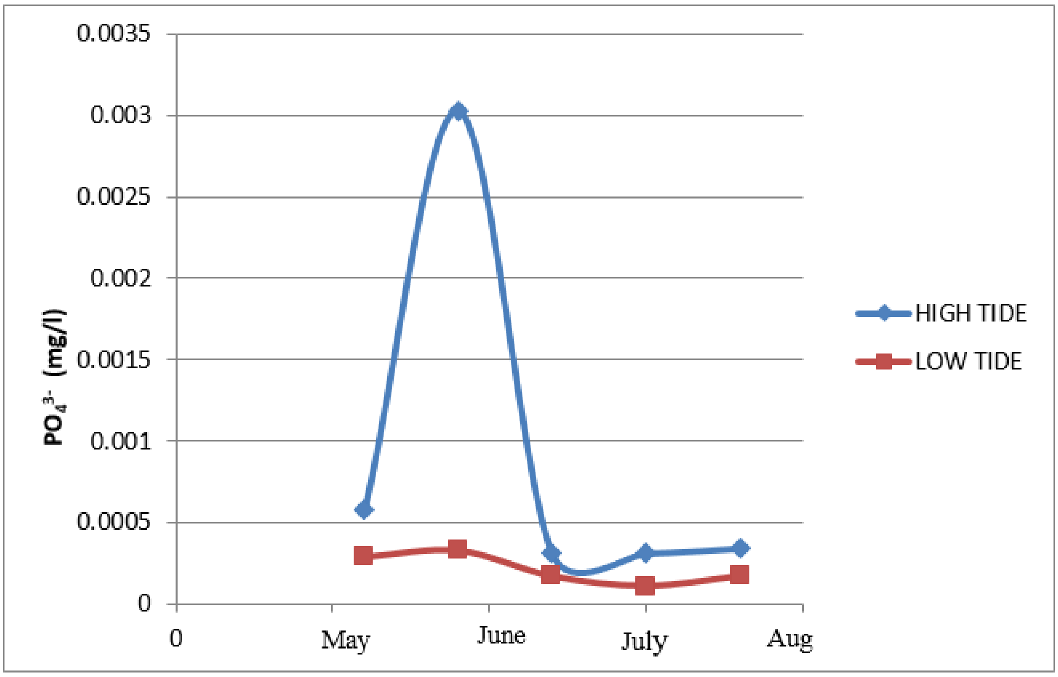

Fig. 3: Variation of phosphate concentration with tides in Great Kwa River Estuary in April, May, June, July & August, 2019

This increase maybe due to the intrusion of saline water while the decreased in value at ebb tide may be related to fresh water input. Parson et al; (1998) observed that the interaction between flood tide and sediment makes the estuary to have high concentration of phosphate even during ebb tide.

Nitrate

From fig. 4, the values of nitrate concentration ranged from 0.001-0. 0065 and 0.001-0.0082 mg/L respectively. In July and August, nitrate concentration was maximum (0.0082mg/L) at high tide

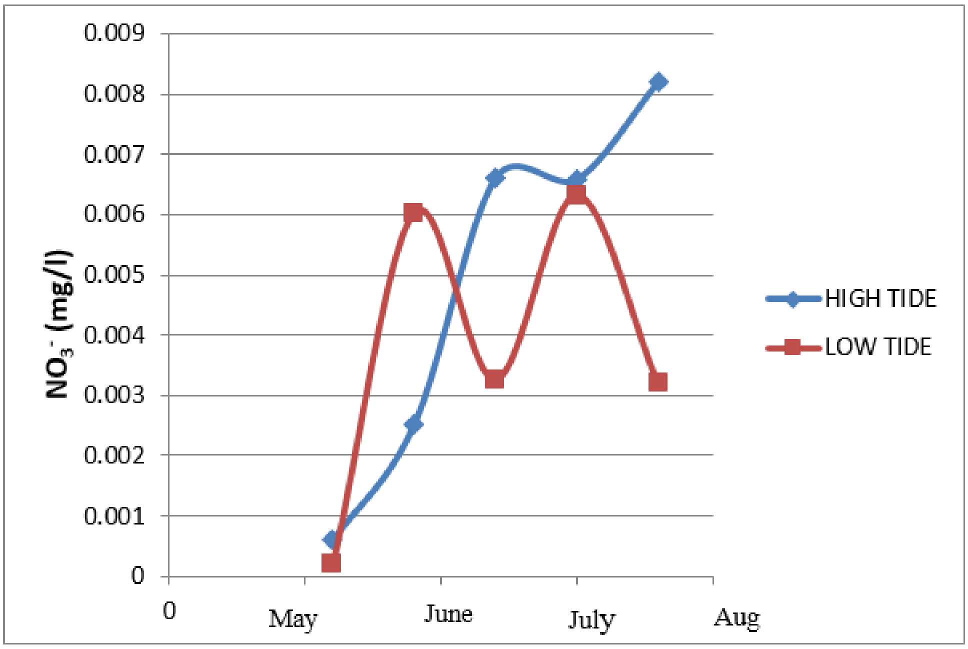

Fig. 4: Variation of nitrate concentration with tides in Great Kwa River Estuary in April, May, June, July and August, 2019

Nitrate levels were higher than the ammonium levels indicating that the nitrate resulted mainly from bacteria decomposition and oxidation of the freshly put organic matter in the estuary. Fatema, et al; 2015, are of the same view that the high concentration of nitrate during high tide may be due to agricultural land run off and nitrification in the sediments and decomposition of organic matter. In July, nitrate levels attained its maximum value of 0.007mg/L at low tides. Low value of nitrate at low tide is an indication of increased in nitrate through fresh water input of organic matter which increased concentration at flood tide may be attributed to dilution with nitrate poor sea water.

Nitrite

Fig. 5 shows the variation on the concentration of nitrite in relation to tides with values ranging from 0.00-0.001 and 0.001-0.0018mg/L respectively.

The concentration of nitrite remain at 0.00 throughout the low tide and increased to maximum (0.018mg/L) during the high tide this increased may be attributed to intrusion of sea water into the estuary. Duedal et al; 2001 observed at the sandy hook that the major source of nitrate is tidal activity.

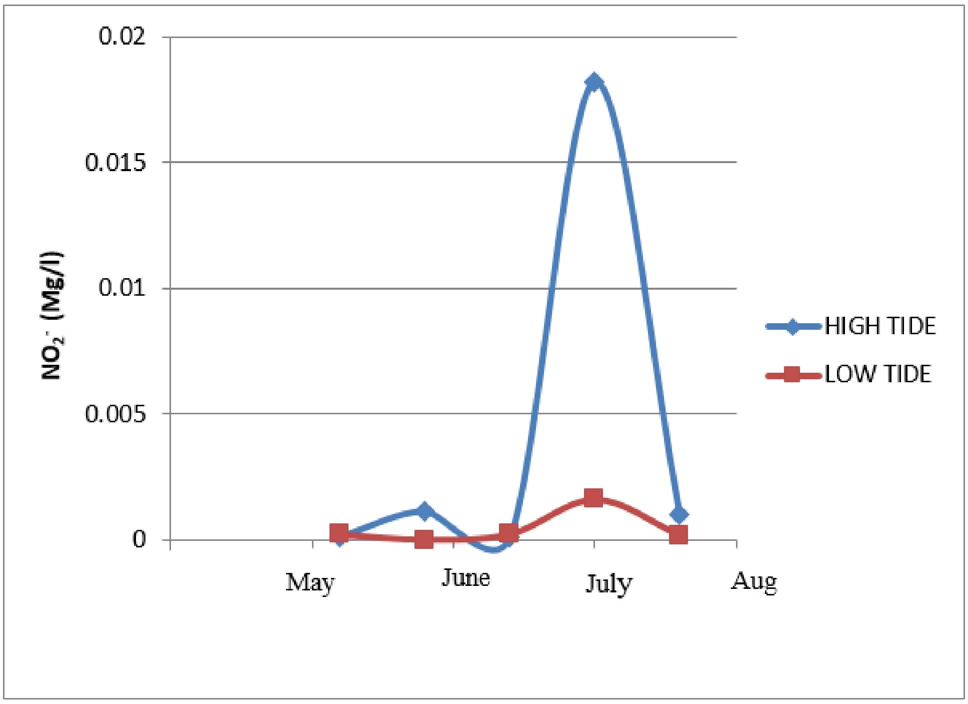

Fig. 5: Variation of nitrite concentration with tides in Great Kwa River Estuary ion April, may, June, July and August, 2019

Table 1: Result of Nutrients Measurement in Great Kwa River Estuary covering Low and High Tide in May, June, July, August and September 2019

NUTRIENTS	HIGH	LOW	MEAN	RANGE	STANDARD
	Tide	tide			Deviation
Ammonium	0.001	0.017	0.8155	1.38-0.458	4.021
Phosphate	0.001	0.03	0.256	0.027-.0.022	2.179
Nitrate	0.0052	0.001	3.211	0.61-0.611	1,740
Nitrite	0.001	0.018	1.0322	1.811-0.161	0.565

Turbidity

Variation of turbidity in relation to tide in May, June, July, August and September are shown in fig 6. With values ranging from 0-4-0.42 and 0.63-0.89 NTU repetitively.

In May, turbidity is high at the beginning of high tide. This may be attributed to the tidal motion which causes the mixing of fresh water and perhaps sea water leading to the resuspension of particles from the bottom.

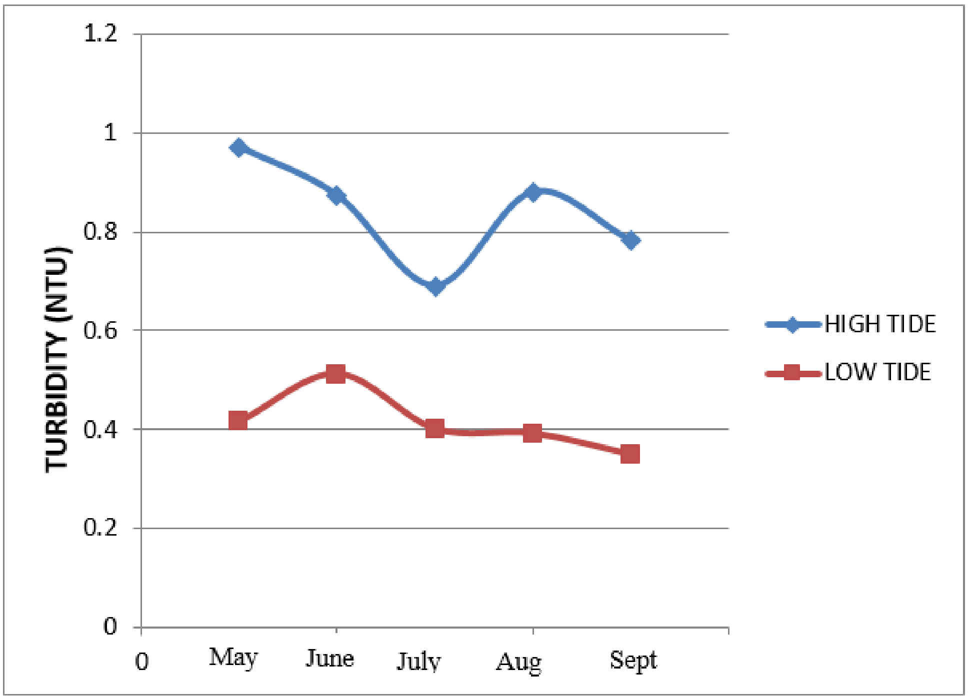

Fig. 6: Variation of turbidity worth tides in Great Kwa River Estuary in May, June, July, August and September, 2019

The tides induced re-suspension of particles. The riverine input also plays an important role in horizontal distribution of suspended sediments associated with input of turbid water from the Cross River estuary. Both river discharge and sea water intrusion are important sources of suspended sediments in the river. The river discharge being more important at low tide while the sea water intrusion was important at flood tide. Turbidity only increase during the high tide decreases during the low tide (as shown in fig.5) more so, the increase of turbidity during low tide is seasonal during raining season the estuary will be highly turbid due to river discharge and surface run off.

<u>Salinity</u>

Variation of salinity in relation to tides in May, June, July, August, and September are shown in fig. 7 with Values ranging from 0.00-0.001 and 0.0001-0.0002 ppm respectively. In May, June and August, the salinity increased during intrusion of seawater reaching its maximum during tidal change from low tide to high tide.

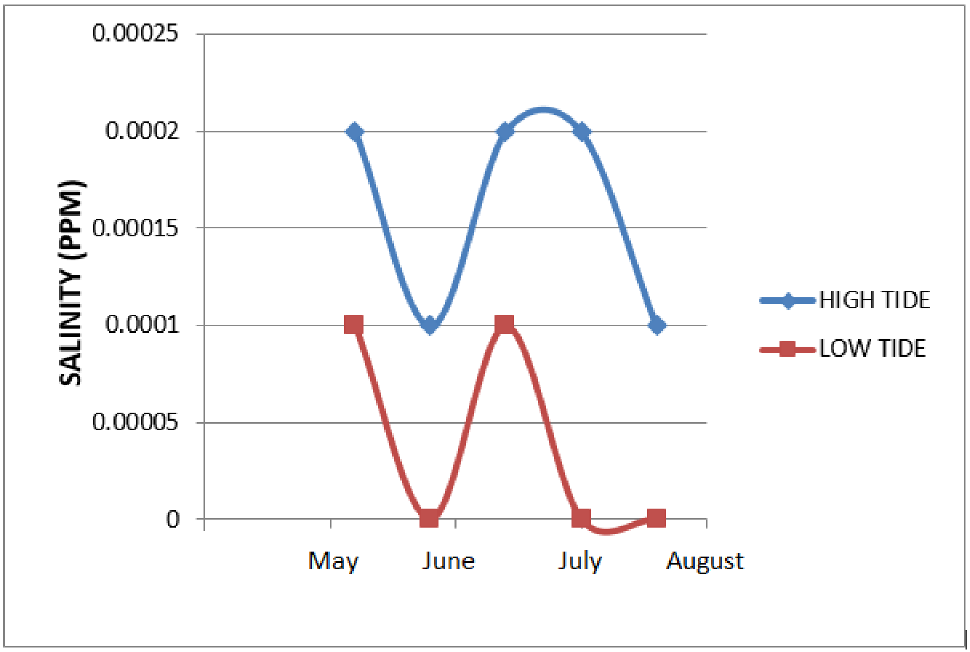

Fig. 7: Variation of Salinity with tides in Great Kwa River Estuary in May, June, July, August and September 2019.

This situation May be attributed to the dominant effect of fresh water discharge which must have pushed the head of the salty water intrusion out of the river. An increase in salinity occurred again during tidal change from low tide to high tide due to recession of fresh water discharge and increased tidal input of salt water. Hence, salt intrusion is determine by rive discharge, channel shape and tidal forcing (zhiming et al, 2010).

Table 2: Result of physicochemical parameters of Kwa River Estuary covering High Tide and Low tide in May, June, July August and September, 2019

PARAMETERS	HIGH Tide	LOW Tide	MEAN	RANGE	STANDARD Deviation
PH	7.0	8.0	7.815+1.230	1.50-0.001	1.230
Tempt (^{0}c)	29.9	28.0	71.85+5.744	0.02-57.9	5.744
Conductivity (µs/cm	0.0062	0.0059	3.91+1.213	29.01-0.56	1.213
Salinity (ppm)	0.002	0.001	0.144+0.013	0.00-0.01	0.013
Turbidity (NTU)	0.9	0.5	13.2+1.7834	16.2-28.1	1.7834
TDS (mg/L	15.2	35.9	7.128+1.513	3.149-1.471	1.573
TSS (mg/L)	0.0035	0.0038	1.360+0.127	0.30-3.228	0.127

KEY TDS=Total dissolve solid
TSS = total suspended solid

Hydrogen ion concentration (pH)

Variation of pH in relationship to tide in May, June, July, August and September are shown in fig. 8. with values ranges from 0.062-0.08 and 0.07-0.017 respectively.

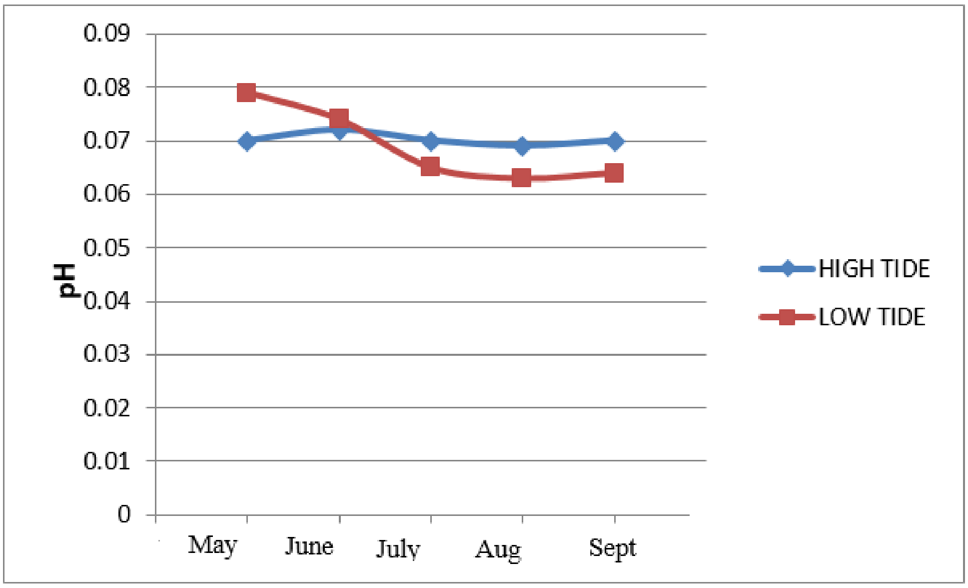

Fig. 8: Variation of hydrogen ion (pH) concentration with tide in Great Kwa River estuary in May, June, July, August and September, 2019

In May, pH was lowest during flood tide but maximum during low tide. The pattern of pH may be attributed to the combine effect of river discharge and input of materials from the mangrove swamps. The influence of sea water is low due to high fresh water discharge associated with proceeding rainy season. During low tide pH of river increases considerable due to the high pH of sea water entering the estuary. In August, pH decreased compared to the value in May. This may be attributed to input of acidic rain water into the estuary.

Temperature

Fig. 9 shown the variation of temperature in relation to tides in May, June, August and September with values range from 28-29.1 ºC and 28.2 ºC-29.9 ºC respectively. In September, The surface increased gradually and reached its maximum value of 29.9^{0}C during high tide.

The surface water temperature was related to solar irradiation cycle .In Columbia River estuary, the surface water temperature was closely related to solar irradiation cycle lara et al; (1990). The exposed mud flats receive the full complement of solar irradiation and heat up faster than the water. This heat is transferred to the water during diurnal inundation, the degree of homogeneity depending on the extent of mixing.

In August, temperature values decreased compared to that of September. Temperature is related to weather condition and temperature attained its maximum value during flood tide because it occurred in the afternoon (Lara et al 1990).

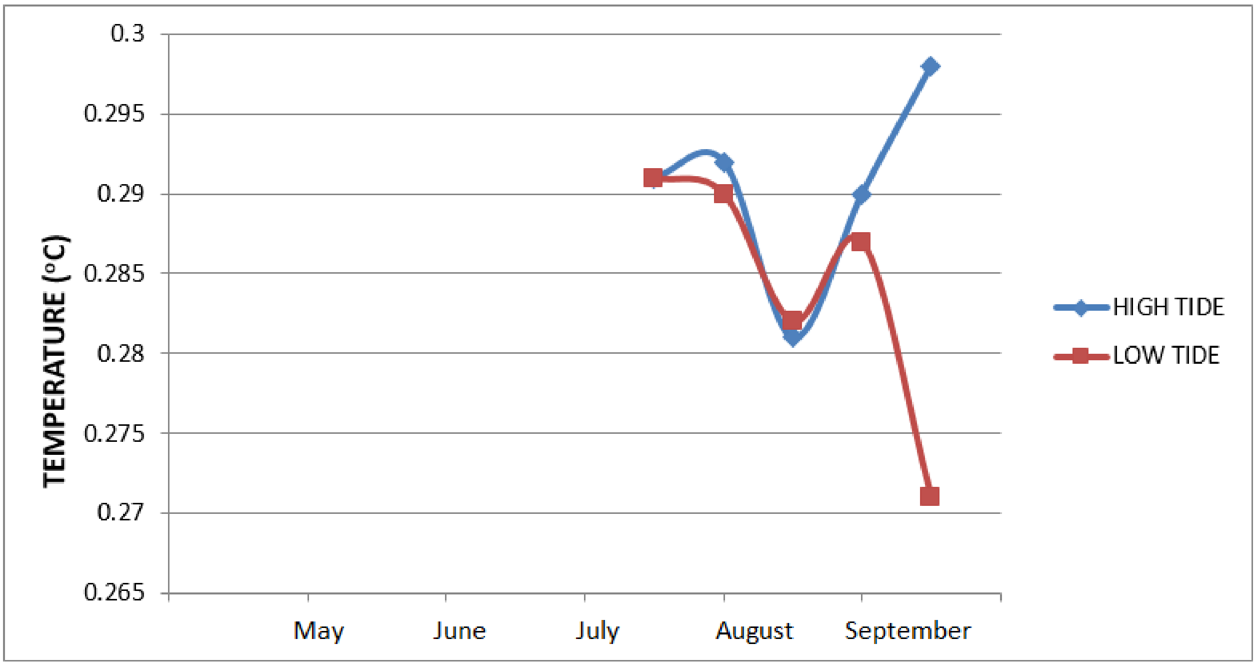

Fig. 9: Variation of temperature with tides in Great Kwa River estuary in May, June, July, August and September, 2019

Conductivity

Tidal variation of conductivity in May, June, July, August and September are shown in fig.9 with values ranged from 0.00-0.0059 and 0.01-0.0662µs/cm respectively. In August, conductivity increased during flood tide but decreased during low tide.

A rise was observed during tidal change from low tide to high tide. The increase in conductivity may be attributed to the intrusion of salt water and the amount of electrolytes in water. The decrease in conductivity during low tide may be attributed to fresh water intrusion which lowers the salinity of water and according to Eddy et al; 2005, "seasonal variation in conductivities is due to seasonal changes in fresh water discharge and dilution from rainfall. Higher conductivities encountered during high tides is a direct result of increased salt water intrusion.

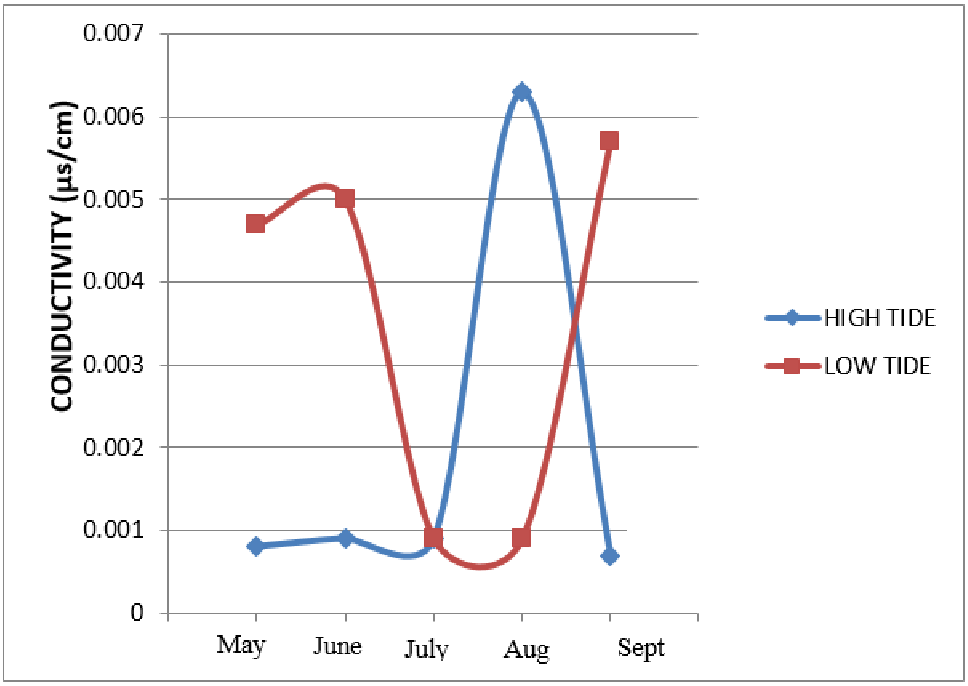

Fig. 10: Variation of conductivity with tides in Great Kwa River Estuary in May, June, August and September, 2019

<u>**Total Dissolved Solid (TDS)**</u>

Tidal variation of total dissolved solid in May, June, July, August and September are shown in fig 10. Values ranged from 0.005-035.9 and 0.00-015.2 respectively.

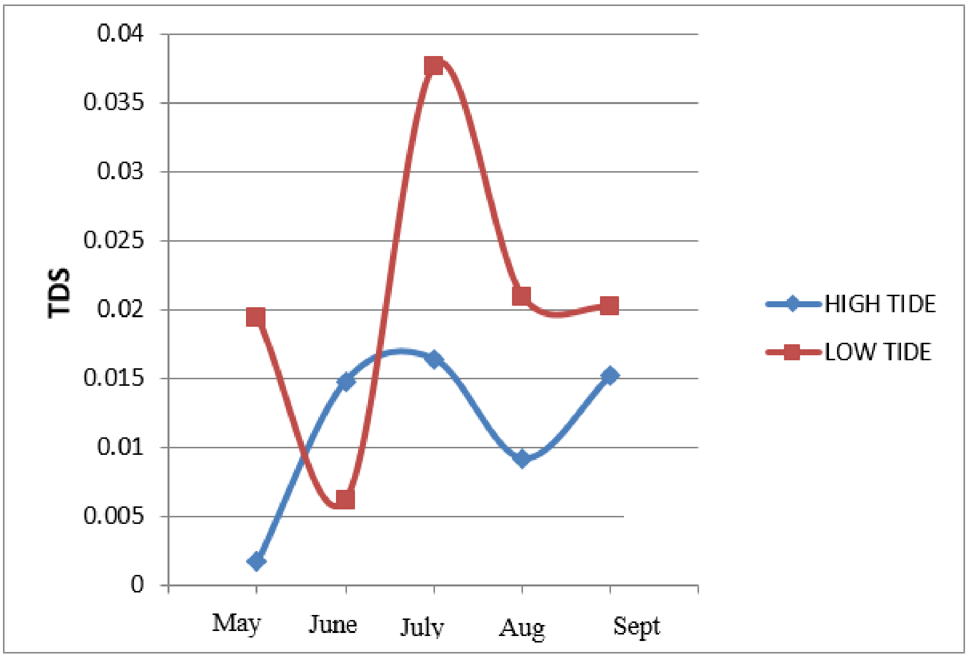

Fig. 11: Variation of total dissolved solid with tides in Great Kwa River Estuary in May, June, July, August and September, 2019

In July, total dissolved solid increased during intrusion of fresh water reaching its maximum during the low tide. This situation may be attributed to the dominant effect of fresh water discharge in Great Kwa River.

Total Suspended Solid (TSS)

Tidal variation of total suspended solid in May, June, July, August and September is shown in fig. 12. Values ranged from 0.005-0.0035 and 015.9-03.6 respectively.

In August, total suspended solid increased during intrusion of fresh water reaching its maximum value (0.0035) during tidal change from high tide to low tide which was due to high rainfall. During that period, the surface was run off gulley erosion and a lot suspended load were being discharged into the Great kwa River estuary but decreased during high tide because of the dominant effect of steady fresh water discharging into the estuary. And transport of nutrients from catchment enhances the nutrient concentration in sediment. (Trott and Alongi, 1999).

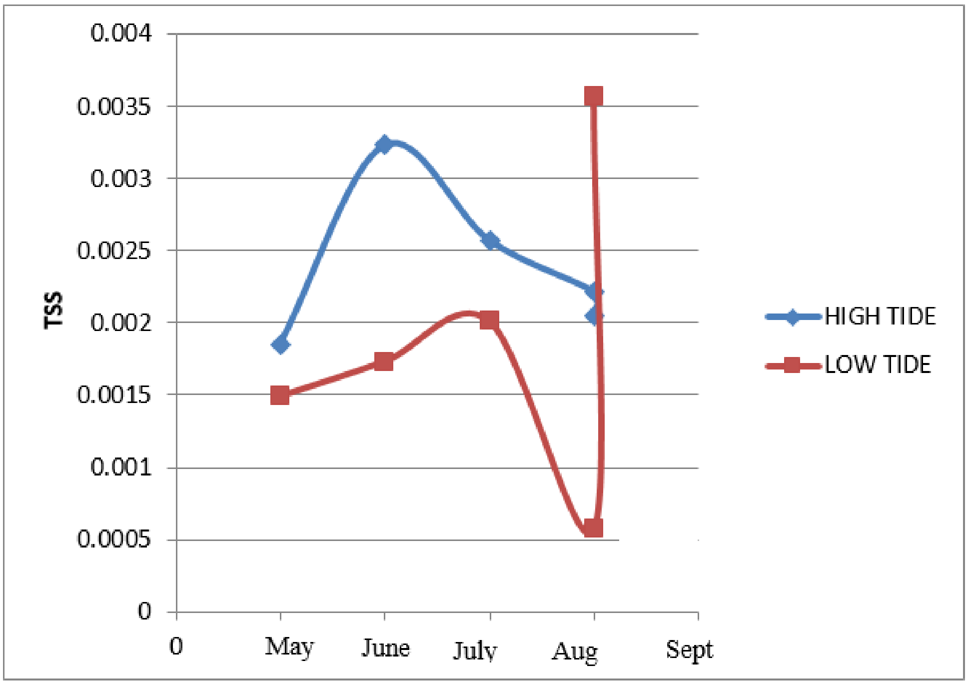

Fig. 12: Variation of total suspended solid with tides in Great Kwa River estuary in May, June, July, August and September, 2019

5. Conclusion

It is crystal clear that tides have a great influence on the distribution of nutrients and physico-chemical properties of the Great Kwa River estuary. The nutrients varied markedly with tidal oscillation. Variation was mainly attributed to re-suspension of sediment, displacement of interstitials water exchanges with intertidal flats and mangroves swamps caused by tidal activities. Other factors include sewage and industrial waste discharge, bacterial activities, removal of nutrient from solution into particulate material. This research has shown visible variations in all the parameters studied, such as nutrient concentration, physicochemical parameters suspended and dissolve matter, etc.

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