

THE DYNAMICS OF NITRATE CONCENTRATIONS IN WATER COLUMN AND SEDIMENTS IN A TROPICAL COASTAL RIVER (QUA IBO RIVER, NIGERIA) IN RELATION TO PRECIPITATION

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ABSTRACT

The dynamics of nitrate concentrations in water column and sediments in Qua Iboe River was investigated for two years at six stations to establish patterns of spatial and seasonal variations. Nitrate concentrations in the river was low ($0.00 - 53.00 \mu\text{gdm}^{-3}$), varied significantly between stations and increased downstream with discontinuities. Temporal patterns indicated the diluting effect of rainfall and concentration patterns varied with recurring trends. Nitrate concentrations exhibited strong seasonality regimes with higher levels during the dry season; correlated significantly with rainfall and gave higher coefficient of variability during the wet season indicating that rainfall is the most important hydrometeorological variable influencing its concentration in the river. Nitrate concentration peaks usually occurred at specific time during early rainy season (March/April) and peak concentration in sediment did not correspond with that in water column. The amplitude of intra-annual variability was lower in sediment than water column and demonstrated stochasticity (non-synchronous temporal variation) than nitrate in water column. Nitrate concentrations were higher in sediment than surface water and fluxes between overlying water and sediment were probably dominated by redox conditions.

KEYWORDS: Nitrate, River, Sediment, Precipitation, Variation.

INTRODUCTION

Nitrogen is known to be a critical component of living systems and its emissions from combustion processes have also been responsible for damaging impacts on the environment. Nutrient enrichment and soil acidification have now been identified as the major causes of these negative impacts particularly as a result of nitrogen losses to the environment (Dalton and Brand-Hardy, 2003). Excesses of ammonia have been known to cause streams and lakes to become acidic through the conversion of ammonia to nitrate and its subsequent leaching to aquatic systems including underground water. It is estimated that about 43% of total nitrogen deposited annually is in the form of nitrate and that the emission of nitrate is generally greater than that of NH_3 (NEGTAP, 2001). Nitrate loss from agricultural land drainage has therefore raised a lot of concern about the quality of drinking water and its detrimental effects on the aquatic environment especially through eutrophication. This is important considering the fact that about 80% of nitrate in aquatic systems is from agricultural land drainage (Pretty *et al.*, 2000) and nitrate pollution in aquatic systems is increasing though largely ignored particularly in the developing countries.

Nutrient composition in river water is known to depend on a wide variety of physical, chemical and biological features (Gibbs, 1970; Akpan, 1992, 1996, 2002). However, Gibbs (1970) identified three basic mechanisms controlling surface water chemistry and these include rainfall, the nature of the bedrock and the evaporation - crystallization process. The allochthonous sources of nutrients into aquatic systems include fertilizers from agricultural land drainage, animal wastes, atmospheric discharges, leachates from waste dump, domestic and industrial sewage, discharges from automobile exhausts, combustion processes and losses from mineralisation of soil organic matter (NAS, 1972, Emteryd *et al.*, 1999). However, Barbieri and Simona (2001) identified anthropogenic sources of nutrients as constituting 85%, industrial 10% and agricultural sources (5%). Welcomme (1985) noted that in most of the large tropical rivers, the ionic composition of water derives primarily from the rain and the rock or sediment over which the river flows, and secondarily from macrophytes and phytoplankton. The autochthonous

sources of nutrients in a river include release during decomposition of plant and animal remains and sediment - water exchanges, among others.

Nutrients in water bodies are lost from the water column to the sediments through a variety of ways including the dead remains of plants and animals particularly algae. Although nutrients may be released from the sediments, it is known that on balance, substances are sedimented than released. The reasons why nutrients are trapped in sediments are both physical and chemical. According to Marsden (1989) there are dense sediments at the bottom of a river where the turbulent mixing induced at the surface is negligible. Some of the nutrients which may be released into the interstitial water of the sediment during the mixing, have little chance of being mixed with the overlying water. Some of them may become locked up in the sediments in insoluble form as complexes with other substances. However, the surface sediment layers are usually not anaerobic because oxygen can diffuse and be mixed into them from the overlying water. The insoluble ferric and other metal complexes are known to form a crust which is generally coloured brown as compared to the dark/black anaerobic sediment underneath (Marsden, 1989).

Nitrate-nitrogen is very important in phytoplankton growth, abundance and productivity in waters and seems to be the critical nutrient in tropical waters (Henry *et al.*, 1984). There is paucity of information on the dynamics of nutrient concentrations in Qua Iboe River despite its importance as the major hydrographic feature in Akwa Ibom State (Nigeria) and its contribution to the fisheries potentials of the nation. The objective of this study was to determine nitrate concentration patterns both in the water column and in the sediments and to investigate the pattern of seasonal variations and fluxes.

MATERIALS AND METHODS

Study Area

Nutrient concentrations were measured both in the water column and in the sediments at six stations (Fig. 1) fortnightly. Water samples for the determination of nitrate concentrations in the water column were collected using clean 1 litre plastic containers. Triplicate samples were usually collected at each site within a station and three such sites

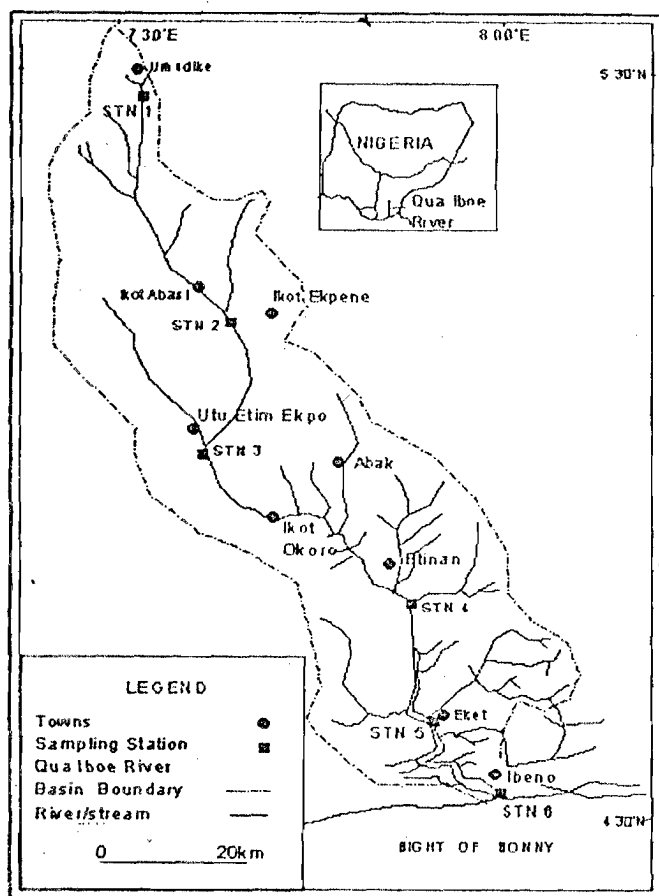


Fig. 1 Map of Qua Iboe River showing the sampling stations
Inset: Map of Nigeria showing the location of Qua Iboe River.

were usually chosen per station. Nutrient determinations were therefore made on composite samples:

Nitrate - nitrogen ($\text{NO}_3\text{-N}$) was determined by the Brucine-sulphanilic acid method (APHA, 1980). The reaction between brucine and strongly acidified nitrate solution yields a deep red colour which quickly changes to sulphur yellow. 2.00cm^3 sample was pipetted into a 50.0cm^3 beaker, and 1.00cm^3 of brucine-sulphanilic acid reagent added using a safety pipette. 10.00cm^3 of H_2SO_4 was measured into another 50cm^3 beaker, and the contents of the two samples were mixed by carefully adding the sample with brucine - sulphanilic acid reagent to the beaker containing acid. The reagents were then poured from one beaker to another for several times to ensure mixing. This was allowed to remain in the dark for 10 mins. After colour development 10.00cm^3 of distilled water was added to the sample and allowed to cool for 20 - 30mins. in the dark. A blank was also prepared with distilled water and all the reagents as above. The nitrate concentration was determined by measuring the absorbance at 410nm wavelength using a uv - visible spectrophotometer.

A standard curve was also prepared by diluting appropriate quantities of standard nitrate solution ($0.0 - 10\text{ml}^{-1}\text{N}$) prepared from 0.7218g of anhydrous KNO_3 in 1dm^3 of distilled water. Appropriate volumes of the standard nitrate were diluted to 100cm^3 with distilled water and the absorbance measured with 2cm^3 of each dilution.

Replicate sediment samples were collected using Erkman grab at the deeper portions of the river and an improvised corer driven into the sediment at the wadeable portions of the river. The concentration of nitrate in the sediments was determined using the methods described by Canfield *et al.* (1982) and Reddy (1983). Sediment samples

were sub-sampled and put in clean plastic containers. The sediment column depth was usually restricted to the upper 25cm^3 when using the corer and to the upper 35cm when the grab was used.

The nitrates were extracted from the sediments using acetic acid/sodium acetate buffer ($\text{pH} = 4.0$). The extraction involved transferring 5g wet sediment into a beaker and adding 30cm^3 of sodium acetate/acetic acid buffer. This was shaken on an electric bottle-shaker for 30 minutes and filtered using Whatman filter paper to remove the extract. The residue on the filter paper was washed twice with 10cm^3 aliquot extractant (buffer) and added to the extract and the total volume of extract adjusted to 50cm^3 . To determine the nitrate concentration in sediment, 2.00cm^3 aliquot of the extract was used (no dilution) using the brucine - sulphanilic acid method as described for the water sample (APHA, 1980).

Rainfall data were collected from meteorological stations close to the sampling stations. Water level was measured from lead sounding cable; water temperature from thermometer; pH with mobile meter (Kent 7010 model, Kent Inc, UK) and conductivity with mobile meter (DC Jenway model, Jenway Inc. Japan). Phosphate-phosphorus and dissolved oxygen (DO) were determined using methods described in APHA (1980), the former by the molybdate-antimony tartrate ascorbic acid method. 50cm^3 of clear sample was mixed with 1.00cm^3 of ascorbic acid reagent. The solution was allowed to stand for 10 - 30 mins for colour development and the absorbance measured with a Pye Unicam Sp 6350 visible spectrophotometer. Dissolved oxygen was determined using the modified Winkler method involving the fixation of DO in the field and titration using sodium thiosulphate with starch as indicator. Concentrations of these parameters were used only in correlation analysis and have been reported elsewhere (Akpan, 2004).

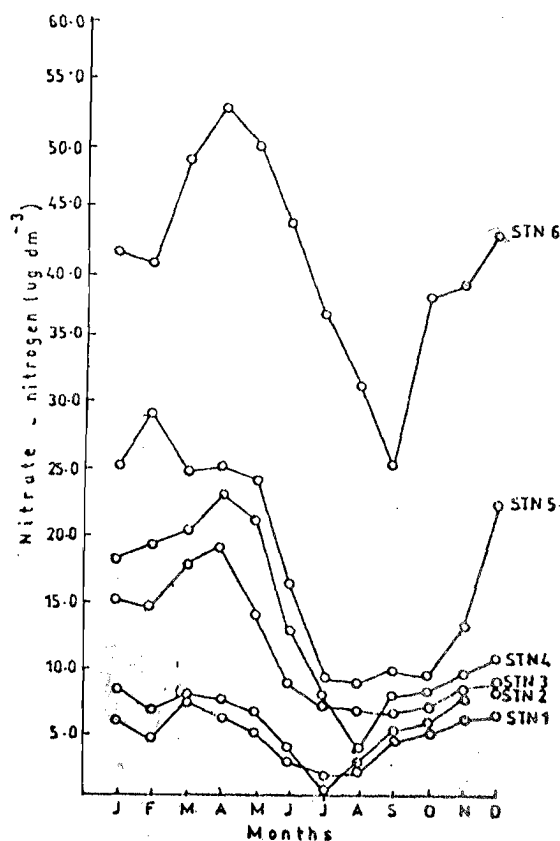


Fig. 2: Seasonal variation in nitrate - nitrogen in Qua Iboe River during the period Jan-Dec. 2000.

Duncan's Multiple Range Test was calculated to determine significant differences in the values of the nitrate at the different stations. Spearman's rank correlation coefficients were also calculated to test for any relationships between nitrate and selected physical and chemical parameters. In addition, t-test was carried out to determine seasonal differences while coefficient of variation was carried out to evaluate intra-seasonal variation.

RESULTS

Nitrate concentrations in water column.

The nitrate concentrations obtained for the six stations in the river were generally low (range of mean = 0.0 – 53.0 $\mu\text{g}\cdot\text{dm}^{-3}$); higher during the dry than the rainy season and exhibited some discontinuity by increasing from station 1 to 2 and decreasing at stations 3 and 4 (Table 1). As a result, mean monthly nitrate level was higher at station 2 than at stations 3 and 4. However, the lowest $\text{NO}_3\text{-N}$ level was recorded at station 1 (annual mean = $4.42 \pm 1.68\mu\text{g}\cdot\text{dm}^{-3}$) and the highest level was recorded at station 6 (annual mean = $41.00 \pm 17.91\mu\text{g}\cdot\text{dm}^{-3}$). The seasonal trends exhibited at the stations were the same with $\text{NO}_3\text{-N}$ levels increasing initially with early precipitation resulting in two peaks, first during February – May and a second peak in November – December

(Fig 2). The $\text{NO}_3\text{-N}$ levels generally decreased during the months with high flow (June – Sept.) with significant difference between stations. The seasonal variation in $\text{NO}_3\text{-N}$ concentrations for the two years (Jan 1990 – Dec 2000) (Fig 3 and 4) showed basically the same trend with higher values during the dry season and lower values during the wet season. The coefficient of variation was higher during the wet (45.60%) than dry season (21.73%) indicating greater variability during the former.

Duncan's Multiple Range Test gave significant difference between the stations at different probability levels. The t – test ($t = 1.88, df = 46, p > 0.05$) showed no significant difference between the two years in $\text{NO}_3\text{-N}$ concentrations. It gave significant negative correlation with rainfall ($r = -0.85, p < 0.001$), water level ($r = -0.63, p < 0.01$) and DO ($r = -0.52, p < 0.05$) and correlated positively with water temperature ($r = 0.50, p < 0.05$). The annual mean values and ranges of $\text{NO}_3\text{-N}$ at the six stations in the river is given in Table 1, while the correlation coefficient values are shown in Table 2.

Sediment Nitrate

The nitrate concentrations in the sediment varied between stations and increased from headwater (annual mean = $24.46 \pm 5.19\mu\text{g}\cdot\text{g}^{-1}$) to downstream ($88.50 \pm 14.24\mu\text{g}\cdot\text{g}^{-1}$). The range of sediment nitrate in the river was wide 15.00 –

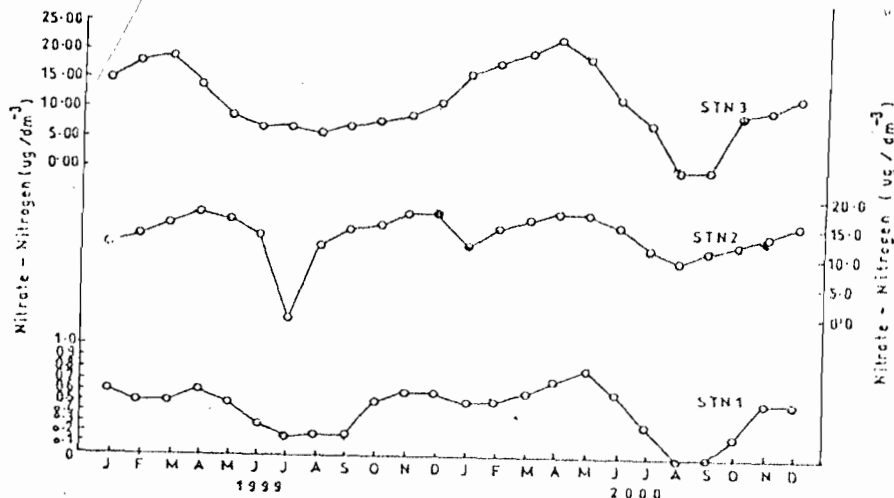


Fig. 3: Seasonal variation in nitrate - nitrogen ($\mu\text{g}\cdot\text{dm}^{-3}$) in stations 1-3 in Qua Iboe River during the two years (Jan.1999 - Dec. 2000)

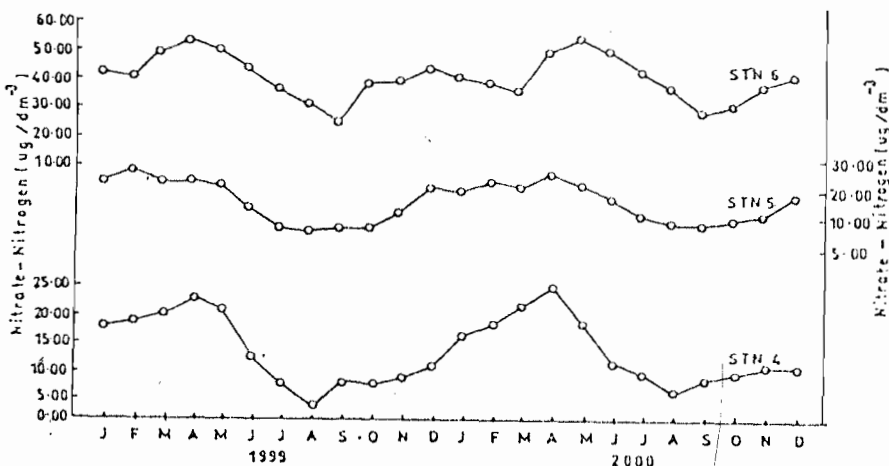


Fig. 4: Seasonal variation in nitrate - nitrogen ($\mu\text{g}\cdot\text{dm}^{-3}$) in stations 4-6 Qua Iboe River during the two years (Jan.1999 - Dec. 2000)

Table 1: Summary of the annual mean concentrations of nitrate-nitrogen both in the water column and in the sediments at the six stations in Qua Iboe River.

PARAMETERS/STRATA	STATIONS					
	1	2	3	4	5	6
Water Column ($\mu\text{g}\cdot\text{dm}^{-3}$)	4.42±1.68	14.00±4.79	10.83±4.55	13.50±6.37	17.83±7.93	41.00±17.91
Range	2.0 – 6.0	0.0 – 17.80	6.0 – 19.0	4.0 – 23.0	8.0 – 29.0	4.0 – 53.0
Sediments ($\mu\text{g}\cdot\text{gm}^{-1}$)	24.46±5.19	35.00±5.92	52.67±7.54	47.25±10.42	64.67±10.21	88.50±14.24
Range	15.00–32.00	24.0 – 39.0	37.0 – 64.0	34.0 – 68.0	49.0 – 77.0	76.0 – 110.0
Ratio	5.53	2.50	4.86	3.50	3.63	2.15
Ratio of N:P in Water column	2.53	3.43	1.46	1.32	1.18	1.20
Ratio of N: P in Sediment	1.40	0.90	1.37	1.00	1.18	1.38

Table 2: Correlation coefficient (r) values between nitrate and some physical/chemical parameters.

	Nitrate	Rainfall	Water level	Water Temp	DO	Conductivity
Nitrate						
Rainfall	-0.85***					
Water level	-0.63**	0.83***				
Water temperature	0.50*	0.53*	-0.08			
DO	-0.52*	0.58*	0.18	-0.62**		
Conductivity	0.09	-0.75***	0.76***		0.18	
PH	-0.15	0.60**	0.70***	0.46*	0.20	0.62**

* Level of significance: * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

$110\mu\text{g}\cdot\text{g}^{-1}$ and varied significantly between stations.

The seasonal variation in sediment nitrate for the six stations exhibited the same trend with high values recorded during the months of Jan. – March (to June in one instance). Maximum values were recorded in February (stations 3 and 4); March (station 6) April, (station 5) and May (stations 1 and 2). The maximum level for station 3 was recorded in June during the rains (Fig 5). Sediment nitrate decreased during the months with maximum precipitation (August – September) with lowest values recorded in August at stations 1,2,4, and 6 and in September at stations 3 and 5. Sediment nitrate exhibited some discontinuity with lower values being recorded at station 4 (annual mean = $47.25 \pm 10.42\mu\text{g}\cdot\text{g}^{-1}$) than at station 3 (annual mean = $52.67 \pm 7.54\mu\text{g}\cdot\text{g}^{-1}$). The sediment $\text{NO}_3\text{-N}$ concentrations increased again during the dry months November – December thereby giving a second peak.

Comparison of nitrate values both in the open water and in the sediments in the freshwater section (stations 1 – 4) indicated similar trends in variation although with slight differences. The amplitude of intra-annual variability was lower in nitrate concentrations than concentrations in water column and demonstrated stronger stochastically (non-synchronous temporal variation) than nitrate in water column. At the freshwater section of the river, nitrate concentration was found to be higher in the sediments than in the open water (Fig.6). In both strata, high nitrate levels were recorded during the dry months January – March and occasionally to June (station 3), with peaks within the period. The values decreased during the rainy season with lowest values at the peak of the rains. Coefficient of variation (CV) was higher during the wet (23.49%) than dry season (9.63%) in sediments nitrate.

The period of maximum nitrate concentration in the open water at the freshwater section of the river did not correspond with that in the sediments and did not appear to follow any definite trend. However, at stations 1 – 3, maximum values were recorded earlier in the open water (March – April) than in the sediments (May – June). Similarly, the period of

lowest concentration did not correspond and appeared to occur earlier in the open water (July – August) than in the sediments (August – September). The trend at station 4 was slightly different with highest values recorded in the sediments before the peaks in the open water.

Further downstream, the seasonal variation in nitrate concentration both in the open water and in the sediments were similar with high levels being recorded during periods with low flow and low concentrations during the rainy season. Differences occurred with respect to period of measured maximum and minimum nitrate concentrations and did not correspond at both the open water and in the sediments. At station 5, the highest value of nitrate in the open water was recorded in February while in the sediments, the highest value was recorded in April. Periods of measured minimum concentrations were July in the open water and September in the sediments. The trend at station 6 (estuary) was remarkably different with highest levels recorded in March in the sediments and April in the open water. Similarly, the lowest measured level was recorded in August in the sediment and September in the open water (Fig. 7). There was significant difference ($t = 8.46$, $df = 46$, $p < 0.01$) between the nitrate concentration in the open water and in the sediments. Duncan's Multiple Range Test gave significant differences ($p < 0.01$) in the sediment nitrate levels between the stations.

DISCUSSION

Nitrate – nitrogen levels in Qua Iboe River were generally low due probably to low tributary and allochthonous inputs from the drainage basin. The concentrations in the water column exhibited pronounced seasonality regime and increased with river order with discontinuities attributed to episodic events. The allochthonous sources include agricultural land drainage, animal wastes and leachates from waste dump sites which yield nitrate to the river system in intermittent pulses including those flushed from wetlands and flood plains. The contribution from atmospheric discharges

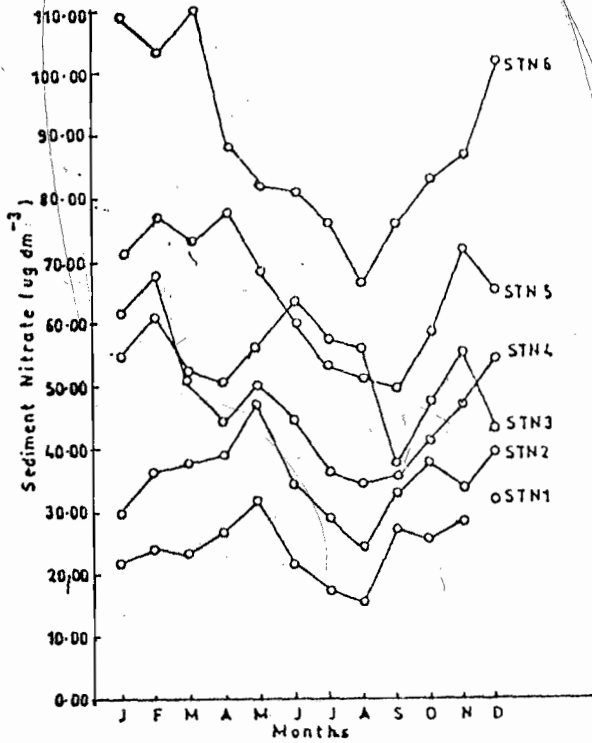


Fig. 5: Seasonal variation in sediment nitrate in Qua Iboe River during the study period Jan- Dec. 2000

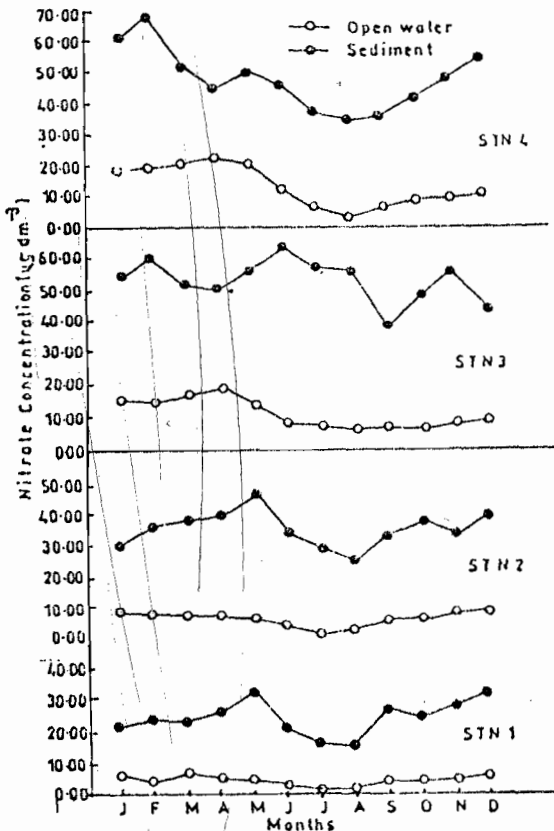


Fig. 6: Seasonal variation in nitrate concentration both in the open water (surface) and in the sediments in Qua Iboe River (stations 1- 4) during the study period Jun - Dec. 2000

could probably be important during the rainy season because of the tropical conditions that prevail in the drainage basin, the area being prone to regular lightening and thunderstorms. In addition, the contribution from agricultural land drainage may be significant than other sources due to the fact that a greater portion of the watershed area is used primarily for agricultural purposes and therefore receive agricultural land drainage from highly fertilised farmlands. Owens (1970) and Holden and Armstrong (1980) also reported that a greater proportion of the NO_3-N in rivers was due to agricultural land drainage. The increase observed during early rains is attributed to surface runoff and atmospheric discharges while the decrease observed during periods of high flow is attributed to precipitation resulting in increased discharge and net dilution. Evaporation - crystallization processes probably account for the increase in nitrate concentration recorded during periods of low flow (Gibbs, 1970; Welcomme, 1985).

It is highly probable that the nitrate concentrations in the river were influenced by hydrometeorological variables, evaporation - crystallization processes and open water - sediment exchange. However, according to Vitousek (1977) and Feth (1966), nitrate concentrations in stream water are mediated primarily by biological factors in the soil and plant community and such processes could also operate within the river system.

NAS (1972) listed different sources of nitrate in water bodies to include fertilizer, animal wastes, atmospheric fall-out, leachates from waste dumps, nitric oxide and nitrite discharges from automobile exhausts, other combustion processes and losses from natural sources such as mineralisation of soil organic matter. Since all these processes operate within the Qua Iboe River drainage basin, it is highly probable that they could have contributed nitrates to the river system. The significant difference observed between some of the stations in NO_3-N concentration is an indication of spatial differences in contribution of this nutrient to the stations. No significant difference was recorded between the two years showing that the variation in NO_3-N followed basically the same pattern with recurring trends. The significant negative correlation between NO_3-N and rainfall, water level and DO is an indication that increase in these parameters resulted in decrease in NO_3-N . The positive relationship with water temperature is an indication that increase in this parameter was followed by increase in NO_3-N probably through accelerating nitrate uptake decomposition processes and sediment releases (Cerco, 1989).

The following levels of NO_3-N have been reported for Nigerian waters: $0.1 - 0.44mg l^{-1}$ for River Sokoto (Holden and Green, 1960); $0.02 - 0.22mg l^{-1}$ for some Ibadan freshwater (Egborge and Sagay, 1979); $0.12 - 0.97mg l^{-1}$ in some south-eastern Nigerian waters (Nwadiaro *et al.*, 1982); $0.30mg l^{-1}$ for Cross River (Moses, 1979); $20-373\mu g l^{-1}$ for River Oshun (Egborge, 1971); $0.07mg l^{-1}$ for River Swashi and $0.24mg l^{-1}$ for River Kpan (Imevbore, 1970); $0.01mg l^{-1}$ for Wikki Warm springs (Egborge and Fagade, 1979); $31.49\mu g l^{-1}$ for Delimi River (Anadu and Akpan, 1986); $3.2mg l^{-1}$ for Nworie stream (King and Ekeh, 1990); $0.05mg l^{-1}$ for Ohoo and $0.05mg l^{-1}$ for Orunro rivers (Ogunkoya and Adejuwon, 1990). The level of NO_3-N in Qua Iboe River: $0.00 - 53.00mg l^{-1}$ with mean range of $4.42 - 41.00\mu g dm^{-3}$ is comparable to those of other Nigerian waters. However, it is less than the values for rivers Oshun, Owena, Ohoo and Orunro. The high level of precipitation in the Qua Iboe River drainage basin followed by dilution could partly be responsible for the low value in Qua Iboe river. The seasonality regime in Qua Iboe River is also in consonance with the results of Imevbore (1970) for River Niger, Anadu and Akpan, (1986) for river Delimi; King and Ekeh (1990) for Nworie stream; Ogunkoya and Adejuwon (1990) for Rivers Owena, Ohoo and Orunro where increases were recorded in

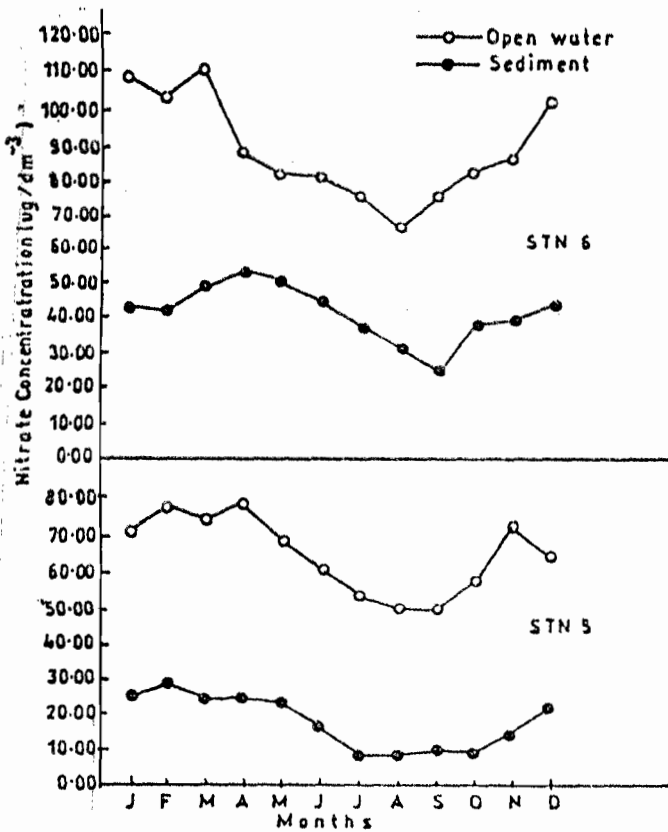


Fig. 7 : Nitrate variation both in the open water and in the sediments in Qua Iboe River estuary during the study period Jan – Dec. 2000

the dry season in $\text{NO}_3\text{-N}$ levels. However, the seasonality regime in $\text{NO}_3\text{-N}$ contrasts with the results of Egborge (1971) for River Oshun (Nigeria); and Sinada and Karim (1984) for the Blue and White Nile (Sudan) and Jimoh (2003) for Tunga – Kawo (Nigeria) where higher concentrations were recorded during the wet season.

Sediment nitrates increased with increasing load of river sediment which on its part increased with river order. Such elevated levels were attributed to increased accumulation of nitrates in the mud through loss from open water and sedimentation of seston. It is known that nitrate is lost from the open water to the sediments through seston that rain down from the open water and accumulate in the sediments (Wetzel, 1977). Cerco (1989) reported that movement of NO_3^- was from the water to the sediments in all observations and that uptake of nitrate was enhanced by high temperature and by low DO, part of which probably becomes refractory and bound up in the sediments. Period of maximum nitrate concentration in the open water did not correspond with that in the sediments probably due to differences in sources, utilisation and sediment uptake. In the freshwater section, maximum nitrate concentration in the water column occurred before the peak in the sediments because nitrate first becomes available to the open water before it is lost to the sediments through the death of planktonic organisms, aquatic macrophytes, and other aquatic life. Wetzel (1977) noted that most of the nitrates in the sediments are considered refractory and therefore the sediments do not contribute appreciable amount of nitrates to the open water by nitrification except during periods of circulation and in the well oxidized superficial layer.

At the estuary, however, the period of maximum nitrate concentration in the open water occurred (in May) well after the peak in the sediments (in March), this being attributed to difference in sources of the nutrient. It is highly probable

that the peak level in the sediments in March was caused by increased enrichment of the sediments by seston following a November – February period of increased phytoplankton bloom and macrophyte production (Akpan, 1992). Sediment nitrate concentration was higher than in the open water probably because the sediment acts as a sink for the nutrient (Cerco, 1989).

Sediment – open water exchanges is partly responsible for the fluxes in nitrate concentration in the Qua Iboe river system, which in turn is influenced by certain physical and chemical variables. Cerco (1989) noted that movement of nitrate was from the water to the sediments in all observations and that nitrate uptake by sediment was enhanced by high temperature and low DO which he attributed to increased denitrification as DO becomes deficient. He further proposed that NO_3^- uptake under anoxic conditions compared to uptake under a water column saturated with DO. The enhancement of NO_3^- uptake under anoxic conditions is known to be affected by several system characteristics such as low rate of NO_3^- reduction relative to that of DO, availability of sufficient NO_3^- in the water column and rapid diffusion of NO_3^- through the sediment. The movement of NO_3^- from water column into sediments accounts for the higher concentration in the sediments than in the water column and is probably enhanced by the high temperatures characteristics of this tropical area. The nitrate concentrations recorded in Qua Iboe were within the levels reported for Nigerian waters and also within the limits reported for unpolluted water bodies indicating that the river is unpolluted with respect to nitrate.

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