

DIURNAL VARIATIONS OF CERTAIN CHEMICAL CHARACTERISTICS IN QUA IBOE RIVER IN SOUTH EASTERN NIGERIA.

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ABSTRACT

The diurnal variations in certain physico-chemical characteristics in Qua Iboe River (Nigeria) was investigated between Feb. – Dec. 2000 at three stations. Measurements were made for pH, conductivity, free CO₂, dissolved oxygen, total alkalinity and salinity. The diel pattern of pH changes showed lower levels in the mornings and night and higher levels during the day. Conductivity did not show any particular diel variation and diel range varied within narrow limits except at the estuary. The pattern of diel variation in DO was similar to that of pH with minimum levels recorded during early morning hours (4.00 – 8.00am). Seasonal pattern in DO was higher at surface than bottom which exhibited narrow differences. Free CO₂ exhibited wide variation over diel periods with minimum levels during day light hours. Total alkalinity exhibited narrow variation over diel periods and bottom levels were higher than surface. The pattern of diel variation in salinity was more remarkable than other parameters particularly at the estuary and also higher at the bottom than surface due to tidal regime and salt intrusion. Diurnal changes in these parameters are attributed to influence of precipitation, evapo-crystallisation process, photosynthetic activity and episodic events.

KEYWORDS: Diel variation, chemical parameters, river.

INTRODUCTION

Measurement of the chemical characteristics of a water body is necessary in order to determine the water quality and identify any deterioration in water quality or the potential for such deterioration. The chemical condition in a lotic ecosystem are usually variable especially in rivers that receive numerous tributaries and with fluctuating hydroregime. Adebisi (1981) considered a knowledge of the physico-chemical conditions of a water body invaluable in determining its productivity and other characteristics. Such knowledge is also important in determining the state of pollution and the influence of these parameters on the distribution of flora and fauna. For example, Forsyth and McColl (1975) noted that density and diversity of flora and fauna depend on the chemical regime of the water. In addition, physico-chemical factors are known to influence the vertical and horizontal movement of organism their distribution and feeding regime (Adeniji, 1975).

Knowledge of the physico-chemical characteristics of water body contributes significantly to fisheries management as any potential damage to fish populations such as low oxygen levels, toxic blooms or anthropogenic pollution can be identified (Henderson, 1977). The fertility of water is said to be related to its chemical properties and according to Imevbore (1970), an understanding of the water chemistry serves as a basis for considering the richness or otherwise of a water body in terms of biological production.

Diurnal studies on lotic ecosystems in Nigeria are extremely scarce and no information is available on the numerous streams and rivers in southeastern Nigeria. However, available information is on lentic systems such as lakes, ponds and reservoirs. Studies of diurnal variation in Nigerian lentic systems include those of Khan *et al.*, (1983) on Jos Plateau water reservoir; Adeniji (1978) on Kainji Lake; Egborge (1979) on Lake Asejire and Hare and Carter (1984) on Opi Lake.

In their diurnal studies, Khan *et al.*, (1983) reported diurnal changes in dissolved oxygen (DO) content as distinct with the water surface being either saturated or super-saturated from 8am to 12 noon in February and from 12 noon to 4pm in April. They also obtained DO super-saturation of 115 – 135% in July throughout the diel cycle. Variations in free CO₂ were more pronounced in July than in February and April.

Concentrations of total alkalinity (due mainly to carbonates) varied between 15 – 16.5mg/l in February with minimum values observed between 12 noon to 4pm. The alkalinity values increased with the onset of dusk with maximum value being recorded at 4am. Total alkalinity values increased in April (25 – 32mg/l). Narrow fluctuations were recorded for pH and chloride. Hare and Carter (1984) reported minimum surface DO concentrations in the late evenings. Surface oxygen concentrations were lower in the harmattan and mid rainy season than at other times of the year.

For pH, they observed no diurnal variation during the rainy season and early harmattan, the pH remaining constant at 6.0, but this varied during the dry season increasing to 6.5. Higher alkalinities were recorded in the rainy season (Aug. – Nov.) than in the dry season and bottom alkalinities were higher than that of the surface waters. They observed that higher alkalinities were usually coincident with low levels of dissolved oxygen.

Egborge (1979) studied the diurnal changes in some physico-chemical factors of Lake Asejire and reported diurnal variations in temperature, density, DO and pH but the total alkalinity and conductivity of the lake waters did not show any such variation. In addition, the diurnal changes affected only the euphotic zone.

The objective of the study was to determine the patterns of diurnal variations in some chemical parameters in Qua Iboe River because of the influence of episodic events such as surface runoff, agricultural land drainage and sundry effluent discharges.

MATERIALS AND METHODS

Study Area

Six sampling stations were selected for the study along the river and were as equidistant as possible to reflect differences in geomorphological attributes. Some of the stations drain watersheds with dissimilar geology and vegetation types. Although they are influenced by similar climatic regimes, they also drain terrain with dissimilar topographic relief. The stations studied therefore differed in specific physical characteristics such as hydrology, width, depth and riparian vegetation (Akpan, 1992). The stations included Umudike (Station 1), Ikot Ekpene (Station 2), Ndiya (Station 4), and

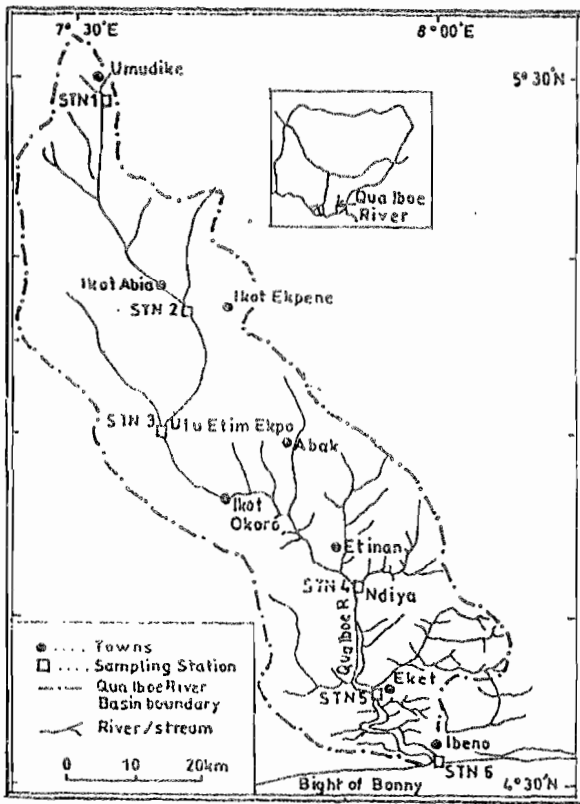


Fig. 1: Qua Iboe River showing stations
 Insert: Nigeria showing the location of Qua Iboe River

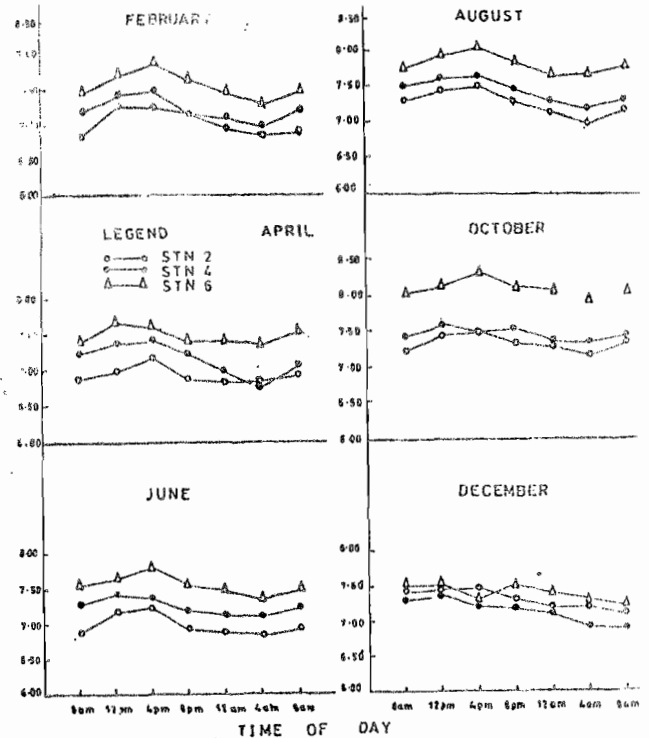


Fig. 2: Diurnal variation in pH in Qua Iboe River during the period Feb - Dec 2000

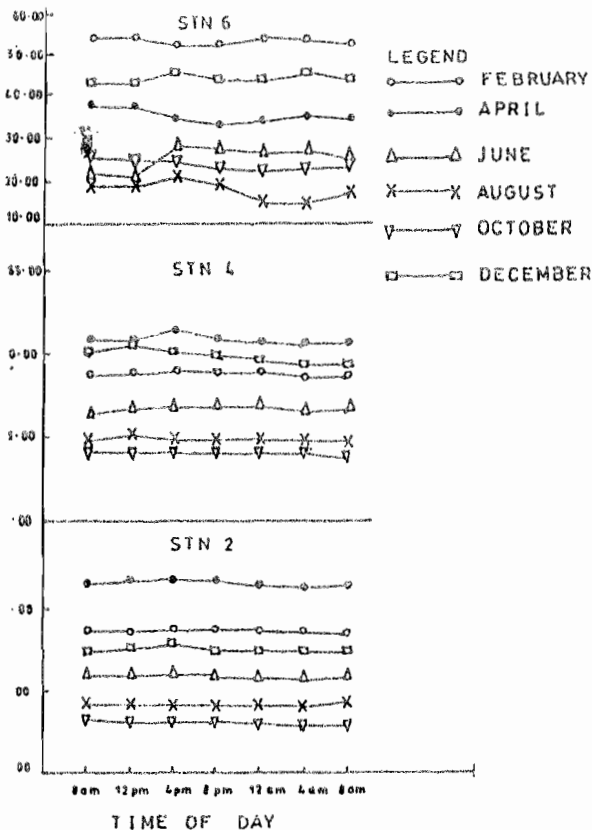


Fig. 3: Diurnal variation in conductivity ($usc m^{-1}$) in Qua Iboe River during the period Feb - Dec. 2000

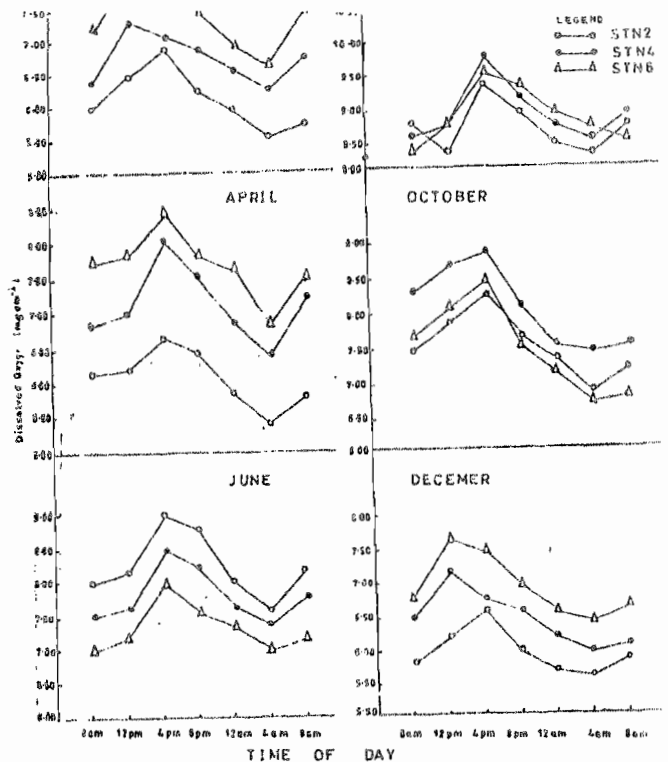


Fig. 4: Diurnal variation in Dissolved Oxygen ($mg dm^{-3}$) in Qua Iboe River during the period Feb. - Dec. 2000

Ibano (Station 6) (Fig. 1) and analysis was done in alternate months.

The diurnal variations were conducted between Feb. - Dec. 2000 on some chemical parameters which did not require electricity but using titrimetric methods. These measurements were carried out bimonthly at three stations (stations 2, 4 and 6) and six sampling occasions were carried out for each station throughout the period. The measurements were carried out at four hourly intervals beginning at 8.00am in the morning and terminating at 8.00am of the following day giving seven sampling periods per each sampling day. Measurements were carried out at both surface and bottom waters. pH was measured in situ using mobile pH meter (orning pH meter) which had been calibrated using a buffer solution of pH = 4.0. Conductivity was also measured in situ using a mobile battery-operated electronic conductivity metre (model DC Jenway). The measurements were done by dipping the probes into the water and the values read off digitally.

Dissolved Oxygen (DO) was measured by the modified Winkler method using the Alsterberg azide method of Brown *et al.*, (1970) and APHA (1980). Surface and bottom water samples for the measurement were collected in 250cm³ amber-coloured bottles without rapping air and fixed immediately after collection. Sodium azide was used to remove nitrate interference. The samples were then titrated using 0.02N solution of sodium thiosulphate with starch as indicator. Water sample for free (dissolved) carbon dioxide was collected without trapping air by means of rubber tubing which discharged gently at the bottom of 100cm³ graduated cylinder. This was titrated drop wise with NaOH using 1cm³ pipette. Water sample for total alkalinity were collected with 1 litre clean plastic containers and titrated with a standard solution of H₂SO₄ to the successive bicarbonate and carbonic acid end points (APHA, 1980). Salinity was determined by titration against AgNO₃ using chromate indicator (APHA, 1980). All the analyses were usually carried out immediately after collection within the four hour period. Analysis of variance (ANOVA) was carried out to test for significant differences between the stations and the diel periods in the levels of the chemical parameters.

RESULTS

The diel pattern of pH changes showed lower pH levels in the mornings and night and higher levels during the day indicating that pH of the water generally increased during mid-day (Fig. 2). The diel variation in pH was similar to that of dissolved oxygen and the variation in pH was also similar at all the stations with no significant difference between the diel periods. The diel range of pH of surface water during morning hours (8am) at station 2 was 6.80 - 7.40 during the months measured. Afternoon pH values were generally higher (diel range = 7.20 - 7.14 at 4pm) but with narrow pH range. Therefore, diel ranges in pH were wide between morning and evening (08 - 1600 hours) and became narrow during the night. The pH also varied between season, and some stations appeared acidic or basic within specific months. For example, station 2 was acidic during the dry months (Feb. mean = 6.96 ± 0.20; April mean = 6.90 ± 0.18) and December (pH = 7.38 ± 0.22). The same station varied between slightly neutral and slightly basic during the months of June, August and October. The diel pattern of pH changes of bottom water did not exactly follow that of surface water and remained nearly constant during morning (0800 hours) and evening (1600 hours) at the different stations.

Conductivity did not show any particular diel variation at any of the stations. However, only slight increases were usually observed during mid-day, except at station 6 where such increases were remarkable. The diel range in conductivity varied per station per month and usually with very

narrow limits. For example, the diel variation for station 2 in February was 28.50µScm⁻¹ at 0800 hours to 2895µScm⁻¹ at 1600 hours. For station 4 within the same month and period, the diel range was from 58.40µScm⁻¹ to 59.00µScm⁻¹. However, the diel range for station 6 was appreciably wide, from 8480.75µScm⁻¹ at 0.400 hours to 8550.93µScm⁻¹ at 1600 hours (Fig. 3). Significant differences existed between the freshwater stations (stations 2 and 4) and estuarine reach (station 6) ($F = 6.85$, $p < 0.05$) in conductivity levels. No significant difference was observed between the diel periods at stations 2 and 4 except at station 6 between low and high tide periods. The pattern of diel variation in DO was similar to that of pH where minimum levels were recorded in the early mornings (4.00am) at the surface and this increased with the rising of the sun. Maximum DO levels were usually recorded between 12 - 4pm during the dry months and this sometimes shifted to 12.00pm during the rainy season especially when there was cloud cover after mid-day. The seasonal pattern of DO variation was highest at the surface water and varied from the freshwater stations (2 and 4) to the estuarine reach of the river. At the freshwater segment, surface oxygen concentration usually exhibit one peak period of concentration during the peak of the rains (June - September). For station 6, peak period of concentration was observed during the dry season (Fig. 4).

Bottom DO concentration exhibited narrower differences between seasons than concentrations recorded at the surface. At stations 2 and 4, DO concentrations at the bottom were higher during the wet season than during the dry season. However, at the estuary, higher DO concentrations at the bottom were obtained during the wet season (4.20mg.dm⁻³) than during the dry months (2.60mg.dm⁻³).

Free CO₂ exhibited wide variation over diel periods. Minimum free CO₂ concentrations were recorded during daylight hours, while maximum levels were generally recorded during the night hours. Concentrations of free CO₂ varied significantly ($p < 0.01$) between stations but generally lower at station 2. Seasonal variation of free CO₂ revealed high values during the dry months with peak concentration in April. Low values were generally recorded during the wet months, with the least value at the peak of the rains (August for stations 2 and 6 and October for station 6) (Fig 5). There were no significant differences between the diel periods. Bottom free CO₂ concentration showed narrow variation over diel periods and were generally lower than surface values, except at station 2 where not much difference was recorded. Values of free CO₂ at the estuary were lower than at station 4 especially during the dry season.

Concentrations of total alkalinity showed narrow diel variation as compared to free CO₂. Minimum levels were recorded during the day while maximum levels were recorded during night hours but not significantly different. Alkalinities were generally higher during dry months (December and February) and were generally lower during the wet months (June, August and October). Maximum values were recorded during the early rains in April (Fig. 6). Bottom alkalinities were frequently higher than surface values especially at stations 4 and 6. Bottom concentrations at station 2 were nearly the same as surface values except during the sampling day in April when some differences were recorded with 24.40 and 23.20mg.dm⁻³ CaCO₃ for surface and bottom respectively at 4.00pm. However, no definite trend was observed as lower alkalinity was sometimes recorded at the bottom than at the surface at the three stations.

Salinity values exhibited the most remarkable pattern of diel variation particularly at the estuary than all the other parameters. Salinity values were generally higher during high tide than low tide. At station 2 which is non-tidal, the diel variation was extremely low with no significant difference observed between the hours. The seasonal trend at all stations revealed high levels in February, while values in

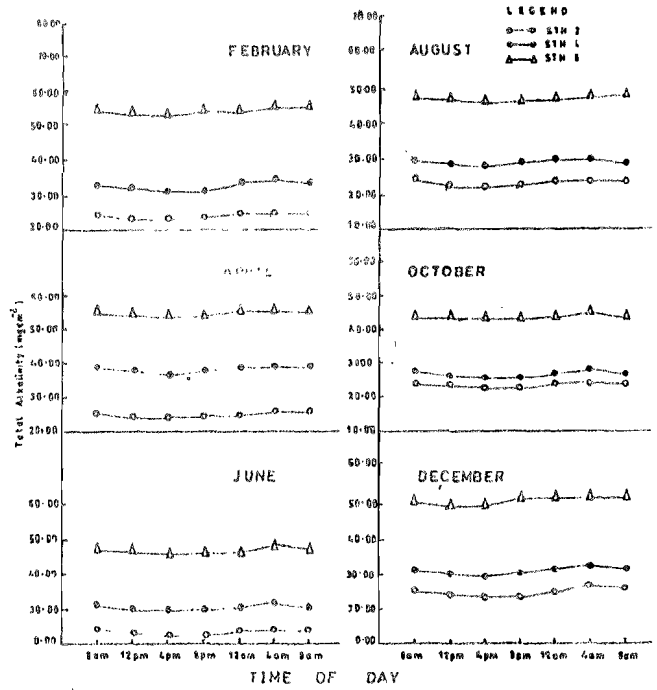
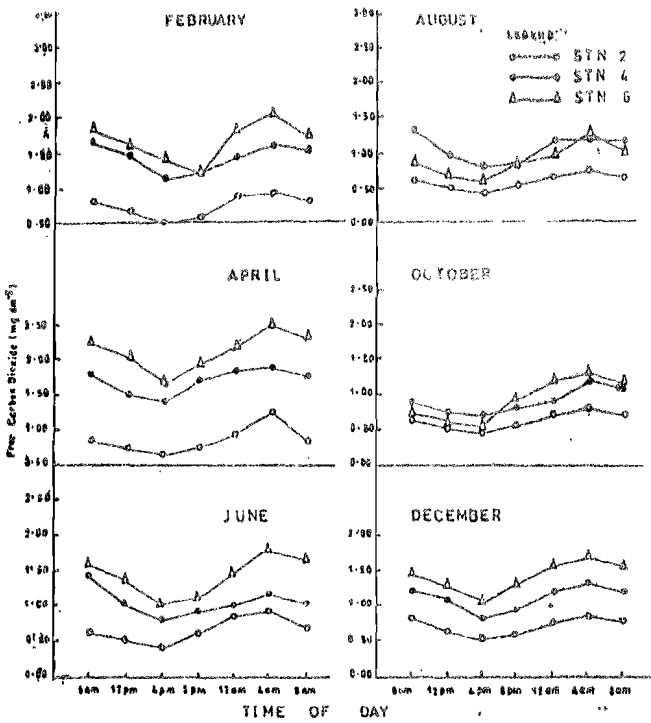


Fig. 5: Diurnal variation in Free Carbon Dioxide (mgdm⁻³) in Qua Iboe River during the period Feb. - Dec. 2000

Fig. 5: Diurnal variation in Total Alkalinity (mgdm⁻³ CaO₃) in Qua Iboe River during the period Feb. - Dec. 2000

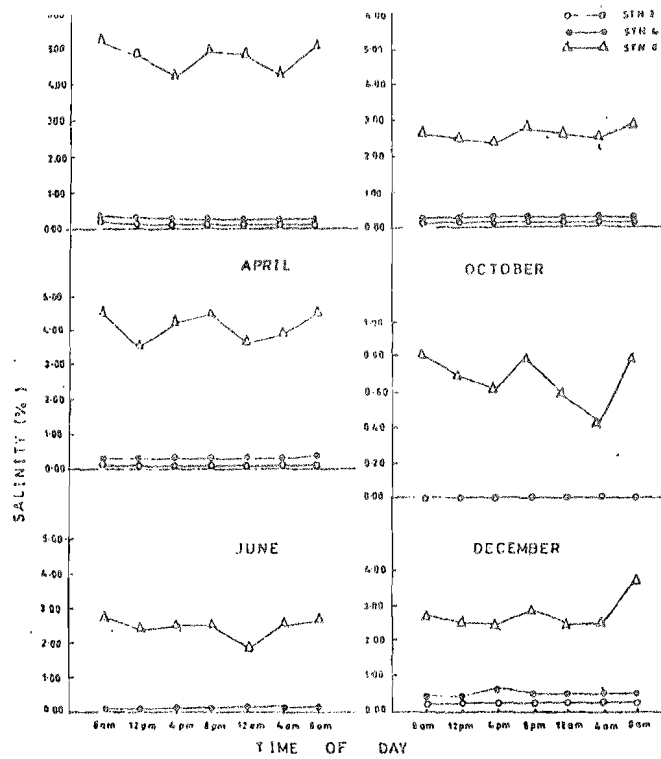


Fig. 6: Diurnal variation in Salinity percentage in Qua Iboe River during the period February - December 2000

June, August and October were below detectable limits. Surface and bottom values were negligible at station 2. At station 4 which is tidal but freshwater, the diel variation was equally low with no definite trend. However, salinity values were higher during the dry months (February and December) while during the peak of the rains (August – October), values were below detectable limits. (Fig. 7).

The pattern of diel variation was stronger and more consistent at the estuary than at other stations. High values were recorded during periods of flood tide and lower values during low tide. For example, during the month of February, the highest value of 5.30‰ was recorded at 12am during high tide at the estuary, while the lowest value of 4.20‰ was obtained at 4pm during low tide. The diel variation was highest during the dry months with wider and significant differences ($F = 10.25$, 10df, $p < 0.01$) between high and low tides. Low variation was observed during the rainy months with no significant difference between flood and ebb tides.

Concentrations of bottom salinity were higher and significantly different ($F = 9.45$, 10df, $p < 0.01$) from surface levels only at station 6 while no statistical difference was observed at stations 2 and 4. The pattern of diel variation at the bottom was wider than at the surface.

DISCUSSION

The chemical parameters measured demonstrated variations over diel periods influenced by biological, hydrometeorological factors and episodic events. The high diel pH levels recorded during the day could be attributed to the photosynthetic activity of phytoplankton. Generally, diel patterns of pH were similar to those of DO, thus suggesting similar influences on both parameters or a relationship between them. The similarity in the diel patterns of pH and DO in the present study, is consistent with the report of Reddy (1981) who noted that diel patterns of pH in all aquatic systems studied generally followed those of DO attributed to photosynthetic activity. Low pH levels were recorded during the morning and night time due to reduced photosynthetic activity and the resultant accumulation of CO_2 , HCO_3^- and CO_3^{2-} ions. Halstead and Tash (1982) indicated that some vascular aquatic plants do cause high diel pH in water. The diel variation in pH in the Qua Iboe River could have been caused by the photosynthetic activity of the fringing macrophytes in addition to periphyton and phytoplankton.

The diel range in conductivity at the freshwater segment (stations 2 and 4) did not show any appreciable variation probably because the ionic content of the river was not influenced by any physical or biological phenomena that could change over short diel periods. It could also include the absence of episodic events that could cause wide diurnal changes. The water at station 2 could be regarded as dilute with conductivity value of 22.20 – 26.35 μScm^{-1} at 25°C. Station 4 had higher conductivity levels (52.40 – 67.15 μScm^{-1} at 25°C). The ionic content of the river at the freshwater segment therefore appeared to be determined by the nature of the drainage basin which is made up of coastal plain with sandy beaches that are highly leached. This is consistent with the report of Egborge (1979) and Reddy (1981) who found that conductivity did not show any particular variation during diel periods in freshwater systems. The high diel variation in conductivity recorded at the estuary could be attributed to the tidal regime and the high diel values were recorded during flood tide as a result of salt inflow from the sea.

Maximum diel conductivity were usually recorded after mid-day (4.00pm) and conductivity levels were higher during the dry months (December – April) and decreased remarkably during the wet months (June – October). The highest conductivity levels for all the stations were recorded at the peak of the dry season. The diel variation at the estuary (station 6) was remarkable with lowest values recorded during

low tide and highest values during high tide. Typical diel difference between high tide and low tide was usually $> 50\mu\text{Scm}^{-1}$. Bottom conductivity did not show any diel pattern for any of the stations but were significantly higher ($p < 0.01$) at the estuary than at the freshwater section. The diel difference in conductivity values between surface and bottom water at station 6 was usually $> 150\mu\text{Scm}^{-1}$ during the dry season. This decreased considerably during the rains, at the peak of which no difference was recorded.

Adebisi (1981) noted that the conductivity of water increases with the increasing values of its total alkalinity and went on to infer that the major ions of Ogun River were CO_3^{2-} and HCO_3^- . The same observation applies to the Qua Iboe River where the conductivity also increased correspondingly with the total alkalinity indicating that some of the major ions in the river are HCO_3^- and CO_3^{2-} . The same observations have been made for other rivers in Nigeria, notably River Sokoto (Holden and Green, 1960) and River Niger (White, 1966).

The high diel variation in dissolved oxygen recorded during daytime coincided with the high diel pH and were similarly attributed to high photosynthetic activity. Egborge (1979) reported changes in dissolved oxygen concentration and pH as indices of phytoplankton activity and this was said to be temperature-dependent. The high diel DO values recorded during daytime hours in the present study is consistent with the report of Khan *et al.*, (1983), Reddy (1981) and Hare and Carter (1984) who obtained unimodal curve in their studies with peaks around mid-day. The low DO values recorded during morning and night hours were probably due to low photosynthetic activity.

The low bottom DO concentrations as compared to surface values and the low diel variation is attributed to the absence of photosynthetic activity at the bottom. DO levels at bottom (3.0 – 6.5m) may therefore be due mainly to diffusion from the surface and mixing brought about by wind and current flow. In addition, the values of bottom DO were higher at stations 2 and 4 during the rainy season due to mixing brought about by the flood and water currents. The lower levels recorded during the dry season were probably due to decomposition of organic matter by micro-organisms and the respiratory activity of bottom fauna.

Dissolved carbon dioxide exhibited the same diel trend at the three stations. The high free CO_2 recorded during the night were probably due to its accumulation as a result of cessation of photosynthetic activity. Low levels were recorded during the daylight hours due probably to utilisation during photosynthesis. In general, high levels were obtained during the dry period with low flow due to evapo-transpiration and dissolution from the atmosphere, while low levels recorded during rainy months can be attributed to the effect of precipitation resulting in net dilution. Reddy (1981) indicated that changes in dissolved CO_2 , HCO_3^- and CO_3^{2-} levels of water are controlled by changes in the pH of water and equilibrium reactions among them. Bottom free CO_2 were higher than surface values and showed diel variation due probably to its accumulation as a result of diffusion from surface and as a by-product of decomposition and respiratory activities.

Total alkalinity exhibited basically the same diel trend as free CO_2 suggesting that they were influenced by the same physical and/or biological processes. The low levels recorded during daylight hours could be attributed to utilisation during photosynthesis while the high values recorded during night hours maybe attributed to accumulation due to non-utilisation. The pattern of diel variation of salinity was influenced markedly by the tidal regime. The remarkable pattern of diel variation at the estuary as compared to that in the fresh-water stations, emphasizes the importance of tide as a determining factor in the chemical composition of the estuary. The levels of salinity were generally higher during flood tide due to salt inflow from the sea. As the flood tide receded, the salinity decreased due

to in-flow of fresh-water. The weak pattern of diel variation at station 4 even though tidal, maybe attributed to the long distance from the sea. Station 2 is predominantly fresh-water and non-tidal and therefore had little salt content. The salinity at the bottom was higher than at the surface at the estuary due to the fact that sea water is denser than fresh water and therefore, flows beneath the fresh water. This results in higher salinity at the bottom than at the surface due to salt intrusion from the sea.

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