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Research

Variation of chemical constituents of a brackish water prawn habitat in Southern Nigeria

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Abstract
Seven chemical parameters (pH, conductivity, dissolved oxygen, salinity, calcium, nitrate-N, phosphate-p) were analyzed for the tidal zone of the Benin River water samples at fortnightly intervals. Three (I, III, V) of the five study stations were situated along the main river channel while two (II, IV) were located on creeks entering the main river. The ranges of the chemical characteristic at the study stretch throughout the study period are as follows: pH (6.70 – 2.80); conductivity (2000.00 – 10.00 µScm^{-1}); dissolved oxygen (16.4 – 2.3 mgL^{-1}); salinity (6.17 – 0.01 ‰); calcium (252.0 – 17.0 mgL^{-1} x 10^{-1}); NO_3-N (6.90 – 0.15 mgL^{-1}); PO_4-P (5.70 – 0.0 mgL^{-1}). However, fluctuations in dissolved oxygen, salinity and phosphorus only were significantly different ($P < 0.05$) at the study stations in the two years. Generally, the chemical characteristics of the creek stations were similar and different from those of the main river stations. The chemical heterogeneity of the study stretch as reflected by the variations of the chemical conditions at the creeks and the main river sites seem to have influenced the distribution and abundance of prawns at the study area.

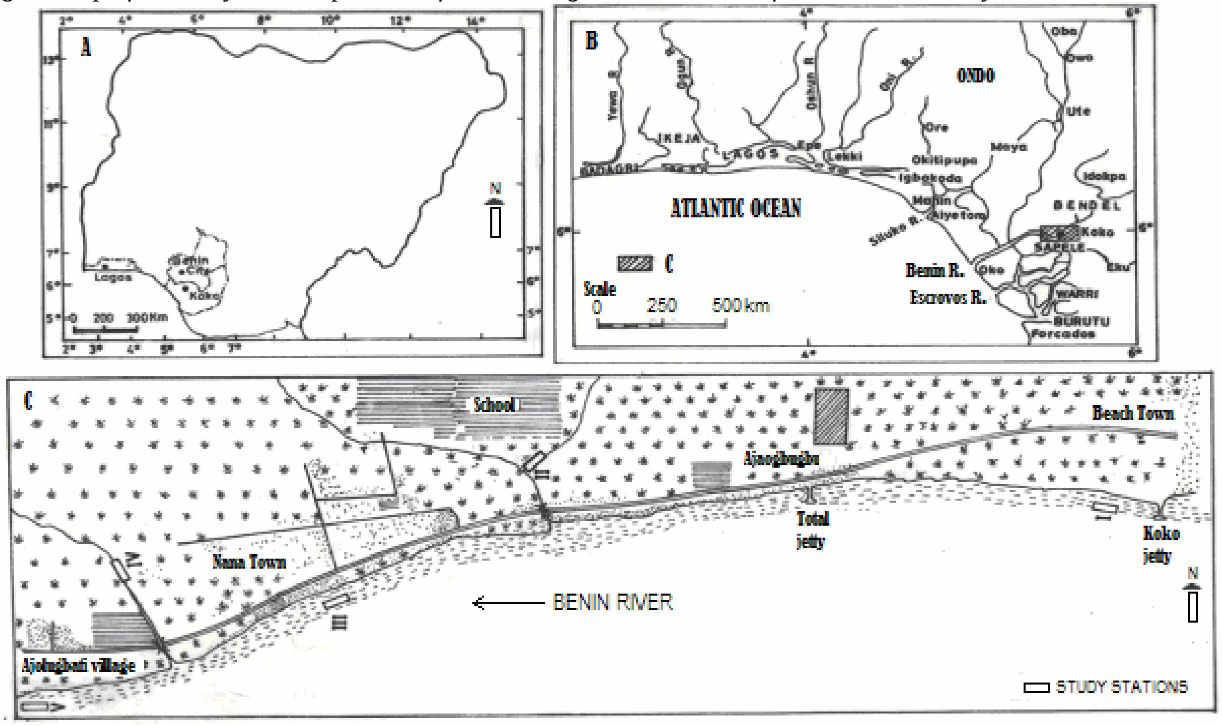
Keywords: Chemical constituents, brackish water, prawn habitat, creeks, Nigeria

Introduction
In Nigeria, the intensive culture of prawn is not economically feasible at present, because of the difficulties involved in larval rearing. The direct development and management of wild populations through habitat alterations has been suggested as feasible alternatives (Powell, 1982).

The Benin River with its associated creeks at Koko, southern Nigeria (Figs. 1a and 1b), supports a thriving artisanal prawn fishery. *Macrobrachium macrobrachion* Herklots, 1851 and *Macrobrachium vollenhovenii* Herklots, 1857 are common and abundant species at these sites (Edokpayi, 1989). Attempts at culture and management of these two species require a thorough understanding of the habitat requirements of these two species. Observation on the variations in the physical conditions of the Benin River is available (Edokpayi *et al*., 2001). This present paper provides the needed baseline data on the chemical characteristics at the tidal zone of the Benin River and two of its tributaries.

Material and methods
The study area
The study stretch represents the near-shore brackish water prawn habitat of the Benin River. It was chosen because of the occurrence and high abundance of *Macrobrachium macrobrachion* and *Macrobrachium vollenhovenii*. The freshwater upstream portion of this stretch is dominated by prawns of the family Atyidae and some Palaemonidae such as *Desmocaris trispinos*, Aurivillius, 1898 and *Leander tenuicornis* Sars, 1818; the downstream portion, characterised by high salinity, is dominated by prawns of the family Penaeidae such as *Parapenaeopsis atlantica* Balss, 1914, *Penaeus kerathurus* Foskal, 1975 and *Penaeus notialis* Perez-Farfante, 1967.

Fig. 1: Map of the study area, a. position of Koko in Nigeria b. Location of Benin river c. study stretch and stations



Southern Nigeria experiences a distinct seasonality in weather typical of the humid tropical climate governed by rainfall. This is characterized by a rainy season lasting for eight months (March – October) and a dry season with duration of four months (November – February). Details of the climatic conditions during the study period have earlier been described (Edokpayi *et al*., 2001).

Sampling Stations

Five sampling stations were selected for this study. Three of the stations I, III, and V were located along the main river channel, while the other two stations, II and IV were along two of the creeks (Fig. 1c). The following range of water depths were recorded at stations I (0.14 – 0.95m), II (0.26 – 0.96m), III (0.51 – 1.18m), IV (0.23 – 0.85m) and V (0.20 – 1.05m) throughout the study period. The aquatic vegetation was made up of submergents, emergents, and floaters. Submergent and emergent plants were restricted to the main river channel. *Ceratophyllum submersum* L. and *Utricularia* sp. account for the submergents, while the only emergent was the water lily, *Nymphea odorata* AIT. The floating vegetation made up of water lettuce, *Pistia stratiotes* L., *Lemma* sp. and *Azolla africana* Desv., occurred both in the creeks and the main river channel. However, the water hyacinth, Eichhornia crassipes (Mart.) Solms-Laub., a dominant floating plant which invaded the river during mid 1987, was never found in the creeks.

The substratum of the main river stations was sand covered with silt. The creek stations bottom sediments were mud with lots of allochthonous matter, mainly leaves and fallen tree trunks. Generally, human activities at the study sites includes fishing, washing of clothes and household utensils, bathing, defecation, and the various activities associated with the local transport terminals and idol worship.

Sample Collection and Analysis

Sub-surface water samples were collected directly in one-litre bottles from each station at fortnightly intervals for a period of two years. Water samples for determining dissolved oxygen were collected in 250-ml glass bottles and fixed in the field. In all, 260 water samples were collected and six chemical parameters were determined.

The pH was measured using a pH meter (Griffin, EIL 716) standardized with a pH 7 buffer. Conductivity was determined using a battery-operated conductivity bridge (Model MC-1, Mark V) at the temperature of the water samples; conductivity at 25^{o}C was estimated using the equation of Mackereth *et al*. (1978). Winkler's method (APHA, 1975) was used in determining the dissolved oxygen content of the water. Silver nitrate titrimetric method (APHA, 1975) was used to measure the salinity. The calcium content

Table 1.Chemical characteristics of the Benin River surface water at the study stations in the first year

	STATION I			STATION II			STATION III			STATION IV			STATION V			ANOVA
Chemical Conditions	Min	Mean ± S.E.	Max	Min.	Mean ± S.E.	Max	Min.	Mean ± S.E.	Max.	Min.	Mean ± S.E.	Max.	Min.	Mean ± S.E.	Max	F-value
pH	3.40		6.30	3.20		6.20	3.20		6.30	3.20		6.40	3.00		6.40	N.C.
Conductivity (μScm^{-1})	20	143.0 ± 2.8	400	18	140.5 ± 2.3	380	20	140.5 ± 2.3	390	20	114.0 ± 2.0	350	20	148.6 ± 3.0	410	0.27
Dissolved oxygen (mgl^{-1})	5.0	9.35^{a} ± 0.5	15.7	2.3	7.13^{b} ± 0.5	13.3	5.6	8.16^{a} ± 0.5	14.5	3.6	6.75^{b} ± 0.4	11.7	5.0	8.51^{a} ± 0.2	14.0	78.57**
Salinity (‰)	0.01	2.39^{c} ± 0.3	6.17	0.02	2.12^{c} ± 0.2	3.64	0.02	2.41^{c} ± 0.3	5.26	0.10	1.78^{d} ± 0.2	3.82	0.10	2.29^{c} ± 0.3	4.82	25.54**
Calcium (mg L^{-1}x10^{-1})	52.8	117.6 ± 1.9	252	38.4	115.0 ± 1.7	224	32.8	104.9 ± 7.4	117.6	35.2	110.5 ± 7.2	162.	24.8	105.1 ± 7.8	182	0.48
NO_3-N (mgL^{-1})	0.45	1.8 ± 0.23	4.10	0.35	2.02 ± 0.3	6.90	0.15	1.68 ± 0.2	4.49	0.45	2.17 ± 0.2	5.50	0.45	1.17 ± 0.2	4.60	0.63
PO_4-P (mgL^{-1})	0.00	1.16^{e} ± 0.2	3.50	0.25	2.07^{f} ± 0.2	3.80	0.00	1.20^{e} ± 0.2	2.89	0.30	2.27^{f} ± 0.3	5.70	0.20	1.61^{e} ± 0.3	4.20	4.45**

n=26 (no. of samples); same lower case alphabets indicate no significant difference (P > 0.05; Duncans New Multiple Range Test)
**significance (P < 0.05); **significance (P < 0.01). N.C.= Not calculated*

Table 2. Chemical characteristics of the Benin River surface water at the study stations in the second year

	STATION I			STATION II			STATION III			STATION IV			STATION V			ANOVA
Chemical Conditions	Min.	Mean ±S.E.	Max.	Min.	Mean ±S.E.	Max.	Min.	Mean ±S.E.	Max.	Min	Mean ±S.E.	Max.	Min.	Mean ±S.E.	Max.	F-value
PH	2.80		6.50	3.00		6.70	3.20		6.00	3.00		6.10	3.20		5.60	N.C.
Conductivity (μScm^{-1})	10.0	453.7 ±11.	2200	14.0	485.7 ±13.0	2600	10.0	452.6 ±10.0	1900	12.0	216.2 ±7	1500	13.0	417.0 ±10	2000	1.08
Dissolved ox -ygen (mgl^{-1})	5.4	9.72^{g} ±0.5	16.4	4.4	7.53^{h} ±0.40	10.2	3.3	8.48^{g} ±0.50	15.3	4.4	7.18h ±0.4	13.2	3.3	8.68^{g} ±0.50	15.3	4.48**
Salinity (‰)	0.10	2.02^{i} ±0.19	2.80	0.10	1.87^{i} ±0.20	2.70	0.10	2.05^{i} ±0.20	2.70	0.10	0.88^{j} ±0.10	0.80	0.10	2.09^{i} ±0.20	2.80	2.80*
Calcium(mg L^{-1}x10^{-1})	17.0	76.42 ±7.5	144.8	22.3	73.56 ±7.9	154.2	28.4	75.99 ±7.1	142.4	25.3	72.47 ±7.7	155.2	18.4	73.69 ±7.0	153.5	0.05
NO_3-N (mgL^{-1})	1.04	2.36 ±0.21	4.50	1.0	2.62 ±0.30	5.0	0.89	2.39 ±0.20	4.26	0.64	2.23 ±0.20	4.50	0.64	2.04 ±0.20	4.18	1.11
PO_4-P (mgL^{-1})	0.0	1.07 ±0.16	2.80	0.0	1.17 ±0.10	2.66	0.12	1.49 ±0.10	3.41	0.12	1.05 ±0.10	3.41	0.18	1.05 ±0.10	2.80	2.33

n=26 (no. of samples); same lower case alphabets indicate no significant difference (P > 0.05; Duncans New Multiple Range Test)
**significance (P < 0.05); **significance (P < 0.01). N.C.= Not calculated*

was determined by the EDTA titrimetric method (APHA, 1975). The Spectrophotometric method (APHA, 1975) was used to determine the nitrate-nitrogen content using a SP6-500UV Spectrophotometer (PYE UNICAM model). Phosphate-phosphorous was measured by the Vanado-Molybdo-Phosphoric acid colorimetric method (APHA, 1975). Coloured water samples were decolourized before analysis by shaking 50ml of the water with 200mg activated carbon (Darco G 60) in an Erlenmeyer flask and filtered through a filter paper (Whatman No. 42).

Statistical Analysis

All statistical procedures were adopted from Zar (1984). One-way ANOVA was carried out to compare the variations in parameters among stations over time. When significant variations are detected a Post-Hoc analyses using Duncan's New Multiple Range Test were performed to determine the location of significant differences. Data analyses were carried out using Statistica 5.0 software.

Results

Tables 1 and 2 shows the summary of the chemical conditions in the Benin River study stretch for the first (March 1986 - February 1987) and second (March 1987- February 1988) years respectively.

The (pH) was relatively uniform along the

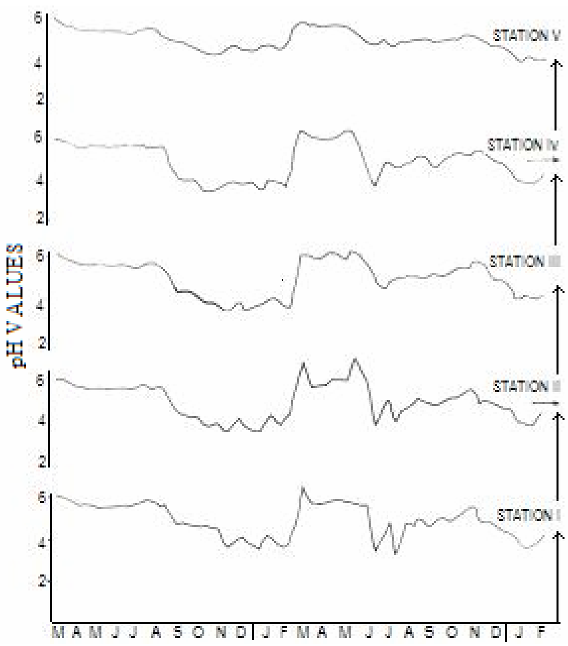


Fig. 2. Forthnight variations in pH, Benin River (arrow between stations indicate flow direction)

length of the study stretch with slight temporal variations during the study period (Fig. 2). Generally, relatively high pH (>5 pH units) was observed between March 1986 - early June 1987 and March 1987 – June 1988; while low values (<5 pH units) were recorded between September 1986 - February 1988 and July 1987 – February 1988 (Fig. 2).

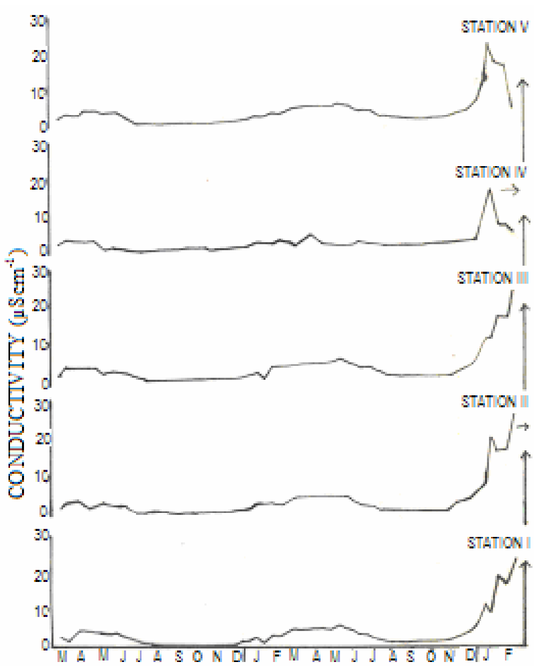


Fig. 3. Forthnight variations in conductivity, Benin River (arrow between stations indicate flow direction)

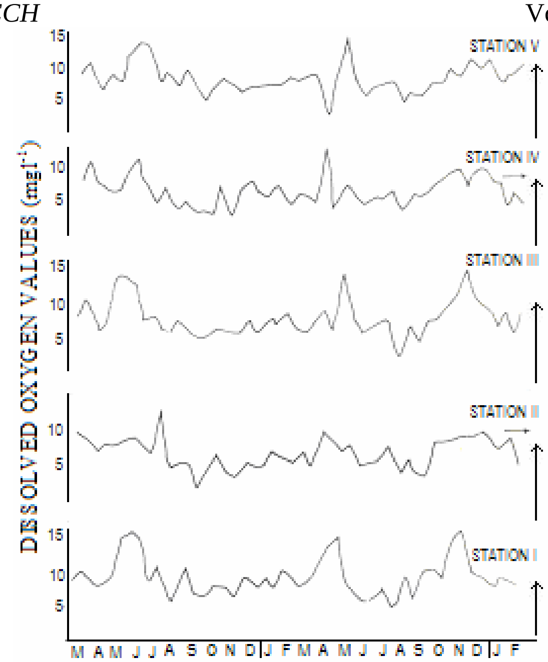


Fig. 4. Forthnight variations in dissolved oxygen, Benin River (arrow between stations indicate flow direction)

Conductivity was not found to be statistically different (P >0.05) at the five stations in both years (Fig. 3; Tables 1, 2). Unexpectedly high values (>1500 μScm^{-1}) were recorded at all stations between January and February 1988 (Fig. 3). Trace values (<10 μScm^{-1}) were reported at all stations between July and December 1986 as well as between August and early

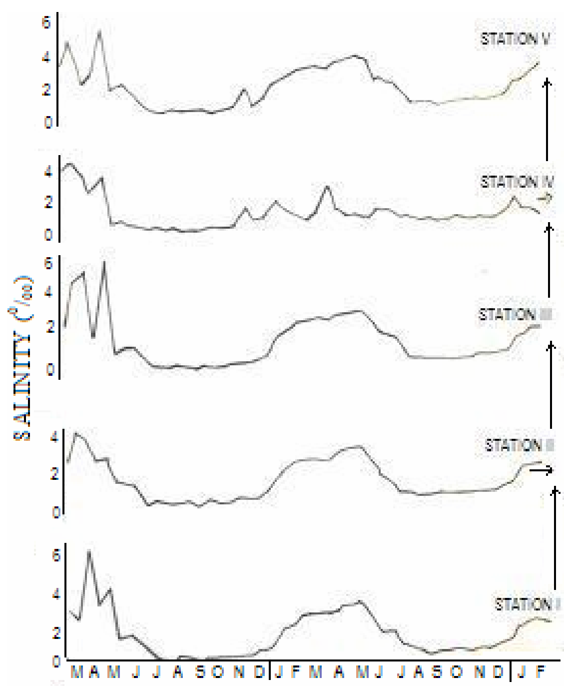


Fig. 5. Forthnight variations in salinity, Benin River (arrow between stations indicate flow direction)

November 1987 (Fig. 3).

The fortnightly and longitudinal variations in dissolved oxygen are shown in Fig. 4. Dissolved oxygen concentrations at stations II and IV (the two creek stations) were statistically lower ($P <0.05$) than those of the three river stations within both years (Fig 4; Tables 1, 2). The lowest value (2 mgl^{-1}) was recorded at station II.

Fluctuations in salinity were uniform among stations with slight temporal variations (Fig. 5). Salinity values at station IV (a creek station) were significantly lower ($P <0.05$) than those reported for the other stations during both years (Tables 1, 2).

Irregular variations in calcium concentrations were observed at all stations (Fig. 6). The calcium content in the first year was relatively higher than those observed in the second year at all stations (Fig. 6; Tables 1, 2). The highest (252 $mgl^{-1} \times 10^{-1}$) and the lowest (17 $mgl^{-1} \times 10^{-1}$) values were recorded at station I, the farthest upstream station (Fig. 7). The calcium content at all five stations were not significantly different within each year ($P >0.05$; Tables 1, 2).

The pattern of nitrate-nitrogen fluctuations at all stations was similar in the first year, but dissimilar with wide variations in the second year (Fig. 7). Peak values (>4.1 mgl^{-1}) were recorded in August 1986 and very low values (<0.5 mgl^{-1}) in late January 1986 at all stations (Fig. 7). There were however, no significant differences ($P >0.05$) in the mean nitrate-N among the stations in the two years (Tables 1, 2).

Irregular fluctuations of phosphate-phosphorus at all stations were observed throughout the study (Fig. 8). Undetectable phosphate-P values were recorded at stations II and III in both years. The mean phosphate-P was significantly different ($P <0.001$) among the five stations in the first year (Table 1). The mean phosphate-P in the first year at stations II and IV were similar to each other ($P >0.05$) but were stati-

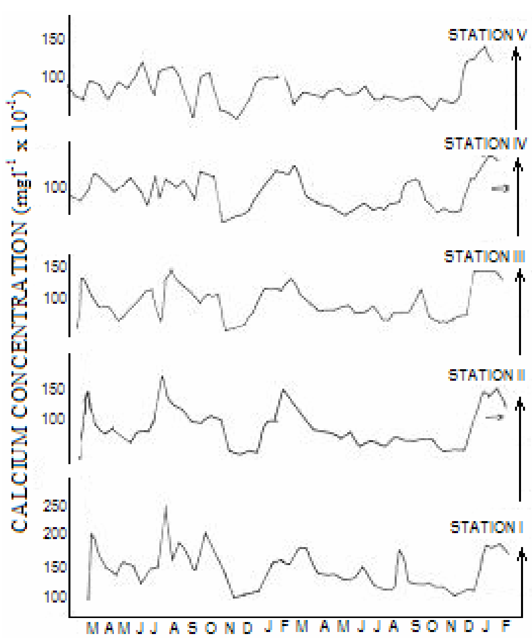


Fig. 6. Monthly variations in calcium, Benin River (arrow between stations indicate flow direction)

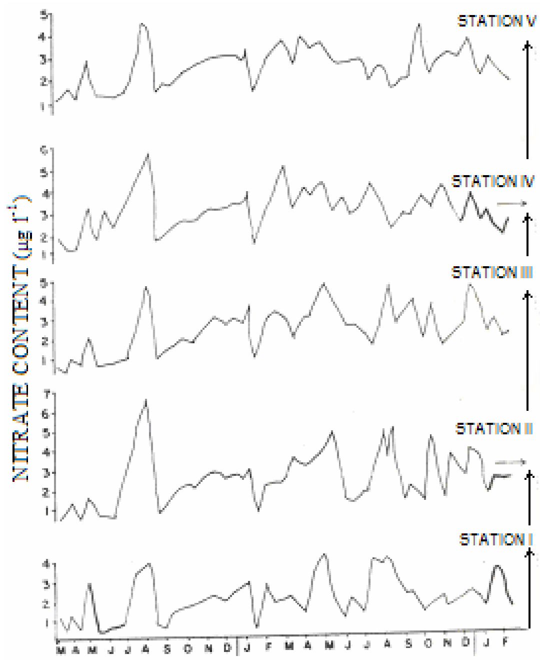


Fig. 6. Monthly variations in nitrate-n, Benin River (arrow between stations indicate flow direction)

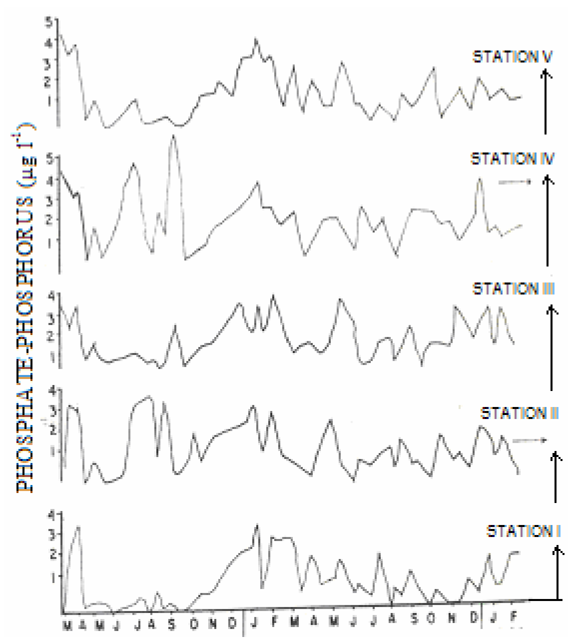


Fig. 8. Fortnight variations in phosphorus-p, Benin River (arrow between stations indicate flow direction)

stically higher ($P < 0.05$) than those of the other three stations. In the second year, however, the station means were not significantly different ($P > 0.05$; Table 2).

Discussion

The Benin River water was acidic with a pH range of 3.0 - 6.7 except in late July 1987 at station l when an exceptionally low pH of 2.8 was recorded. The observed pH values were lower than those recorded for most African rivers (Hall *et al*., 1977), and some Nigerian rivers (Courant *et al*., 1987).

The pH 2.8 recorded at station I is the lowest ever reported for an African river (Awachie, 1981; Courant *et. al.*, 1987). Onwudinjo (personal communication) however, reported a similar low pH (2.7) at the bottom of the mid-waters of the Benin River at Koko. Because of the low water level (39cm) at this station on the sampling day, water samples were collected near the substratum. The low pH was probably due to the release of hydrogen sulphide from the peaty soil as a result of sulphate reduction by bacteria within the sediments (Wetzel, 1975). Laterite and peaty types of soil common in tropical regions are capable of reducing the water pH (Kellman & Tackaberry, 1997). The flooding of associated acidic swamps into the river channel may be an additional reason (Tait & Dipper, 1998). The only unidirectional flow velocity (5 cms^{-1}) measured at this station in the second year was recorded on that sampling day.

Conductivity is a measure of the total ionic composition of the water and therefore, its overall chemical richness (Awachie, 1981). Seasonal variations in conductivity were observed with high values recorded in the dry months (December – March) and low values in the rainy months (July – October). Similar trends have been observed in many African rivers (Ogbeibu & Victor, 1989; Ogbeibu & Victor, 1995). High ionic content in the dry season was likely due to the concentration of nutrients by evaporation (Jefferies & Mills, 1990). The decomposition and mineralisation, of allochthonous organic matter during this period could also increase the conductivity (Victor & Al-Mahrouqi, 1996; Tait & Dipper, 1998). The lower conductivity observed during the rainy season is not an indication of ionic paucity, but a reflection of dilution by rainfall (Nybakken, 1997).

In running water, dissolved oxygen is usually not limiting (Hynes, 1970). The range of dissolved oxygen content estimated here (2.3-16.4mgl^{-1}) is similar to ranges reported for most Nigerian rivers (Egborge *et al*., 1986; Courant *et al*., 1987; Ogbeibu & Victor, 1995). The mean oxygen concentrations at the five sampling stations were significantly different ($P < 0.001$). The low oxygen content in the Creek was comparable to those of the Escravos River, New Calabar River, the Nun floodplains (Courant *et al*., 1987), and the polluted stretch of the Ikpoba River (Edokpayi, 1988) in Nigeria. The low oxygen level is probably the result of high oxygen demand caused by microbial breakdown of allochthonous input, mainly fallen leaves of the riparian trees (Hynes, 1970; Nybakken, 1997). The relatively high oxygen content in the main channel may be due to greater volume of water, lack of shade, and low allochthonous input, in addition to wind and tidal wave actions along the river bank (Townsend, 1980).

The reported salinity range (0.21 - 11.17‰) is within the brackish water range (0.21 – 30‰) given by Tait & Dipper (1998). The salinity of the Escravos, Brass, and New Calabar Rivers (Courant *et al*., 1987) were higher than those reported in this study. The Benin River at Sapele, upstream of the study stretch, is fresh as indicated by its lower salinity (Egborge *et al*., 1986).

Although, there were slight variations in salinity among stations, its seasonality was obvious. Generally, salinity values were low during the rainy months and high during the dry months. Similar observations have been reported for most Nigerian rivers and creeks (Courant *et al*., 1987). The dilution effect of increased river inflow during the wet season is responsible for the reduction in the salinity. The salinity values at station IV were lower than the other four stations throughout this study. The upper reaches of this creek was freshwater, and the local villagers were using this water for drinking and cooking purposes. The relatively low salinity recorded at this station resulted from the continuous input of freshwater from upstream.

The calcium content of the Benin River at the study stations was higher (mean >70 mgl^{-1}) than those of many African waters in general (Beadle, 1974) and Nigerian rivers in particular (Egborge *et al*., 1986). The recorded high values were probably due to the release of calcium from peaty clay and soft mud that made up the substrata of this river, in addition to the eroded calcarous materials of biogenic origin common in the study stretch (RPI, 1985).

The observed nitrate-nitrogen levels were higher than those of many African waters (Hall *et al*., 1977). Lower values have been reported for many Nigerian rivers (Egborge & Benka-Coker, 1986; Egborge *et al*., 1986; Edokpayi, 1988).

The high level of nitrate-nitrogen observed in the present study is attributed to the natural processes of organic mineralization both *in-situ* and those washed in by surface run-off from adjacent forest and human communities. Plants in the river also release nitrogen as leacheate (Hynes, 1970; Wetzel, 1975; Kellman & Tackaberry, 1997). The dependence of nitrate levels in African rivers on litter breakdown has earlier been reported (Harrison & Ranking, 1976). Cow dung deposited along the riverbanks and the direct human defecation into the river are common features of the study area. Raw and treated mammalian excreta can mineralize rapidly in water and contains high proportions of inorganic nitrogen and phosphate (Stewart *et al*., 1975; Cosgrove, 1977).

The mean nitrate-N concentrations were significantly different ($P < 0.05$) among the stations. The high level in the creeks was likely due mainly to the leaching of allochthonous leaf litter that covers the bottom sediment at the creeks in addition to the contribution from human waste deposited directly into the creeks. Nitrate depletion by seasonal macrophytic blooms (Harrison & Rankin, 1976) maybe responsible for the low levels in the main channel.

Phosphate-phosphorous plays a major role in biological metabolism. Its relatively small amount in the hydrosphere is of ecological interest (Roger & Adams, 1996; Tait & Dipper, 1998). The reported phosphate-P levels were high compared to those of many African waters (Ogbeibu & Victor, 1989). A combination of environmental impact through surface run-off, precipitation and the leaching of dead macrophytes (Stewart *et al*., 1975; Sutcliffe *et al*., 1982) probably contributed to the high levels of phosphate-P recorded here. The importance of dead macro-vegetation as a source of phosphorous in aquatic ecosystems has been reported (Kellman & Tackaberry, 1997). Phosphate-P recycling from sediments by aquatic macrophytes (McRoy *et al*., 1972) could be another important source of phosphate-P along the study stretch. Soap and detergents used for bathing and other domestic purposes are high in phosphate-P (Wetzel, 1975). Their moderate contribution should not be overlooked as a possible source in this study area.

The observed variable seasonal pattern of phosphate-P is not uncommon in most Nigerian rivers (Nwadiaro & Umeham, 1985; Ogbeibu & Victor, 1995). The relatively higher phosphate-P levels at the creeks than the main channel were probably due to rapid leaching from the dry leaf litter. Wetzel (1975) observed that leaching of phosphate-P from dried plants was more rapid than that of freshly dead plants.

Generally, the chemical conditions at the creek stations were similar and slightly different from the main river stations, which were similar. The dominance of *Macrobrachium macrobrachium* at the creek and *Macrobrachium vollenhovenii* at the main river channel (Edokpayi, 1989) could be a reflection of this differential habitat conditions.

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