

PHYSICO-CHEMICAL CHARACTERISTICS AND ANTHROPOGENIC POLLUTION OF THE SURFACE WATERS OF CALABAR RIVER, NIGERIA.

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ABSTRACT

Investigation of the variations in water quality characteristics, hydrocarbon levels and Fe contents of the Calabar River, a major tributary of the Cross River, Nigeria, was conducted between October 1994 and March 1996. The study showed that the river is relatively fresh (salinity < 0.56 ppt) from 25km upstream indicating a remarkable diminution in salinity when compared to previous measurements. The river has high total hydrocarbon (THC) levels (22.0 - 55.8 mg/l, mean 27.3 ± 3.9 mg/l) depicting anthropogenic additions and low Fe content (0.5 - 2.0 mg/l, mean 1.55 ± 0.42 mg/l). THC was above the limit (10 mg/l) and Fe below limit (20 mg/l) recommended for nearshore waters (FEPA 1988). Generally, all the measured water quality parameters were higher at flood tide than ebb tide except turbidity and temperature, suggesting that tidal regime is the predominant factor influencing changes in the river water quality. A statistical analysis using coefficient of determination, r^2 gave no relationship between THC levels and current speed ($r^2 = 0.05$ for station 1 and $r^2 = 0.03$ for station 2). The potential sources of pollution such as occasional spills, residual oils from ships during the discharge of petroleum products at the jetties and the discharges from motorised boats commuting between Creek Town, Calabar and Oron have been identified as point sources of pollution. Pollutant toxicity to fish, bioaccumulation and surface water contamination are also discussed.

Key Words: Water quality, hydrocarbon pollution, tidal regime, point sources.

INTRODUCTION:

In the present decade, much concern is focused on ascertaining the quality of the environment due to increased human activities (domestic and industrial). The advancement in science and technology is associated with environmental problems that require both local and international attention. The notion that water, one of the nature's greatest gifts to man is an inexhaustible resource that can assimilate and diffuse anything put into it is fast fading out. The rapid deterioration of coastal and inland water qualities in Nigeria due to anthropogenic additions are quite alarming (Imevbore, 1970; Ajayi and Osibanjo, 1981; Adeniji and Mbagu, 1983; Ntekim *et al.*, 1993). Solid wastes that are biodegradable aggravate the situation by exerting an immediate oxygen demand on the ecosystem. The extent to which contamination has occurred in most Nigerian aquatic systems including the Calabar River is yet to be thoroughly quantified. The Calabar River, a major tributary of the Cross River, originates from the Oban Hills, Nigeria, and flows through black shale and siltstone, clayey sand and silt deposit. It also passes through an alluvial deposit before entering the Cross River at Alligator Island. The present study was carried out to examine the extent of pollution of the Calabar River ecosystem by investigating its physicochemical characteristics and the pollution status of the river.

MATERIALS AND METHOD:

Monthly samples were collected from the Calabar river at two locations: Okurikang bridge (station 1) and Calcemco Jetty (station 2), Fig. 1. Sample collection was done for eleven months (between October 1994 and March 1996). Parameters investigated included physicochemical factors, organic pollution indicators, total hydrocarbon contents (THC) and Fe concentrations.

In situ measurements were carried out for dissolved oxygen and water temperature using oxyguard MK11 electronic meter, ± 1.0 units. pH and E^h were measured with WTW pH 90 meters ± 0.1 units and electrical conductivity was measured with WTW LF - 90 conductivity meter, ± 1.0 $\mu\text{S}/\text{cm}$. Water samples for nutrients and metals were collected in one litre plastic bottles and kept frozen (at 4°C) until analysis.

THC samples were collected in glass bottles and preserved by adding 10ml of 4M H_2SO_4 . Extraction was carried out with distilled n-hexane (Analar Grade) and quantified by gravimetry $\pm 0.0001\%$, Rump and Krist, 1985). Turbidity and total suspended solids (TSS) were measured spectrophotometrically at 450nm and 810nm respectively. Biochemical oxygen demand (BOD₅) was determined as the difference between

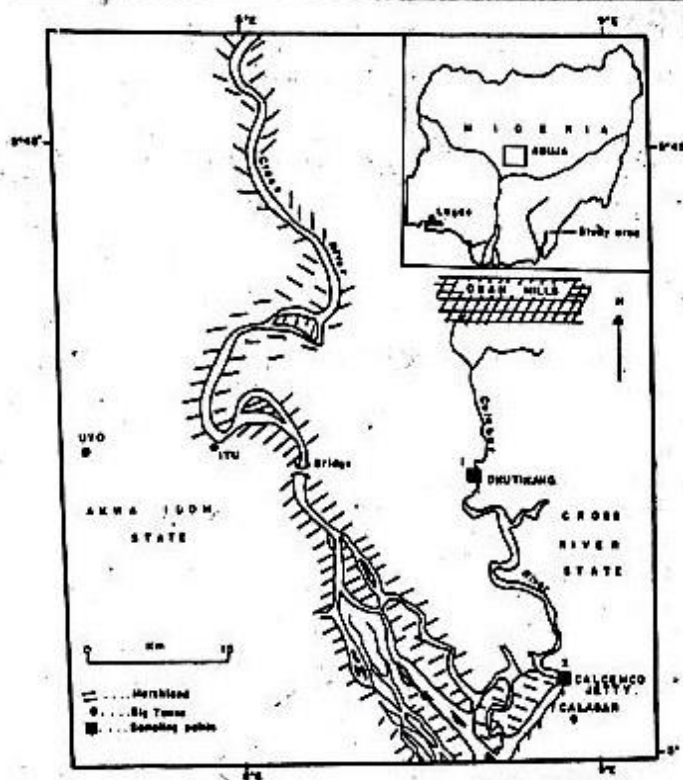


Fig. 1. Map of the Calabar river indicating the sampling points 1 - Drukiang bridge, 2 - Calabar Jetty.

The highest mean temperature for the river was $28.3 \pm 1.6^\circ\text{C}$ at station 2. Fluctuations occurred in water temperature levels as a result of tidal perturbations (ebb tide values, $25.3 - 30.9^\circ\text{C}$ and flood tide, $25.0 - 29.9^\circ\text{C}$). Low temperature at flood was attributed to high degree of turbulence associated with mixing process between surface and subsurface waters. Water temperature reached their maximum (30.90°C) in February/March each year.

The redox potential (E^h) measured the oxidation/reduction ability of the aquatic environment. Reducing environments are found where there is low oxygen tension or where marshy condition predominates. The highest mean E^h observed was -14.0 ± 4.5 mv at station 1 (ranged from -30 to 8.0 mv at ebb tide and -9 to 14.0 mv at flood tide). E^h values determined showed a slightly reduced environment at both locations (Table 1). The river showed a considerably reduced state at ebb than flood tide and station 1 was at a higher oxidised state than station 2 (Fig 2a). The reduced state of station 2 especially at low tide is greatly influenced by the addition of low oxygenated water coupled with the microbial activities (anaerobes) which create anoxic conditions in the subsurface. Anoxic conditions favour the inter-conversion of oxidised forms and the incorporation of reduced species into muddy sediments. This is consistent with the high levels of heavy metals (Fe^{2+} , Cu^{2+} , Zn^{2+}) as reported in the riverine sediment (Nickim et al. 1993).

Salinity regime in the Cross River system is highly fluctuating. High salinity up to 10ppt was reported at the outer Cross River estuary (RP1 1985). At about 20 km upstream, 7.0 ppt was recorded at flood tide during the dry season (Asuquo, 1989). During the present study, a drastic reduction in salinity was observed 0.56 ppt (mean salinity, 0.249 ± 0.14 ppt, Table 1). The notable change in salinity regime is as a result of the dredging and widening of the navigational

channels of the Calabar river by the Nigerian Ports Authority (NPA) to enable large cargo vessels to berth at their jetty. The dredging of this river facilitates an increased discharge of fresh water such that incoming estuarine water is highly diluted by large volume of inland drainage. Generally, the salinity varied with tide, season and with location. Minimum salinity was observed during the wet season (April to October) and at ebb tide, while maximum salinity occurred during dry season (November to March) and at flood tides. Highest salinity was measured at station 2 due to salt water incursion. Salinity variation in the surface water of Calabar river is tidally dependent as shown in Fig. 2a. Precipitation contributed remarkably to the net volume of fresh water drainage during the period (range 0 - 782.1 mm).

initial and final dissolved oxygen after incubation for 5 days at room temperature (27°C). Nitrite, nitrate, ammonium and phosphate were determined using conventional colorimetric methods (APHA, 1980). Iron (Fe) was determined by O-phenanthroline method (APHA, 1980).

Current velocity (speed) was obtained using the flotation method by noting the time it takes for a float to drift over a known distance while tidal ranges were measured using a tidal pole calibrated in metres.

RESULTS AND DISCUSSION:

The levels and concentration of physicochemical factors and nutrients are presented in Table 1. Table 2 shows the concentration and levels of organic pollution indicators, THC and Fe contents while Table 3 represents the changes in tides, rainfall pattern and current speed during the period. Figs. 2a and 2b illustrate the spatial variation of measured parameters at ebb and flood tides where the partially shaded bars depict observed fluctuation in the concentration of the measured variables during tidal regimes. Fig. 3 represents the diurnal variation of THC and current velocity in the Calabar river system.

PHYSICO-CHEMICAL PARAMETERS:

The hydrological characteristics of the river was markedly influenced by tidal incursions and high river discharge. The changes observed and the affected parameters are discussed below.

TABLE 1: Levels of physicochemical factors and nutrients in surface waters of Calabar River between 1994 and 1996.

Parameter/Tide	EBB TIDE		FLOOD TIDE	
	Station 1	Station 2	Station 1	Station 2
Temp. °C	27.4 ± 1.9	28.3 ± 1.6	27.3 ± 2.2	27.7 ± 0.8
pH	6.7 ± 0.3	6.7 ± 0.35	6.8 ± 0.3	7.0 ± 0.3
E _h mv	-16 ± 6.3	-21 ± 6.0	-14 ± 4.5	-28.3 ± 21.7
Cond. µm/cm	27.2 ± 5.9	30.2 ± 3.2	27.1 ± 1.6	33.7 ± 6.5
NH ₄ mg/l	0.26 ± 1.4	0.18 ± 1.6	0.28 ± 0.12	0.26 ± 0.17
NO ₂ mg/l	0.003 ± 0.004	0.004 ± 0.003	0.004 ± 0.01	0.01 ± 0.01
NO ₃ mg/l	0.09 ± 0.07	0.20 ± 0.16	0.15 ± 0.11	0.18 ± 0.11
PO ₄ mg/l	0.37 ± 0.8	0.20 ± 0.06	0.39 ± 0.11	0.01 ± 0.02
SiO ₂ mg/l	0.73 ± 0.49	0.59 ± 0.39	0.86 ± 0.55	0.78 ± 0.7
TDS mg/l	22.9 ± 0.7	26.91 ± 3.2	23.7 ± 0.8	27.9 ± 3.9
Salinity ppt	0.895 ± 0.04	0.194 ± 0.12	0.148 ± 0.14	0.249 ± 0.14
SO ₄ mg/l	5.8 ± 5.9	15.8 ± 15.0	3.3 ± 6.0	28.8 ± 13.1
Tot. Hard mg/l	23.4 ± 7.3	37.7 ± 28.7	15.9 ± 7.9	24.1 ± 8.0
Tot. Alk. mg/l	28.1 ± 3.2	22.3 ± 3.7	20.0 ± 2.6	27.0 ± 8.3

Levels of parameters are the means obtained from more than 11 measurements at ebb and flood tides. Not less than 2 measurements were made for in situ parameters.

The measurements of tidal levels (at flood and ebb tides) gave the highest tidal range of 25.0 to 76 cm at flood tide during the wet season. The river is characterised by two tidal regimes - flood tide (high water) and ebb tide (low water). At the upper reaches of the river, flow is unidirectional. The shoreline is characterised by thick vegetation changing from fresh water swamp ecology to mangrove swamp towards the mouth of the estuary. The flushing characteristic is enormous being influenced by the presence of more than six tributaries discharging large amount of fresh water into the drainage basin. Artisanal fisheries are dependent on the tidal pattern and fish catch is dominant during the ebb and neap tides than at flood or spring tides. The latter being characterised by turbulent mixing especially at periods after noon generated by sea-land breeze motion.

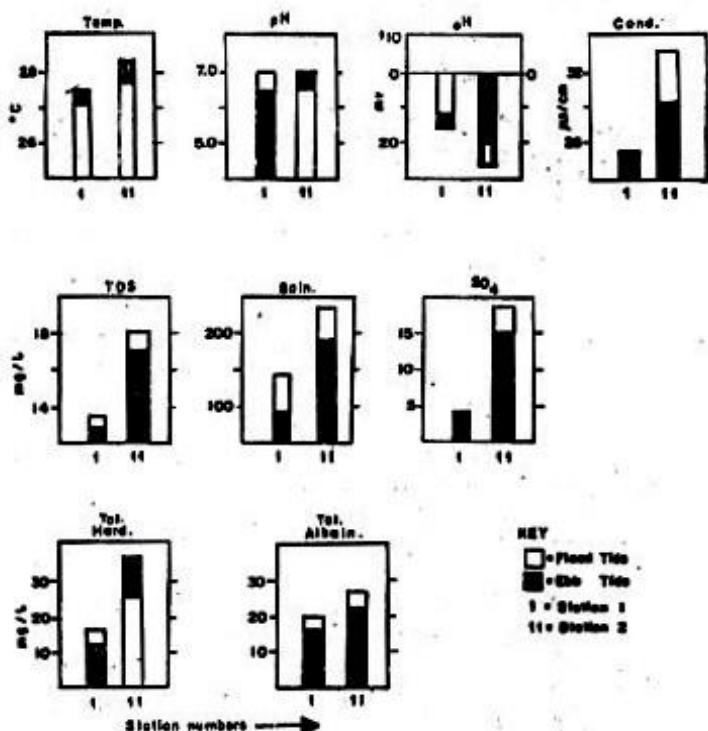


Fig. 2a. Spatial variation of physical and conservative parameters in Calabar river (1994-1996)

TABLE 2: Levels of organic pollution indicators and total iron in surface waters of Calabar River.

Parameter/Tide	EBB TIDE		FLOOD TIDE	
	Station 1	Station 2	Station 1	Station 2
DO mg/l	5.5 ± 0.8	5.2 ± 0.9	5.5 ± 0.5	5.4 ± 0.8
BOD ₅ mg/l	21 ± 0.8	3.4 ± 1.1	2.2 ± 1.0	3.6 ± 2.2
TSS mg/l	7.4 ± 3.7	9.7 ± 4.1	8.1 ± 3.5	10.7 ± 4.7
Turb. NTU	9.5 ± 4.2	12.1 ± 6.2	8.4 ± 3.4	10.8 ± 4.8
THC mg/l	27.3 ± 3.9	21.9 ± 5.3	26.4 ± 10.2	23.6 ± 5.6
Fe mg/l	0.15 ± 0.1	1.1 ± 0.3	0.19 ± 0.13	1.53 ± 0.40

Levels of parameters are the means obtained from more than 11 measurements.

The diurnal current velocity measured ranged from 2 to 24cm/sec. At station 1 (upstream), current speed was relatively higher (24cm/sec) than station 2 downstream (20cm/sec.), and current was higher during ebb tide and decreased during the flood tide. Dissolved and particulate materials are transported by surface currents from the estuary into creeks and upper reaches of the river during semi-diurnal tides. From diurnal studies of the relationship between current speed and pollutant concentration, it was observed from a pair-wise correlation analysis that current speed did not exhibit any direct relationship with pollutant concentration (coefficient of determination, $r^2 = 0.05$, $Y = 10.95 - 0.05 X$ for station 1 and $r^2 = 0.03$ and $Y = 12.05 - 0.02 X$ for station 2, where $Y =$ THC concentration and $X =$ current speed). Current speed aided the dispersion, distribution and

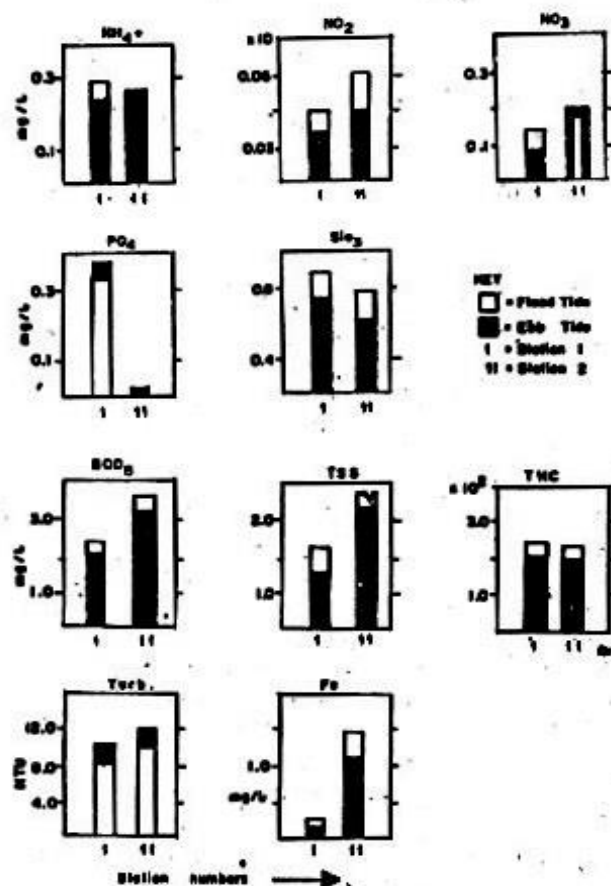


Fig. 2b. Spatial variation of nutrients, organic pollution indicators, THC and Fe in Calabar river (1994-1996)

exchange of dissolved and particulate pollutants between the estuary and the upper regions of the river. For instance, the diurnal concentrations of THC at both locations monitored fluctuated within a range of 80 to 120 mg/l (Fig. 3).

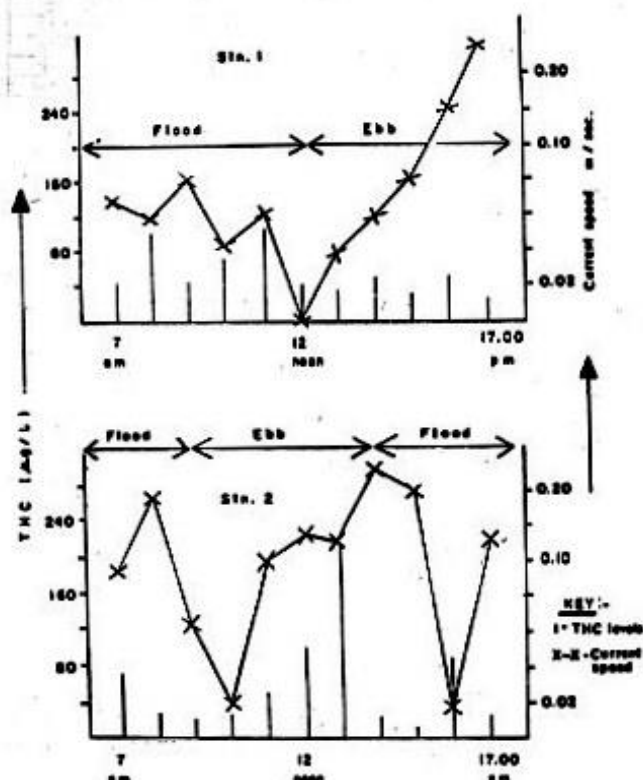


Fig. 3 Diurnal variation of THC levels and current speed at Stns. 1 and 2 of Calabar river

The electrical conductivity measurements were low (highest mean $33.7 \pm 6.2 \mu\text{s/cm}$ at station 2). This highest value measured at station 2 located close to the estuary and at high tide is relatively small depicting that the river has a low dissolved salt content (salinity < 1 ppt) being influenced primarily by high fresh water discharge from inland drainage.

Chemical factors such as phosphates (range 0 - 0.05 mg/l), silicates (range 0.14 - 2.44 mg/l), total alkalinity (range 15 - 50 mg/l), total hardness (range 5.5 - 113.8 mg/l), SO_4 (range 0 - 0.6 mg/l), NO_2 (0 - 0.03 mg/l) and NO_3 (0 - 0.6 mg/l) showed minimal fluctuations during the period. Observed values were higher at flood tide than ebb tide and this was attributed to salt water intrusion from the estuary. NH_4^+ levels (0.08 - 0.55 mg/l, highest mean 0.28 ± 0.12 mg/l) were slightly higher than previous measurements (Asuquo, 1989) depicting anthropogenic addition from municipal waste dumping and domestic sewage from non-point sources. Higher levels of ammonium than nitrate observed may have originated from faecal matter addition to the river and the inter-conversion (biochemical speciation) of nitrates into other nitrogenous forms especially NH_4^+ in a chemically reduced environment.

Organic Pollution Indicators and Fe:

The dissolved oxygen (DO) content of the Calabar river system was generally near saturation (80.9 %). The highest mean DO concentration 5.5 ± 0.8 mg/l occurred at station 1 (range 2.40 - 7.0 mg/l). Low oxygen levels were measured at ebb tide and high levels observed at flood tide. The fluctuation is associated with the mixing and alteration processes occurring during the discharge of highly turbid waters from the creeks and mudflats into the river system at ebb tide. This is similar to the observation of Reid and Wood (1976) that fluctuation in dissolved oxygen can arise as a result of large inflow of fresh water especially during the rainy season. The microbial degradation of organic matter determined as BOD_5 (Biochemical Oxygen Demand) gave low values (highest mean 3.6 ± 2.2 mg/l at station 2) for the Calabar river system which is within the acceptable limit (10.0 mg/l) for nearshore waters (FEPA, 1988). Comparatively, the BOD_5 values were remarkably lower than values obtained from the streams and rivers of Jakarta which ranged from 50 - 100 mg/l (Bilal et al., 1975). BOD_5 values were higher at station 2 (2 - 10.0 mg/l) than station 1 (1.4 - 4.0 mg/l) and higher at flood than ebb tide.

The highest mean level of total suspended or filterable solids (TSS) measured was 10.7 ± 4.7 mg/l at station 2 (range 4 - 20 mg/l). Turbidity measurements gave 12.1 ± 6.2 NTU at station 2 (range 4 - 20 NTU). These values are comparatively low despite additions from surface runoff. TSS and turbidity levels fluctuated with tides. Turbidity was higher at ebb and low at flood tide, while TSS was high at flood tide and low during ebb tide (Fig. 2). Both parameters were higher at station 2 than station 1.

TABLE 3. Levels of tides, rainfall and current speed measured during the period.

Parameters	Wet Season ^a	Dry Season ^c	Ebb Tide	Flood Tide
Tide Range (cm)	76.0 maximum	54.0 maximum	58 - 35.0	25 - 76.0
Rainfall (mm)	788.4 - 782.1	9 - 326.9	-	-
Current speed (cm/sec)	2 - 24.4	5 - 24.8	24.0 maximum	20.0 maximum

- Rainfall data were obtained from the meteorological unit, Geography Dept; University of Calabar, Nigeria.
- Wet season: Sampling and measurements were made in October 1994, June, July, and October 1995.
- Dry season: Sampling and measurements were made in November and December 1994, Jan, Feb, March 1995, January 1996 and March 1996.

THC levels measured in the surface waters were exceedingly high. At station 1, THC values ranged from 22 - 55.8 mg/l (mean 27.3 ± 3.9 mg/l) while station 2 values ranged from 15.1 - 35.8 mg/l (mean 23.65 ± 5.6 mg/l). The THC

levels showed high variation with tides. Generally, higher values were obtained during flood tide than ebb tide indicating contribution from occasional spills emanating from oil production facilities at the outer estuary. The THC levels previously reported for the Cross river system was 2.2 mg/l (RPI, 1985). Measurements during the present

study were several orders of magnitude higher reflecting a polluted environment. THC concentrations determined were higher at station 1 than station 2. Diurnal distribution of THC showed a bimodal pattern at station 1 giving a higher peak at flood tide and low at ebb tide (Fig.3) while at station 2 the levels were low at flood and high at ebb tide. These variations are indicative of anthropogenic input influenced by maritime activities of cargo ships and oil tankers berthing at the Nigerian Ports Authority (NPA), Nigerian National Petroleum Corporation (NNPC)/Pipeline Products Marketing Company (PPMC) jetties all located downstream of station 1 but upstream of station 2. At flood tide, discharge at these jetties are transported upstream beyond station 1 and when the river recedes (ebb tide), the pollutants are carried downstream towards the estuary. This indicates that the tidal movement of the river assists in the dispersion and distribution of associated pollutant. THC levels above 10mg/l in coastal waters depict a polluted ecosystem (FEPA, 1988).

The concentration of total Fe was surprisingly low. Fe concentrations varied from 0.01 - 0.5mg/l at station 1 and 0.2 - 2.0 mg/l at station 2. Concentrations of Fe changed with tides. High concentrations were obtained during flood tide than ebb tide. Fe concentrations showed minimal fluctuation during the period. The concentrations were higher at station 2 than at station 1 (Fig. 2b). However, these concentrations are below FEPA limits (20mg/l) for coastal waters. The observed low value could be due to the reduction of dissolved and particulate Fe by microbial fauna and subsequent adsorption by the riverine sediments which have been reported to be grossly contaminated (Ntekim *et al.*, 1993). Silty sediments can act as sink for particulate Fe.

The proximity of station 2 to the estuary influenced both the levels, and diurnal variations of the physico-chemical and organic pollution indicators measured during the study. The generally low BOD observed is a reflection of the low input of organic matter in the Calabar river system. The hydrocarbon pollution of the river depicts the contribution of maritime activities (motorised boats and ships), uncontrolled discharge of oil at harbours and addition from surface erosion of vehicle maintenance workshops (mechanic workshop) from the municipality.

Potential sources of pollution:

Changes in water quality are expected depending on the nature of human activities prevalent in the area. The Calabar river shoreline is sparsely populated with few cottage industries still in operation. These include the Calabar Cement Company (CALCEMCO), Calabar Wood Company, Pipeline Products and Marketing Company (PPMC), Nigeria Ports Plc, Calabar Plastic Company among others. Liquid and solid wastes arising from the routine activities of these industries are channelled directly or indirectly into

the surrounding waters. Maritime activities such as cargo transportation, loading and off-loading of petroleum products at the jetties, conveyance of transit passengers between the riverine communities by motorised engine boats and sand mining are some of the routine operations carried out directly on the Calabar river. Environmental pollution emanating from each of these operations are yet to be fully investigated.

The Calabar river resources contribute substantially to the sustenance of Nigeria's economy in terms of fishery resources, navigation and tourism. Moses (1987) estimates the fishery yield of Cross river to be 6500 tons. At present, efforts are underway to develop the Calabar Port into an Export Processing Zone (EPZ). Unchecked discharge of effluents and solid wastes directly by households and operating industries shall alter the water quality of the system and may result in a prolonged degradation of the river as a resource vis a vis the adjoining estuary. Consumption of contaminated fishes are a potential health risk to both the local fishermen and the coastal communities. Recently, the impact of petroleum input (oil spillage) into the river has been quantified and the environmental effects observed were physiological stress on fish, reduction on fish fecundity and bio-accumulation of THC and heavy metal (Zn, Fe, Cr) by pelagic fishes (*Ethmalosa Fimbriata*) and dermal fishes (*Chrysichthys sp.*), (Mobil Report, 1988). Higher levels of hydrocarbon above the observed value can be lethal to fish.

RECOMMENDATION:

The deterioration of the surface waters can be minimised if the responsible governmental organs ensure regular monitoring and strict adherence of polluters to existing rules limiting the discharge of effluents into the aquatic systems. Presently, effective waste handling techniques are yet to be put in place by the responsible Federal Authorities (FEPA) to check unnecessary discharge of petroleum products and also the dumping of domestic/municipal waste into river. Strict policies such as "polluter pay principle" should be adopted in an effort to limit industrial effluent discharge into the system. Additionally, it will be necessary to improve oil handling facilities at the jetties and harbours. Oil released directly during cruises should be curtailed and the discharge of oily waste at harbours by motorised boats and ships prohibited.

CONCLUSION:

The present study has revealed that the Calabar river is heavily contaminated by hydrocarbons and that there is great fluctuation in the water quality factors changing with tides and from one station to another. All the measured water quality parameters were higher during the flood tide than the ebb tide with the exception of turbidity and temperature. No direct relationship

between pollutant concentration and current velocity was noticed and the observed diurnal variation in pollutant concentration was induced by changes in tidal flux.

The protection of the quality of coastal waters must be reasonably ensured. Life on earth depends on water and environmental impacts on water and its resources originating from man's activities are finally received by man through an elongated vicious cycle.

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REFERENCES:

- Adeniji, H. A. and C. I. Mbagwu, 1983. Study and Appraisal at the Water Quality of the Kantogora and Eku Rivers-Kainji lake Research Institute (K.L.R.I) Annual Report: pp. 17-22.
- Ajayi, S. O. and Osibanjo, O. 1981. Pollution studies on Nigerian Rivers 11 Water Quality of some Nigerian Rivers. Environ. Poll. Ser. B. Applied Science Publishers Ltd. England, pp. 87-95.
- APHA. 1980 Standard Methods for examination of water and waste water. Washington DC. American Public Health Association APHA 15th Edition.
- Asuquo, F. E. 1989. Water quality of the Calabar, Nigeria. Tropical Ecology 30: pp. 31-40.
- Bilal, J. S. Wahyu, Mulyono and Abuyiwono, A. Inventory data in the Bay of Jakarta. Caraka Lingkungan 1: pp. 3-6.
- FEPA 1988: National Interim Guideline and standard for industrial effluents: gaseous emissions and hazardous waste management in Nigeria. Decree 58 of 1988, 238 p.
- Inevbore, A.M.A. 1970. The chemistry of River Niger in the Kainji lake Reservoir area. Arch, Hydrobiol. 67: pp. 412-413.
- Mobil Report 1998. Port Impact Assessment (P.I.A) of Cross River State Coastal waters affected by Mobil (Idoho) oil spill. Report by Devman Konsult for C.R.S. Government, June 1998, 69p.
- Moses, B. S. 1987. The influence of flood regime on fish catch and fish communities of the Cross River State flood plain ecosystem, Nigeria. Environ. Biology of Fishes 18: pp. 51-56
- Ntekin, E. E. U., Ekwere S. J. and Ukpong, E. E. 1993. Heavy metals distribution in sediments from Calabar river, south-eastern Nigeria. Environ Geology 21: pp. 237-241.
- Reid, G. K. and Wood, Rd 1976. Ecology of Inland water and Estuaries, 2nd Ed. Van Nostrand, New York.
- RPI. 1985. Environmental Baseline studies for the establishment of control criteria and standards against Petroleum - related Pollution in Nigeria. Research Planning Institute (RPI), Inc USA. Final Report for NNPC. Lagos, Nigeria pp. 118-127.
- Rump, H. H. and Krist, 1988. Laboratory Manual for examination of water, waste Water and soil. Weinheim VCH, Verlag 190p.