Patterns of Total Hydrocarbon, Copper and Iron in Some Fish from Cross River Estuary, Nigeria

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Abstract

Muscle tissue of *Ethmalosa fimbriata* and *Chrysichthys nigrodigitatus* were collected between the period March and August 1999 from the Cross River Estuary, Nigeria, in order to assess possible anthropogenic impacts on these species. Levels of total hydrocarbons (THC > 6.0 p.p.m.) and Cu (> 2.6 p.p.m.) exceeded their WHO permissible limits (0.0001 and 0.02 p.p.m. respectively) in the fish tissues. Fe levels also exceeded the permissible limit (300 p.p.m.) in more than 13.3% of *C. nigrodigitatus* and 22.2% of *E. fimbriata* collected during the period. Lead was not detected in any of the fishes sampled. Inter-locational variation in mean concentrations of THC, Cu and Fe were minimal and insignificant ($P > 0.05$) except for *C. nigrodigitatus* sampled from Anantigha area ($P < 0.05$). Pollution pattern was in the order: Obufa Esuk (upstream) < Henshaw Town (midstream) < Anantigha (downstream), independent of weight and length of fish ($r < 0.3$, $P > 0.05$) but time –dependent ($P < 0.05$, ANOVA), especially in the accumulation of THC in *E. fimbriata* and Fe in *C. nigrodigitatus*. Linear relationship was found between Cu and Fe levels in *E. fimbriata* as described by the equation: $Y = 0.45 - 29.39 X$ ($r = 0.98$, $n = 18$, $P < 0.05$). *E. fimbriata* showed a higher affinity for Cu and Fe than *C. nigrodigitatus*. These results provide the baseline levels of these pollutants in the species investigated and also suggest that long term bioaccumulation of the toxins by these species is potentially hazardous, especially to coastal dwellers who consume them in large quantities yearly.

Introduction

It is well known that fish and shell fish commonly accumulate water-soluble petroleum products as well as heavy metals through their diet (Davies *et al.*, 1981; Denton & Burdon-Jones, 1986; Blackmore *et al.*, 1998). The Cross River Estuary is the largest estuary along the West African sub-region. It is located between longitude 8° 15' and 8° 30' E and latitude 4° 32' and 5° 12' N (Fig. 1). Sources of pollution include industrial discharges and municipal dumps (Ntekim, 1987; Etim & Akpan, 1991) and oil spills from point and non-point sources (Asuquo, 1998; Asuquo, 1999; Olagbende *et al.*, 1999). Its principal tributaries are the Calabar and Great Kwa Rivers (GKR) which are usually affected by oil spills (Devman Konsult, 1998). Observations in the Cross River system indicate the presence of enhanced level of pollutants such as lead, mercury, arsenic, total hydrocarbons and copper in the coastal waters and superficial sediments (Ntekim, 1987; Etim & Akpan, 1991; Asuquo, 1998).

E. fimbriata and *C. nigrodigitatus* are found spawning in the inshore waters of Nigeria. They were chosen for this study because they are the second and third major components (12.2% and 10.8%, respectively) of fisheries in the Cross River Estuary, after *Pseudotolithus elongatus* (66.5%), (Holzlohner *et al.*, 1998). The paper presents data on the levels of total hydrocarbons, copper, iron and lead in the tissues of resident and migratory *E. fimbriata* and *C. nigrodigitatus* from the Calabar and Great Kwa Rivers of southeast Nigeria. It further relates the size of fish to pollution patterns of hydrocarbons and heavy metals in coastal fishes.

Materials and methods

E. fimbriata and *C. nigrodigitatus* of total length 6 cm to 8 cm were obtained fortnightly directly from fishermen at three fishing stations; Obufa Esuk (upstream) at Great Kwa River, Henshaw Town (midstream) at Calabar river and Anantigha (downstream GKR) (Fig. 1.) Samples were collected from March to May 1999 for *E. fimbriata* (due to its natural seasonal occurrence) and from March to August 1999 (except June) for *C. nigrodigitatus* using drag nets. On collection, fish samples were immediately weighed and their total length measured to the nearest 0.1g or 0.1 cm respectively. They were then frozen and transported in plastic bags to the laboratory for analysis.

Individual fish was filleted in a manner as to remove all skin, scales, bones and excess blood. All filleted muscle samples were cut from the left side of the fish for analysis (Santoro & Koepp, 1986). For total hydrocarbon (THC) determinations, 3 g wet weight of fresh fillet muscle were digested with methanol: 20% brine solution in a soxhlet apparatus and later determined by UV Spectrophotometry (HACH DREL 3000,450 nm).

Copper, iron and lead concentrations were determined by digestion of 1 g of ground oven-dried tissue samples (175 °C for 3 days) in a mixture of 40% nitric and 80% sulphuric acids. The digested samples were allowed to stand over-night at room

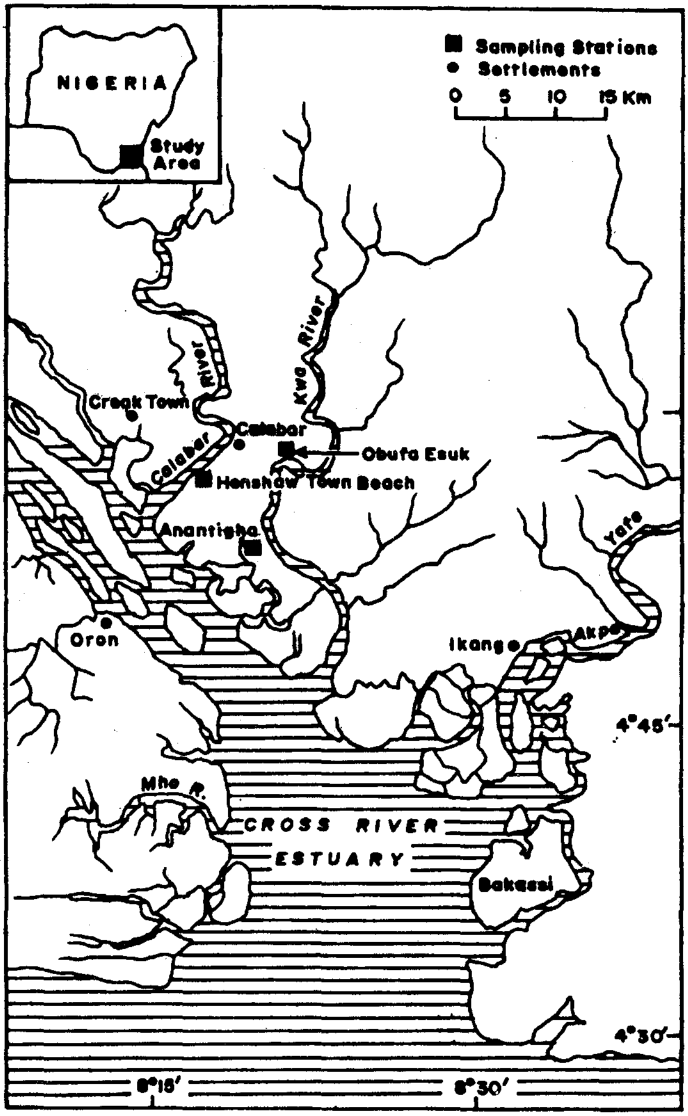

Fig. 1. Map of the Cross River Estuary showing the locations of the Calabar River and Great Kwa Rivers and the sampling stations

temperature before AAS analysis (Asuquo, 1998; Kotz *et al.*, 1972). To ensure quality assurance and control of determination, each sample analysis was duplicated and compared with standard solutions (reference material) of the specific metal. Coefficients of variation were less than 4% for the parameters investigated. All results were subjected to statistical analysis using linear regression and ANOVA techniques.

Results

Average total hydrocarbon and metal concentrations in the fish species analysed over the sampling period for each station are presented in Table 1. Lead concentrations were very low and undetectable (< 0.05 p.p.m.) in all fish analysed. Mean concentrations of total hydrocarbon, copper and iron in *E. fimbriata* were 6.91, 7.02 and 206.75 p.p.m., respectively. The iron content was considerably higher than other pollutants (THC and Cu). In *C. nigrodigitatus* the order of increasing magnitude for metals was Fe < Cu, each pollutant being markedly different from the other (F-test, $P < 0.05$). *E. fimbriata* showed a higher affinity for Cu and Fe than *C. nigrodigitatus.*

There was no significant spatial variation ($P > 0.05$) per pollutant concentration in the three sampling stations except for total hydrocarbon concentrations in *E. fimbriata* where the levels in fish samples from Obufa Esuk were significantly lower ($P < 0.05$) than those obtained from Henshaw Town and Anantigha (Table 1). Mean Fe concentration (*ca* 204 p.p.m.) was similar for both species at Anantigha. However, an F-test of the cumulative mean pollutant concentration per species per site revealed that *C. nigrodigitatus* and *E.*

TABLE 1

Levels of total hydrocarbon, copper and iron (in dry tissues weight) per sampling station

Sampling station	* *Mean pollutant level (p.p.m.)*		*Minimum*		*Maximum*		*S.E.*	
	Total hydrocarbon							
	C.N.	*E.F.*	*C.N.*	*E.F.*	*C.N.*	*E.F.*	*C.N.*	*E.F.*
Obufa Esuk (OE)	17.97	5.26^a	5.0	3.48	30.44	7.16	2.68	0.49
Henshaw Town (HT)	9.47	7.67^b	3.84	4.43	17.12	13.36	1.51	1.22
Anantigha (AN)	17.3	17.80^c	2.20	4.43	35.92	14.76	2.78	1.46
Cumulative	14.78	6.91	2.20	3.48	35.92	14.76	1.33	0.37
	Copper							
OE	2.70	6.87	1.41	5.23	4.02	11.76	0.30	1.01
HT	2.82	6.18	1.67	5.23	4.02	7.90	0.25	0.38
AN	2.28	6.94	1.77	2.84	4.02	12.65	0.25	1.82
Cumulative	2.60	7.02	1.41	2.84	4.02	12.65	0.10	0.46
	Iron							
OE	135.39	234.13	73.08	154.5	242.58	346.28	16.44	35.22
HT	128.92	182.02	52.20	153.8	367.80	232.20	37.65	11.09
AN	205.54	204.11	39.12	83.46	506.10	372.02	54.33	53.47
Cumulative	149.95	206.75	39.12	83.46	506.10	372.02	21.19	13.53

* Pb concentration in all the samples were consistently below limits of analytical detection (< 0.05 p.p.m.); + = on wet weight basis; abc = means ($\bar{x}$) in each column having the same superscript are not significantly different ($P > 0.05$). C.N. = *C. nigrodigitatus*; E.F. = *E. fimbriata.*

fimbriata sampled from Anantigha (downstream) were significantly ($P < 0.0001, n=30$) contaminated with Cu, when compared to other locations. Generally, the results obtained disclosed that both species show a low degree of variability for copper and total hydrocarbons (SD < 9.0; max. SE $= 2.78$) within the sampling stations compared to that observed for iron (SD > 28, max. SE $= 54.33$).

Maximum pollutant concentrations in individual fishes are shown in Table 1. Only 22.2% and 13.3% of *E. fimbriata* and *C. nigrodigitatus,* respectively, from these areas accumulated iron in their tissues above permissible levels. Much of this cane from those sampled from Anantigha (Table 3). All fish sampled had accumulated total hydrocarbon and copper levels above the World Health Organization permissible limits (Fig. 2).

Pairwise correlation analysis was performed on the data. Cu and Fe were haphazard and independent of fish length and fish weight ($P > 0.05, r < 0.03, n=18$). The only significant r value ($P < 0.05, r = 0.98, n = 18$) was found between Cu and Fe in *E. fimbriata*: $Y = 0.45 + 29.39\,X$. This suggests a linear average between the two metals in this fish and similar source of pollution.

Discussion

During the study, all the fish samples analysed accumulated Cu and total hydrocarbons above the WHO permissible level (0.02 and 0.0001 p.p.m., respectively). The iron content of more than 20% of the fish sample during the study exceeded the minimum permissible limit (300 p.p.m.). The range of pollutant concentrations in the study are in agreement with those obtained a year earlier by Asuquo (1998). This pollution level is alarming and is attributed to the industrial, oil exploration/production and water transportation activities around the Calabar and Great Kwa Rivers of the Niger Delta region of Nigeria. No lead pollutant was detected in the fishes sampled.

The patterns of accumulation of the pollutants by the species investigated are clearly visible (Table 1). While Cu showed a decreasing trend from *E. fimbriata* to *C. nigrodigitatus* (asterisked *), Fe and THC

TABLE 2

Monthly levels of THC, Cu and Fe (in dry tissue weight)

Fish	*Month*	*Means ± SE (p.p.m.)*		
		THC	*Cu*	*Fe*
E. fimbriata	March	6.94 ± 0.49^{a}	5.62 ± 0.92	165.73 ± 25.42
	April	6.32 ± 0.39^{a}	7.99 ± 1.49	234.96 ± 43.74
	May	7.92 ± 2.01^{b}	8.23 ± 1.49	230.45 ± 40.93
	Grand mean	6.91 ± 0.37	7.02 ± 0.46	206.75 ± 13.53
C. nigrodigitatus	March	13.67 ± 2.99	2.78 ± 0.26	196.96 ± 46.51^{a}
	April	16.99 ± 3.58	2.75 ± 0.25	140.81 ± 47.46^{b}
	May	9.98 ± 3.51	2.78 ± 0.46	225.02 ± 98.33^{a}
	July	14.66 ± 4.15	2.24 ± 0.42	119.35 ± 34.21^{a}
	August	13.25 ± 1.10	2.74 ± 0.38	78.64 ± 8.85^{b}
	Grand mean	14.78 ± 1.33	2.60 ± 0.10	149.95 ± 21.19

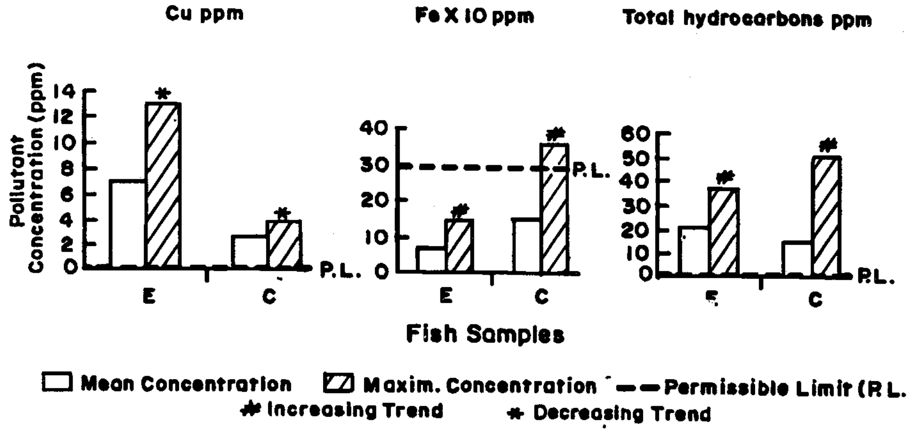

Fig. 2. Mean and maximum total extractable metals and hydrocarbons in fish species compared to permissible limits.(P.L.) (E - *Ethmalosa fimbriata*; C - *Chrysichthys nigrodigitatus*); # Increasing trend, * Decreasing trend.

TABLE 3

Relative levels of THC, Cu, and Fe in the study area

Above permissible level (WHO)	*Obufa Esuk* *N% month*	*Henshaw Town* *N% month*	*Anantigha* *N% month*	*Cross River Estuary (cumulative)*
		E. fimbriata		
> 0.01 – 0.02 p.p.m. Cu*	100%, a.t.s.p	100%, a.t.s.p	100%, a.t.s.p	100%
> 300 p.p.m. Fe	33%, Apr, May	0%, a.t.s.p	33%, Apr., May a.t.s.p	22.2%
>0.0001 p.p.m. THC	100%, a.t.s.p	100%, a.t.s.p	100%, a.t.s.p	100%
		C. nigrodigitatus		
>0.01 – 0.02 p.p.m. Cu*	100%, a.t.s.p	100%, a.t.s.p	100%, Apr, May	100%
> 300 p.p.m. Fe	0%, a.t.s.p	20%, Apr, May	20%,May	13.3%
>0.0001 p.p.m. THC	100%, a.t.s.p	100%, a.t.s.p	100%, a.t.s.p	100%

N = Occurrence frequency (%); a.t.s.p = all through study period; GKR – Great Kwa River.
* Cu levels above unpolluted nearshore waters (Chung & Brinkhuis, 1986).

increased (marked #). This observation portrays the characteristic conservative behaviour of Cu during estuarine mixing (Roux *et al*., 1998). It further suggests that the Cu is bio-accumulated more in their suspended particulate matter (SPM) than the dissolved fraction, which explains why *E. fimbriata* (pelagic) had a higher accumulation of Cu than *C. nigrodigitatus* (dermesal) in their tissues (Fig. 2). On the other hand, THC is available for absorption principally as dissolved fraction especially during accidental oil spills.

Accumulation of total hydrocarbons in *E. fimbriata* and Fe in *C. nigrodigitatus* were shown to be seasonal–dependent ($P < 0.05$) especially in wet season, probably due to the inputs of oil and metal–contaminated detrital matter washed from vehicle maintenance (motor mechanic) workshops during heavy rains (Table 2). Heavy rainfall starts from May in the study area annually.

The variability in the concentrations of Cu and THC is similar to that observed by Denton & Burdon–Jones (1986). The low variability suggests that both *E. fimbriata* and *C. nigrodigitatus* employ different mechanisms in their bio-accumulative tendencies of Cu and THC, on one hand, and iron on the other. However, further examination revealed marked inter-species differences in mean iron content of *E. fimbriata* and *C nigrodigitatus* at Obufa Esuk sampling station: 234 and 135 p.p.m., respectively. This is affirmative of the finding that the potential for bio-accumulation is strictly dependent on the type of fish, nature and the characteristic behaviours of the chemical species during estuarine mixing.

Significant differences in the concentrations of the pollutants were observed in all the sampling stations (Table 1). This could be due to the proximity of the area to pollution sources and the retentive ability of each environment to added pollutants. Higher concentrations found in 65% of fish caught downstream (Anantigha) are indicative of a more anthropogenically perturbed area than the other (middle and upstream) locations. The characteristic network of rivulets and creeks in the Anantigha area and the meandering system of these channels restrict free flow of coastal water such that the circulation and bio-accumulation of pollutant by migratory fish species are enhanced.

Characteristically, the rivers (Calabar and GKR) are semidiurnal and shallow. The upstream sampling station at Obufa Esuk is, therefore, likely to be influenced by pollutants transported upstream through tidal incursions and water movement (current reversal). The impact of this movement is observed in the mean pollutant concentration of Fe (approx. 234.0 p.p.m.) in *E. fimbriata* at Obufa Esuk being markedly higher than could be expected in the upstream segment of the estuary (Table 1).

Since *E. fimbriata* and *E. nigrodigitatus* constitute the major food fishes of the coastal population, the danger of bio-accumulation of Cu, Fe and THC in humans through the food chain is a great possibility and needs to be checked. Cu is known to exert physiological stress on early stages of Kelp, *Tamineria saccharina* (Chung & Brinkhuis, 1986) and persistent accumulation could lead to death of fish and harm to local consumers. Presently in Nigeria, combating pollution is more of a local effort rather than regional and or international. With limited scientific capability, pollution monitoring and assessment is often neglected. International organizations and environmental agencies in collaboration with the recognized national environmental bodies must show concern towards developing sustainable and practical policies in the management and utilization of both fisheries and natural resources derived in these areas. Such policies are highly desirable since they help to check anthropogenically induced pollution and the conservation of the aquatic environment.

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