PRESENCE OF HYDROCARBONS AND HEAVY METALS IN SOME FISH SPECIES IN THE CROSS RIVER, NIGERIA.

8

Olaifa, F.E. and Ayodele, I.A.
Department of Wildlife and Fisheries Management University of Ibadan, Nigeria.

ABSTRACT

The study was undertaken to determine the total hydrocarbon (THC) and heavy metal contents of fish (finfish and shellfish) in the Cross River, Nigeria. Fish Samples were collected in the dry (March) and rainy (October) seasons between 2000-2002. The finfish species identified in the study were Synodontis clarias, Sarotherodon galilaeus, Heterotis niloticus, Schilbe mystus, Parachanna obscura, Citharinus citharus, Mormyrus rume, Phago loricatus and Petrocephalus ansorgii and the shellfish were Macrobrachium vollenhovenii and Tympanotonus fuscatus.

Significant differences ($P<0.05$) existed between finfish and shellfish in both THC and heavy metals contents. The levels of THC in fish exceeded the World Health Organization's limit of 0.0001 ppm by an average of 3.2 and 15.57 mg/kg in fin and shellfish respectively. High concentrations of vanadium and THC in fish samples were the main indicators of pollution from petroleum sources.

Key words: THC, heavy metals, finfish, and shellfish, Cross River, Nigeria.

INTRODUCTION

Nigeria has a rich variety of fin and shellfish resources. The exploited fishery resources in Nigeria are basically pelagic and demersal (Mabawonku, 1993). The environment in the coastal areas is subjected to the effects of pollution, which may be from industrial effluents, solid wastes, domestic sewage, crude oil spillages, atmospheric fallouts from gas flares, spent lubricating oil, tanker ballast water, leakages from sea-going or marine vessels and outboard engines.

These wastes usually contain various proportions of toxic metals such as zinc, lead, copper, vanadium, antimony, arsenic, beryllium, mercury, cadmium, nickel and chromium. Apart from direct toxicity, these trace metals may accumulate in the food chain and threaten human health (Mason, 1992).

Within the concept of monitoring, the chemical concentration of substances in organisms are regarded as indicators of bio-available fractions in the environment (Zauke *et al*,1995). At low concentrations, many trace elements act as micronutrients and may be essential for growth but higher concentrations may be toxic. The gap between the optimal and toxic concentration is usually very small (Santschi, 1988).

The rate of accumulation depends on the concentration of the pollutant in water (Kelly, 1988; Barak and Mason, 1989), temperature and salinity (Philips, 1980). The internal factors that affect bioaccumulation include the physiological conditions like fat content, (Sagiura *et al*, 1978) and periods of fast growth, which correlate with low accumulation (Mance, 1987). Fishes with higher metabolic rates accumulate pollutants faster and feeding results in a greater uptake of pollutants across the gills (Douben, 1989). The accumulation of a contaminant is also a function of its uptake and elimination.

The objective of this study is to assess the hydrocarbon and heavy metal content of some fish species present in the Cross River, Nigeria.

MATERIALS AND METHODS

Fish samples were obtained directly from fishermen at the study sites (fig. 1) and frozen before analysis. Each fish was allowed to thaw partially, skinned and filleted (avoiding skin, bones and scales). For hydrocarbon (THC) determination, 3g wet weight of fresh muscle fillet was digested with methanol: 20% brine solution in a soxhlet apparatus and quantified using UV Hach spectrophotometer (DREL 3000) while heavy metals presence was analyzed using the method of FAO/SIDA (1983).

RESULTS

The fin and shellfish species identified in the study area are presented in table 1.

Table 1: Fish species identified in the study area.

Fin Fish		Average Length (cm)
Station 6		
	Synodontis clarias	17.5
	Sarotherodon galilaeus	10
	Heterotis niloticus	48.0
	Schilbe mystus	16.5
	Parachanna obscura	37
Station 7		
	Citharinus citherus	11.5
	Mormyrus rume	1.5
	Phago loricatus	12
	Parachanna Obscura	15
	Petrocephalus ansorgii	14

UNIVERSITY OF IBADAN LIBRARY

Shellfish:

Macrobrachium vollenhovenii was present at many stations except 3, 5 and 8 while *Tympanotonus* fuscatus (periwinkle) was found at stations 5, 6 and 7.

Total hydrocarbon content of the fish:

Measurable quantities of hydrocarbon were recorded in both fin and shellfish studied. The total hydrocarbon contents of fish are given in table 2.

Table 2: Total hydrocarbon content of the fish *(mg/kg)*

Station 6 Finfish species	Dry Season	Rainy Season
Heterotis niloticus	2.8	1.0
Schilbe mystus	3.0	1.0
Sarothendon galilaeus	0.9	0.4
Synodontis Clarias	2.5	1.2
Parachanna obscura	3.5	1.5
Station 7		
Citharinus citherus	2.5	1.0
Mormyrus nime	15.5	8.0

Shellfish

1. *Macrobrachium vollenhovenii*

Stations	Dry Season	Rainy season
1	20.5	15.0
2	25.3	18.5
3	NA	NA
4	39.2	20.1
5	NA	NA
6	13.0	7.0
7	14.3	7.0
8	NA	NA
9	15.5	8.0

2. *Tympanotonus fuscatus*

Stations	Dry Season	Rainy season
5	0.8	0.6
7	1.0	0.9

NA = not available

The THC contents of fish ranged from 0.9 - 15.5 mg/kg in the dry and 1.0 - 8.0 mg/kg in the rainy season. The THC content of *M. vollenhovenii* ranged from 13.0 to 39.2 mg/kg and 7.0 to 20.1 mg/kg in the dry and rainy seasons respectively, while in *T. fuscatus* the ranges were 0.8 to 0.1 and 0.6 - 0.9 mg/kg in the dry and rainy seasons respectively. The mean dry and wet season THCs were 4.39 and 0.99 mg/kg (finfish), 21.5 and 12.9 mg/kg (*M.vollenhovenii*) and 0.9 and 0.75 mg/kg (*T. fuscatus*) respectively.

Heavy metal content of fish

All the heavy metals of interest were recorded in all fish species (fin and shellfish). The contents of heavy metals in fish are shown in table 3.

It was not possible to assess the fish and shellfish at stations 3 and 8 due to the inability to obtain samples.

DISCUSSION

Total Hydrocarbon Content of fish

The presence of hydrocarbon, especially floating oil disturbs the respiration of aquatic organisms and lowers the productivity of the impacted area (Tait, 1978). It may also affect the biological diversity (Clark *et al.*, 1997). This was observed during this study as fish could not be obtained at some locations and fishermen complained of low catches. This observation is similar to that of low abundance of fish and shellfish reported in the area during fecundity studies (Mobil Report, 1998; Asuquo *et al*, 1999).

The content of hydrocarbons in the different fish species were observed to be time-dependent as higher concentrations were observed in the dry than rainy seasons. All fish studied accumulated hydrocarbons above the World Health Organization permissible limits of 0.0001 ppm. The highest THC was recorded for *M.vollenhovenii* and the least in *T. fuscatus*. The accumulation of THC in fish followed the order:

Macrobrachium sp > finfish > *T. fuscatus*.

THC is available for absorption mainly as the dissolved fraction especially due to oil spills. The accumulation of hydrocarbons may be organism-specific for example, *Mormyrus rume* is a bottom dweller and insectivorous, which may allow more avenues for hydrocarbon absorption. The accumulation of hydrocarbons may also be as a result of more absorption than excretion allowing more retention of hydrocarbons within the organism.

Heavy Metal Content of fish

In most fish studied, Fe or Zn was the dominant metal while Pb or Cd was least. The content of Cu, Zn, Pb and Cd in fish were generally below the WHO acceptable limits (Kakulu *et al*, 1987a). The concentrations of the

UNIVERSITY OF IBADAN LIBRARY

metals recorded during this study were higher than those obtained for the Niger Delta Area inland water fish (Greichus *et al*, 1978a). The iron content of fish recorded was generally less than the 300-ppm minimum permissible limit recommended by WHO. Cr is both essential and carcinogenic and needs to be properly monitored. Cr (III) is not harmful but Cr (VI) is. The presence of vanadium is an indication of contamination from petroleum.

This study considered heavy metal concentration in fish muscle only. However, Sadik (1990) reported higher concentrations of some heavy metals in the liver of tuna species than muscles, the croakers showed the lowest content while the Bonga species contained little or no heavy metals. It has also been suggested that Cd and Pb are not significantly regulated in the liver (Philips,1977). Significant differences ($P < 0.05$) of heavy metals in fish tissues have been reported with fish muscles having the least (Chaohua, 1994).

Shellfish species have been useful as indicators of pollution in biomonitoring (Zauke, *et al*, 1995; Viera, *et al* 1995 and Roesijadi, *et al*, 1997). Higher concentrations ($P<0.05$) of heavy metals were recorded in shell than finfish. Other workers observed a lower bioaccumulation potential for *T. fuscatus* than other mollusks (Momoh, 1995; and Oyewo, 1998).

CONCLUSION AND RECOMMENDATION

Pollutants like hydrocarbons and heavy metals are present in the rivers and coastal waters of Cross River and Akwa Ibom States of Nigeria. Shellfish species generally concentrated more hydrocarbons and heavy metals than finfish due to their more sedentary nature. Bioaccumulation of metals usually occurs due to the competition between uptake and elimination of elements. The accumulation of metals in fish observed in this work could be due to the absorption of element directly across body surfaces, membranes and diets at a faster rate than excretion. There is a need to carry out regular monitoring of the environment to evaluate and enforce effluent and emission standards. Negative industrial processes that allow pollutants into the environment should be discouraged and improved waste management such as recycling and reuse be encouraged.

Table 4: The Correlation matrix for heavy metals in fish muscle

Variable	Cu	Fe	Zn	Mn	Pb	Cd	Cr	V
Cu	1							
Fe	-0.2	1						
Zn	0.23	-0.5	1					
Mn	0.99*	-0.13	0.19	1				
Pb	0.16	0.78*	-0.39	0.17	1			
Cd	0.56	-0.9	-0.48	0.53	0.3	1		
Cr	-0.15	0.12	-0.19	-0.1	-0.4	-0.35	1	
V	0.27	0	0.18	0.23	0.3	0.44	0.76*	1

Table 5. Mean Heavy Metal Contents (ppm) of Fish in the Dry and Wet Seasons

	Heavy Metals							
Wet Season	Cu	Fe	Zn	Mn	Pb	Cd	Cr	V
Finfish	3.15	79.92	75.74	18.31	0.29	0.31	1.18	0.93
shellfish:								
M. vollenhovenii	24.71	122.23	122.5	49.23	3.08	1.3	2.09	1.43
T. fuscatus	27.26	147.95	16.2	54.81	4.13	1.1	1.35	1.75
Dry Season								
finfish	3.98	79.96	74.04	16.79	0.59	0.36	1.5	1.1
shellfish:								
M. vollenhovenii	26.02	127.93	126.42	54.4	4.44	1.1	2.63	2.05
T. fuscatus	25.15	138.5	14.1	49.75	2.52	1.8	1.23	0.78

UNIVERSITY OF IBADAN LIBRARY

Table 3: Heavy Metals in biota

Station 6	Cu		Fe		Zn		Mn		Pb		Cd		Cr		V
Finfish species	March	October	March	October	March	October	March	October	March	October	March	October	March	October	March
Heterotis niloticus	0.875	1.125	65.5	64.75	74.5	75	7.05	5.125	0	0.25	0.125	0.125	2.375	2.125	0.625
Schilbe mystus	11.75	14.75	68.75	70.625	84.15	82.5	76.5	74.875	0.25	0.75	0.5	0.625	1.75	1.5	1
Sarotherodon galilaeus	1.875	2.625	59.5	58.375	54.25	52.5	7.25	5.875	0.125	0.5	0.625	0.625	1.625	1.375	1
Syndontis Clarias	1.625	2.125	73.25	72.375	98.5	96	8.375	6.875	0.125	0.375	0.25	0.125	1.875	1.25	1.125
Parachanna obscura	1.335	1.375	133.75	136.25	56.5	55	7	6.25	0.625	0.875	0.2	0.375	1.875	1.75	0.875
Station 7	2	3.125	101.2	99	64.5	62.5	14.5	13	0.5	0.875	0.375	0.375	1.5	1.25	1
Citharinus citherus	2.55	2.75	57.5	58.375	97.75	95	7.5	5.5	0.375	0.5	0.125	0.25	1.25	1.35	0.9
Mormyrus rume															

Shellfish Species (1) *Macrobrchium sp*																
Stations	Cu		Fe		Zn		Mn		Pb		Cd		Cr		V	
	March	October	March	October	March	October	March	October	March	October	March	October	March	October	March	October
1	40.5	45.625	152.35	155.625	126.5	135.5	101	105.5	2	4.375	1.125	1.05	2.05	3	1.5	2.5
2	19.75	20.375	125.25	145.375	121	120.5	13.25	15.75	1	2.625	1	0.95	0.75	1.5	1	1.1
3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4	44.25	43.375	140.5	143.375	118.75	117.5	102.5	112.13	5.5	5.375	1.75	1.25	3.25	2.75	1.5	2.5
5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
6	21.75	22.625	145.5	148.625	198.5	207.5	60	69	3.75	7.375	2	1.75	2	2.875	2.05	3
7	12	12.5	47.25	49	50.75	57.5	10.15	13.75	1.5	1.625	0.85	0.75	0.5	1.125	1.5	2
8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
9	10	11.6	122.5	125.5	119.5	120	8.5	10.25	4.75	5.25	1.05	0.875	4	4.5	1	1.2

Shellfish (2) *Tympanotonus fuscatus*																
Stations	Cu		Fe		Zn		Mn		Pb		Cd		Cr		V	
	March	October	March	October	March	October	March	October	March	October	March	October	March	October	March	October
5	25.75	24.75	144.25	134.75	14.25	13.7	53.75	49.25	3	1.78	1	0.75	1.55	1.7	1	0.875
7	28.76	25.55	151.65	142.25	18.15	14.5	55.875	50.25	5.25	3.26	1.2	1.05	1.15	0.75	0.5	0.675

UNIVERSITY OF IBADAN LIBRARY

REFERENCES

Asuquo, F.E.; Ogri, O.R. and Bassey, E.S. (1999). Distribution of Heavy metals and Hydrocarbons in Coastal Water and Sediments of Cross River State, South Eastern Nigeria. *International Journal of Tropical Environment,* 1(2) pp 229 - 242.

Barak, N. A. E. and Mason, C.F. (1989). Heavy Metals in Water, Sediment and Invertebrates in Eastern England. *Chemosphere,* 19: pp 1709-1714.

Chaohua, L. (1994). Studies on Heavy Metals in Commercial Fishes from the Northern part of South China Sea. *Journal of Fisheries Science, China/Zhogguo Schichan kexue* Vol. (1) pp 68-77.

Clark, R.B.; Frid, C and Atrill, M. (1997). Marine Pollution. 4th Edition. Oxford University Press, New York.

Douben, P.E.T. (1989). Uptake and Elimination of Water borne cadmium by Fish *Noenacheilus barbatulus* L. (stoneloach).*Archives of Environmental Contamination and Toxicology,* 18 pp 576 -586.

FAO/SIDA (1983). Manual of Methods in Aquatic Environmental Research. Part 9: Analyses of Metals and Organchlorines in fish. *FAO Fisheries Technical Paper* 212.

Greichus, Y.A. *et al,* (1978a). *Bulletin of Environmental Contamination and Toxicology* 19: pp 444-453.

Kakulu, S.E. Osibanjo, O. and Ajayi, S.O. (1987a). Trace metal Content of Fish and Shellfishes of the Niger Delta Area of Nigeria. *Environment International* 13:247-251.

Kelly, M. (1988). Mining in The Freshwater Environment. Elsevier, London.

Mance, G. (1987). Pollution Threat of Heavy Metals in Aquatic Environment. Elsevier,London.

Mabawonku, A.F. (1993). Conflict and Conflict Resolution in the Conservation and Management of the Fisheries Resources of Nigeria. *Proceedings of the National Conference on Conservation of Aquatic Resources* (Eds. Egborge, A.M., Omoloyin O.J., Olojede, A. and Manu, S.A.). Pp 234 - 243.

Mason, C.F. (1992). Biology of Freshwater Pollution. 2nd Edition. Longman Scientific and Technical, John Wiley and Sons, New York pp219-246

Mobil Report (1998). Post Impact Assessment (PIA) of Cross River State Coastal Areas Affected by Mobil (Idoho) oil spill. Government of Cross River State of Nigeria.

Momoh, A.E. (1995). Bioaccumulation of Lead by *Clibanarius africanus* (Aurivillus) Exposed to Sublethal Concentrations of Spent Engine Oil. M.Sc. Thesis, University of Lagos, 25 pp

Oyewo, E.O. (1998). Industrial Sources and Distribution of heavy metals in Lagos Lagoon and their Biological Effects on Estuarine Animals. A Ph.D. Thesis submitted to the University of Lagos. Pp 223.

Philips, D.J.M. (1977). The use of Biological Indicator Organisms to Monitor trace Metal Pollution in Marine Estuarine Environments. A Review. *Environmental Pollution,* 13 pp 281 - 317.

Philips, D.J.M. (1980). Quantitative Aquatic Biological Indicators. Applied Science Publishers, London.

Roesijadi, G.; Hensen, K.M. and Unger, M.E. (1997). Concentration - Response Relationship for Cd, Cu and Zn and Metallothionen. MRNA Induction in Larvae of *Crassostrea virginica. Comparative Biochemistry and Physiology,* Volume 118(3) pp 267 - 270.

Sadik, O.A. (1990). Heavy Metal Contaminants in some Nigerian Marine Fishes of Commercial Imporatnce. *NIOMR Technical Paper,* No. 63 pp 1-16.

Sagiura, K.; Wushino, T.; Hattori, M; Sato, E. and Goto, M, (1978). Accumulation of Organochlorine Compounds in Fishes. Differences of Accumulation factors by Fishes. *Chemosphere,* 9:pp 359-364.

Santschi (1988). Factors Controlling the Biogeochemical Cycles of Trace Elements in Fresh and Coastal Marine Waters as revealed by Artificial Radioisotopes. *Limnology and Oceanography,* 33 (4 part 2) pp 846 - 866.

Tait, R.V. (1978). Elements of Marine Ecology. An Introductory Course. 2nd Edition. Butterworths, London.

Viera, L.M., Alho, C.J.R., Ferreira, G.A.L.(1995) Mercury Contamination in Sediment and in Mollusks of Pantanal, Mato Grosso, Brazil. *Revista Brasileira de Zoologica,* Vol. 12(3) pp 663-670.

Zauke, G.P. Bernds, D. Janssen, H - J, Clason, B., Meurs, H - F. (1995) Metals in Organisms of the lower Saxonian Wadden Sea near Norderney (1991 - 1994). Pb, Cd, Cu, Zn, and Hg in selected Mussels (Bivalvia) and polychaetes (polychaeta) *Ber Forschungsstell Kueste* 1, vol. 40.

UNIVERSITY OF IBADAN LIBRARY

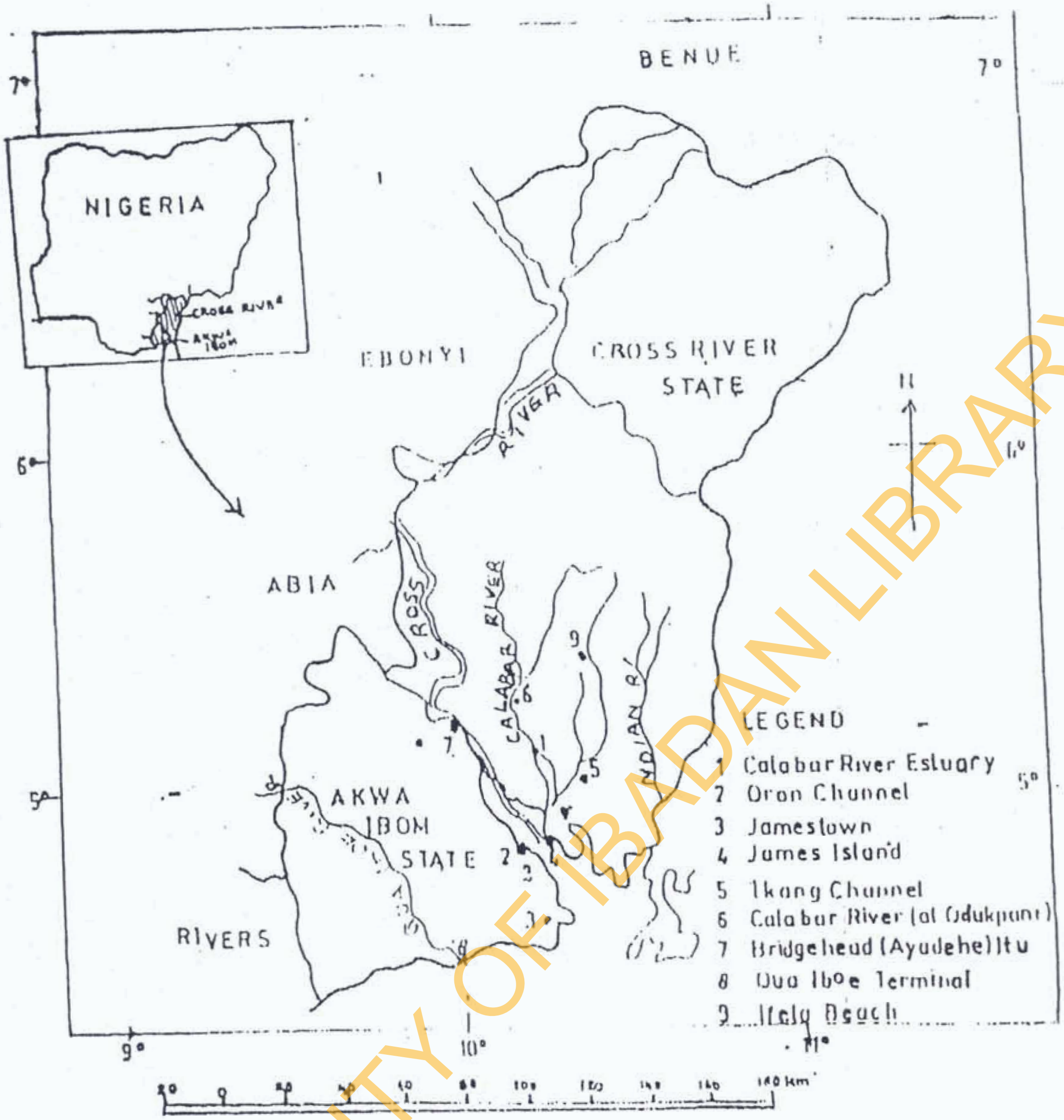

FIG I : MAP OF AKWA IBOM AND CROSS RIVER STATES SHOWING THE STUDY LOCATIONS

UNIVERSITY OF IBADAN LIBRARY