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TRACE METAL LEVELS IN *TYMPANOTONUS FUSCATUS* FROM QUA IBOE RIVER ESTUARY IN NIGER DELTA REGION OF NIGERIA.

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Abstract: *The levels of nine trace metals (Ni, Cr, Mn, Co, Cd, Fe, Zn, Cu and Pd) in Tympanotonus fuscatus samples from six sampling stations in Qua Iboe river Estuary were determined during wet and dry seasons covering May through February of the following year. There was no seasonal significant difference in the levels of these metals but the degree of accumulation differed from site to site. The respective ranges in concentrations for the metals during wet and dry seasons were: 1.99-19.21*mgg^{1} *and 1.92-19.15*m gg^{-1} *for Ni; 0.54-6.96*m gg^{-1} *and 0.58-1.02*mgg^{-1} *for Cr, 12.89-715.72*mgg^{-1} *and 12.23-689.90*mgg^{-1} *for Mn; 036-2.25*mgg^{-1} *and 0.38-2.57*mgg^{-1} *for Co; 0.39-0.97*mgg^{-1} *and 0.37-0.98*mgg^{-1}*for Cd; 5.60-205.99*mgg^{-1} *and 4.35 200.72*mgg^{-1} *for Fe; 6.75 109.95*mgg^{-1} *and 6.54-119.22*mgg^{-1}*for Zn; 0.37-6.51*mgg^{-1} *and 0.30 6.41*mgg^{-1} *and 3.20-31.90*mgg^{-1} *and 1.96 32.37*mgg^{-1} *for Pb. Cobalt showed very high seasonal coefficients of variation of 87.40% and 96.50% at location 1 during wet and dry seasons respectively. On the other hand, very low coefficients of variation were recorded by Ni (1.80%) at location 3 and Mn (0.44%) at location 2 during dry season. The possible health implication of consuming Tympanotonus fuscatus is also discussed.*

INTRODUCTION

Accumulation of toxic and persistent substances in seafood is of great concern to environmentalists. Although aquatic ecosystems naturally contain trace levels of metals essential for the growth of aquatic organisms, the concentration of these metals in seafood in recent times has increased due to anthropogenic inputs of domestic, chemical and industrial wastes often dumped indiscriminately into the aquatic environment. Additional inputs occur through runoff or accidental discharges. According to Hester (1976). concentrations of heavy metals in aquatic environments and marine organisms have been of considerable interest because of their toxicity effect particularly on man. While some of these metals such as Ca, Fe, Cu, Zn, etc., are essential nutrients, some are toxic in higher concentrations while others like Pb, Cd and Hg are never known to be physiologically useful at all (Udosen, 2000). The trace metal becomes highly toxic when present in high concentration and could remain for a long time in seafood and later becomes accumulated in the aquatic food chain. Such seafood when consumed, becomes a source of health problem to man (Fadrus et al., 1979).

Typanotonus fuscatus is a brownish-black mollusc that remains and feeds on the mudflats in the mangrove swamps of Qua Iboe River estaury in Ibeno. They are therefore deposit feeders, hence the decision to use them as indicators of trace metal pollution in aquatic environment. Exxon-Mobil oil terminal and offshore facilities are situated in close proximity of the estuary. Crude oil operational activities are known to release high concentration of trace metals into this environment (Ubong, 1983). It is an established fact that sediment is a major sink of metals in aquatic environment (Voogt et al., 1980). Therefore, because *Typanotonus fuscatus* feeds on the sediment, it stands a high risk of exposure to toxic metals, which could pose a serious health risk to the large number of consumers in the coastal settlements of Akwa Ibom State, where it serves as a major protein supplement. Because of the high consumption rate of this animal, it became necessary to carry out this study to ascertain its safety with regards to trace metal content.

MATERIALS AND METHODS

Study Area

Qua Iboe River originates from Umuahia hills in Abia State in South Eastern Nigeria and flows southwards into the Atlantic Ocean within the Bight of Bonny. The estuary, which is at Ibeno, is mesotidal with tidal amplitude of 1m to 3m. It lies with latitude 4^{0}30'to 4^{0}45'N and 7^{0}00'to 8^{0}00'E. Ibeno, the study area is in Akwa Ibom State, which is located in the Niger Delta Region, South-South of the Federal Republic of Nigeria (Fig.1). This region is characterized by distinct wet and dry seasons. The wet season often begins in late March and ends in late September or mid October, while the dry seasons begins in late October and ends in early March.

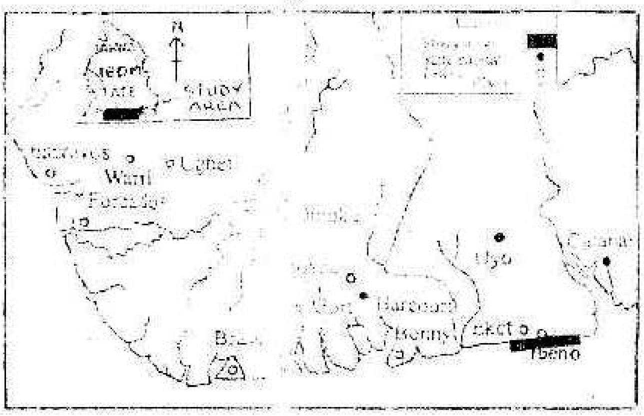

Fig. 1: The Niger Delta region showing location of the study area

Generally, the relative humidity is high in all parts of the study area. During the dry season, humidity is highest along the coast of Qua Iboe River but tends to be higher inland during the wet season. The soil temperature is usually higher during dry season (30^{0}C to 45^{0}C). On the other hand, the soil temperature during wet season ranges from 20^{0}C to 30^{0}C. The soil of Niger Delta region of which Ibeno is a part is generally acidic with pH ranging from 3 -5.8 (Ekwere et al., 1992).

Sample Collection and Analysis

The samples used in this study were collected from the muddy swamp of Qua Iboe River estuary during low tide, at six locations, namely: Ukpenekang (Station 1), Terminal Jetty (Station 2), Ikot Inwang (Station 3), Stubbs Creek (Station 4), Itak Abasi (Station 5) and Okoritak (Station 6). Samples collected were transported in black polyethylene bags (Polprasert, 1982) to the laboratory for analysis. Sampling was carried out once a month for ten months from May to February of the following year. Forty (40) samples collected from each station were washed with distilled water to remove sediment deposit. They were shucked in a mortar with pestle, drained and the tissue removed from the shells. The tissue was dried in an oven at 50^{0}C. The dried samples were ground into fine powder prior to analysis.

The dried sample (1.0g) from each location was added to the crucible that had been charred and placed in a furnace at 500^{0}C to 700^{0}C for 2 4 hours for ashing. The ashed sample was allowed to cool, then leached with 5ml of 6M HCl and filtered through Whatman No.2 filter paper. The aliquots of the *Typanotonus fuscatus* samples were made up to 20cm^3 by volume with distilled water and poured into specimen bottles for metal analysis. Standard solutions of the metals to be analysed (Ni, Cr, Mn, Co, Cd, Fe, Zn, Cu and Pb) were then prepared (Welch, 1963; Whitehead, 1979; A. W. W. A., 1980). A blank solution that served as the control was also prepared with all the reagents used for the sample digestion except that it contained no sample of interest. These samples were aspirated into a Solar System Atomic Absorption Spectrophotometer (Pye Unicam), model 919. The absorbances were recorded and calibrated curves prepared for the metals. The concentrations of these metal were then read from the calibration curves.

The use of ANOVA revealed the significant seasonal variations of these metals per sampling location.

RESULTS AND DISCUSSIONS

The means and standard deviations of trace metal levels in *Tympanotonus fuscatus* from the six sampling stations during dry and wet seasons are presented in Table 1. The result obtained from ANOVA analysis showed no significant seasonal difference in the level of trace metals in *T. fuscatus*. However, a significant different existed in the levels of these metals (Ni, Cr, Mn, Co, Cd, Fe, Zn, Cu and Pd) from one location during both seasons. A significant difference in the level of Cr ($t = 15.6$; $P < 0.01$) was obtained in the dry season at all the locations. Similarly, a highly significant difference in the level of Mn was observed during both seasons at all the locations ($t = 17.4$ dry season and $t = 128.4$ wet season; $P < 0.001$). Moreover, intra-location significance difference was observed in the level of Cd during both season ($t = 6.5$ for wet season and $t = 2.25$ for dry season; $P < 0.001$). A significant intra-location difference also existed in the levels of Fe, Zn and Pb. Nevertheless, significant difference in the level of Cu at all the stations was detected statistically ($t = 34.18$ dry season and $t = 58.761$ wet season; $P < 0.001$). Table 2 shows the seasonal coefficients of variation in the levels of trace metals in *Tympanotonus fuscatus* samples from the six sites. Co had very high coefficients of variation in the samples from location I with coefficients of variation of 96.50% and 87.40% followed by Pb with coefficients of variation of 42.80% and 52.80% for both seasons respectively. On the whole, Ni and Zn had the least coefficient of variation of 1.80% during wet and dry seasons respectively.

The major sources of trace metals in Qua Iboe estuary at Ibeno are industrial activities, leaching of metals from garbage; solid wastes dumps and natural source such as rock weathering.

Nickel concentrations for both seasons were high at all locations (except 1). This result is consistent with concentration range of 7.83 - 11.67ugg^{-1} obtained by Udoh et al. (1999) in the same organism collected from same aquatic environments of Qua Iboe River Estuary at Ibeno in Akwa Ibom State. The ranges and mean Ni concentrations in the samples from all the study sites during wet and dry seasons were equally higher than 0.025mgkg^{1}, i.e. 0.025µgg^{-1} fresh weight as standard for Ni in seafood by W. H. O. (1991). The high Ni concentration in *Tympanotonus fuscatus* in this study presupposes pollution of the estuary by nickel metal that may have been present in wastes and runoff discharge into the estuary.

The mean concentration range of 8.50 - 17.00µgg^{-1} for Cr in *Tympanotonus fuscatus* obtained by Udoh et al. (1999) were higher than 0.54 - 6.96µgg^{-1} range obtained for the same metal in the present study. However, the range of Cr. in *Tympanotonus fuscatus* in this study fell within the lethal dose of 0.01 0.06µgg^{-1} for children and 2.50 5.00µgg^{-1} for adult suggested by Goyer and Myron (1977) except in the sample from Station 6 during wet season.

Although Cr Level in *Tympanotus fuscatus* samples in this study is not such that could pose any heath hazard to the consumers for now and does not seem to pose an instant health problem generally, yet continuous contamination of the estuary by Cr laden wastes and runoff will increase the levels of this metal in the organisms which in will affect the consumers adversely in future. Effluent and wastes laden with Cr should not be discharged into the estuary to avoid future contamination of the organisms by this metal.

When compared with levels of other metals in the organism, the seasonal mean concentrations of Mn were high at all stations particularly during wet season except in samples from station 1 during both seasons. There was no significant seasonal difference in the level of Mn, but a significant spatial difference was observed during both seasons. Ignoring the low concentration level of the metal in samples from station 1, the high range in concentration of 298.12 - 715.72µgg^{-1} obtained in the study compares favourably with the range of 282.50-360.00µgg^{-1} obtained in samples of the same organisms collected from different aquatic environments including Ibeno estuary Akwa Ibom State by Udoh et al. (1999). Although Mn is a growth activator of certain enzymes such as dipeptidase, the discharge of wastes and effluent laden with Mn should be checked since the mean value is already higher than the lethal dose of 2.50- 5.00µgg^{-1} set for adult (Goyer and Myron, 1977) and the standard of 0.10- 3.99µgg^{1} set by W. H. O. (1999) for meat, poultry, eggs and seafood such as *Tympanotonus fuscatus*.

Although there was no significant seasonal difference in the levels of Co in *Tympanotonus fuscatus,* a significant spatial difference was observed. The levels of Co in the study (3.33- 5.00 µgg^{-1}) were lower than the levels in the samples analysed by Udoh et al. (1999) who worked in the same environment. In spite of the low concentration of this metal in the samples its presence in the estuary is dangerous since direct human effects of the metal is said to include dermatitis, heart attack, liver and kidney damage (Schroeder, 1974).

Even though no significant seasonal difference was observed in the concentration of Cd in *Tympanotonus fuscatus,* the level of this metal in samples from the other locations except location I was remarkably high during both seasons. The relatively low level of Cd in samples from Station 1 could be attributed to the remoteness of this station from the point of waste discharge into the estuary. Whereas, Udoh et al. (1991) recorded a concentration range of 0.00- 2.83µgg^{-1} in *Tympanotonus fuscatus* from various aquatic environments in Akwa Ibom State, a range of 0.37 0.98µgg^{-1} was obtained in this study for both wet and dry seasons. The distribution pattern of this metal is above the acceptable W.H.O. levels for mollusks (0.21 -1.40mgkg^{-1}, i.e. 0.01 0.07µgg^{-1} dry weight and 0.01 1.04mgkg^{-1}, i.e. 0.005 0.052µgg^{-1} dry weight) for fish. These levels were equally higher than the Maximum Permissible Limit (MPL) for Cd in fish muscle (2.00mgkg^{-1} i.e. 0.10gg^{-1}) wet weight set up by the US Food and Drug Administration (Adeyeye, 1993). In Belgium, regulatory limits for Cd vary from 10µgg^{-1} (0.05µgg^{-1}) in milk or eggs to 2000gkg^{-1}, i.e. 100µgg^{-1} in fish and shellfish and the established Provisional Tolerance Weekly Intake (PTWI) is 7.0µgg^{-1} i.e. 0.35µgg^{-1} body weight. Eating mussels or kidney once in this country is said to be resulting in a cadmium intake equal to PTWI (UNEP, 1992). Considering the physiology of human beings to be largely similar worldwide, what obtains in Belgium could be said to apply to consumers of this seafood with high Cd content in many other countries including Nigeria. Since the concentration of Cd content in these samples were higher than those of the standards quoted above, and because the inhabitants of this area rely to a great extent on seafood to supplement their protein intake, then it could be said that consumers of large quantities of *Tympanotonus*

Fuscatus obtained from this estuary stand the risk of experiencing health problems such as severe kidney and liver damage, proteinuria, glycosuria, bronchitis, pneumonitis, hypertension, aneamia, emphysema and death often associated with the consumption of seafood with high Cd content (Voogt et al, 1980; W.H.O., 1984). Since increased concentration of Cd in any seafood often worsens the above health conditions (Young and Blevins, 1981), there is need to always analyse any sea food for the presence of Cd since Cd once taken up could be stored in the body and accumulate with age so that damage from long-term consumption becomes irreversible (Spiro and Stigliani, 1996).

Zinc concentration in *Tympanotonus fuscatus* samples from all other sites were significantly higher than levels in samples from station 1 in line with the general trend observed for the other metals. This may be attributed to low commercial activities within and around station 1. The mean concentration of Zn in this study fell below the recommended limit of 1000.00μgg^{-1} for seafood by Australian National Health and Medical Research Council. Udoh et al. (1999) in their study on Tympanotonus fuscatus from different aquatic environments in Akwa Ibom State obtained a concentration range of 85.00 150.00μgg^{-1}. Similarly Horsefall et al. (1993) observed a concentration range of 37.80μgg^{-1} in the muscle of male and 32.00μgg^{-1} in female mudskipper from mangrove swamps of coastal new Calabar River. Since the level of Zn is lower than the recommended limit, health hazard associated with Zn toxicity is not anticipated.

The seasonal mean concentration of Cu ranged between 0.30 and 6.57μgg^{-1} (Table 1). There was no significant seasonal difference in the levels Cu in *Tympanotonus fuscatus* but the levels in samples from station 1 were significantly lower than the levels in samples from other sites. The concentration range of Cu in samples in this study was lower than the 30.00gg^{-1} limit set by Australian National Health and Medical Research Council for Cu in seafood (Bebbington et al., 1977). However, Udoh et al. (1999) observed a concentration range of 101.00- 160.00μgg^{-1}. The remarkable difference in Cu concentration in the two studies could be traced to the sampling times, periods of the study and the locations and points of sample collection. Similarly, Lopez-Artiguez et al. (1989) observed a concentration of 180.00μgg^{-1} in *Gascostra angiata* while Horsefall et al. (1993) recorded a Cu concentration of 4.70μgg^{-1} in the muscle of male and 7.30μgg^{-1} in the muscle of female mudskipper. Although Cu toxicity associated with consumption of this organism has so far not been reported, industrial effluent must be treated before discharging into the estuary to avoid future contamination of the estuary and the aquatic organisms by this metal.

Although no significant seasonal difference in the level of Pb in *Typanotonus fuscatus* was observed, yet concentrations in samples from locations 2, 3, 5 and 6 were significantly higher than the levels in samples from locations 1 and 4 with those from location 6 being the highest. Lead levels in samples during wet season were slightly higher than the dry season levels. The high Pb content in these samples may have resulted from the lead present in the effluent, industrial wastes and runoff from the urban area that flowed through mechanic workshops and petrol filling stations into the estuary. The mudflats in the swamps on which the organism lives may have trapped these. The results obtained were consistent with those of Udoh et al. (1999) and Ibok et al. (1989). Except at station 1 during the dry season, the mean concentration of Pb obtained in *Tympanotonus fuscatus* samples at all stations were higher than the 2.00μgg^{-1}, which is the limit set by the Australian Health and Medical Research Council for Pb in seafood. The overall mean value for Pb obtained in the samples throughout the study period was also much higher than the Maximum Permissible Level of 2.00mgkg^{-1}(ie.0.10lμgg^{-1}) wet weight set for Pb be the US Food and Drug Administration. It is therefore advisable to guard against indiscriminate discharge of effluent and wastes into the estuary since Pb has a cumulative effect. Moreover, Pb is known to inhibit active transport mechanisms involving Adenosine Triphosphate (ATP) to depress the activity of the enzyme cholinesterase, to suppress cellular oxidation reduction reactions and to inhibit protein synthesis (Waldron and Stofen, 1974). Once absorbed, Pb causes deadening of nerve and receptors in man since man is not known to require this metal in any concentration (Bodansky and Latner, 1987).

CONCLUSION AND RECOMMENDATION.

From the results of this study, it is certain that Ni, Cr. Mn, Cd and Pb pollute *Tympanotonus fuscatus* obtained from different locations in the Ibeno estuary of the Qua Iboe River. The higher mean levels of these metals in this environment are suspected to have been associated with the indiscrimate dumping of waste and effluent into the estuary. Runoff and natural sources may have also contributed to the higher levels of these metals in the organism. Although, no toxicity associated with consumption of this organism are reported in the area, it is advisable to guard against

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Table 1: Concentrations of Trace Metals in *Tympanotonus fuscatus* (gg^{-1}) during Wet and Dry Seasons (n =40).

METALS	SEASON	CONCENTRATION (gg^{-1})					
	LOCATION	1	2	3	4	5	6
Ni	Wet	1.99±0.10	18.60±0.44	12.63±0.30	6.23±0.67	19.12±1.84	12.56±1.20
	Dry	1.92±0.10	18.47±0.55	12.98±0.23	6.73±0.38	19.15±1.14	9.71±2.09
Cr	Wet	BDL	1.08±0.10	0.77±0.22	0.54±0.14	0.71±0.20	6.96±0.09
	Dry	BDL	1.02±0.11	0.90±0.09	0.58±0.12	0.69±0.12	1.00±0.05
Mn	Wet	12.89±0.61	715.72±38.46	595.24±58.23	298.59±10.46	347.79±42.76	498.69±87.26
	Dry	12.23±0.74	689.90±3.10	606.97±17.50	298.12±8.66	489.20±41.28	489.20±91.13
Co	Wet	2.25±1.95	0.53±0.07	0.42±0.08	0.36±0.12	0.98±0.08	0.58±0.19
	Dry	2.57±2.48	0.55±0.88	0.40±0.06	0.38±0.12	0.97±0.08	0.80±0.18
Cd	Wet	0.39±0.06	0.85±0.19	0.79±0.11	0.97±0.04	0.79±0.08	0.86±0.13
	Dry	0.37±0.05	0.74±0.16	0.78±0.07	0.78±0.03	0.72±0.07	0.79±0.15
Fe	Wet	5.60±2.07	145.27±5.45	136.63±11.50	147.49±5.72	205.99±46.39	136.94±8.83
	Dry	4.35±1.40	146.00±3.33	138.32±11.29	147.00±6.43	200.72±13.45	138.90±9.52
Zn	Wet	6.75±0.44	100.60±1.84	96.57±4.79	109.95±7.75	94.42±3.79	95.30±6.19
	Dry	6.54±0.46	99.70±2.09	96.73±5.43	119.22±29.85	94.73±5.17	98.61±5.75
Cu	Wet	0.37±9.06	6.09±0.80	5.94±0.95	6.51±0.49	5.78±0.76	5.80±0.88
	Dry	0.30±0.06	5.81±0.49	6.25±0.77	6.41±0.51	5.76±0.78	5.99±0.78
Pb	Wet	3.20±1.69	28.99±2.21	25.30±0.75	13.50±1.15	31.90±0.80	24.32±1.30
	Dry	1.96±0.74	28.5±1.85	25.41±1.08	13.23±1.17	32.37±0.95	24.23±0.81

Table 2. Seasonal Coefficient of Variation (%) of Metal Levels in *Tympanotonus fuscatus*.

METALS	SEASONS / LOCATION	COEFFICIENT OF VARIATION					
		1	2	3	4	5	6
Ni	Wet	4.9	2.4	2.3	10.7	9.6	9.5
	Dry	5.3	2.9	1.8	5.7	5.9	21.5
Cr	Wet	-	9.4	28.3	25.7	27.5	9.1
	Dry	-	10.5	10.1	20.5	17.5	4.8
Mn	Wet	4.7	5.4	8.1	3.5	12.3	17.5
	Dry	6.0	0.44	2.9	2.9	12.6	22.1
Co	Wet	87.4	13.6	18.8	33.0	7.8	32.6
	Dry	96.5	14:5	15.8	32.1	8.5	22.1
Cd	Wet	16.2	17.5	13.3	3.8	10.5	14.6
	Dry	13.8	21.2	8.3	2.9	9.2	18.5
Fe	Wet	40.9	3.8	8.4	3.9	3.1	6.4
	Dry	32.2	2.3	8.2	4.4	6.7	6.9
Zn	Wet	6.5	1.8	4.9	7.0	4.0	6.5
	Dry	7.1	2.1	5.6	25.5	5.5	6.0
Cu	Wet	15.9	13.1	16.1	7.6	13.1	15.3
	Dry	19.7	8.5	2.3	8.0	13.1	15.3
Pb	Wet	52.8	7.6	2.9	8.8	2.6	5.3
	Dry	37.9	5.6	4.2	8.8	2.9	33.3