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Mercury Levels in Sediment, Shellfish and Fish of a Water Body in the Niger Delta

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ABSTRACT

The concentrations of mercury in sediment and the muscle tissues of shellfish and fish of Bonny River and creeks around Okrika were determined in order to identify possible sources and indicator species that can be used to monitor pollution of the ecosystem, as well as assess possible health risk. Sediment samples were taken from ten (10) locations including the refinery effluent discharge channel, while shellfish and fish were randomly taken within the studied area. All samples were prepared and analysed by the cold vapour technique. The mean level of detectable values (ppm) in the sediment was 0.273±0.016. Those of shellfish were: *P. aurita* (0.016±0.012) and *G. rhizophorea* (0.018±0.026), while for fish we have: *P. koelreuteri* (0.014±0.019), *M. cephalus* (0.011±0.010), *S. marderensis* (0.008±0.011) and *T. guineensis* (0.026±0.032). The sediment results reveal largely anthropogenic enrichments mainly from refinery effluent. The pattern of accumulation by both fish types was both physiologically and ecologically characterized an indication that it is only the dissolved forms of metals that are effectively available to fish for bioaccumulation. The remarkable bioaccumulation factor (130.00) was associated with *T. guineensis*, which appeared to be the most efficient accumulator, and therefore a good bioindicator to monitor mercury pollution of the system. Mercury levels in all sample types were however generally low and do not portend serious danger with respect to human health. Nevertheless, the continued discharge of industrial effluents without regular monitoring may have imminent detrimental effect on the flora and fauna, since the metal is detectable in all the samples at sub-lethal concentrations.
KEYWORDS: concentrations, shellfish, fish, mercury, indicator species, Bonny River

INTRODUCTION

Fish and shellfish are of high economic value in Niger Delta, and could be bioindicators of trace metals and hydrocarbon pollutants in marine environments; hence studies are conducted to ascertain the level of concentrations of trace metals in these commercial species (Biney, 1991; Okoye, 1991; Davies *et. al*., 2006; Nsikak and Usoro, 2007).

Mercury is recognized as a toxic metal and stringently regulated in waste discharges (Gress and Lord, 2002). It has been reported to be in fish and shellfish. Fodeke (1979) in determination of heavy metals concentrations in whole as well as different parts of tilapia species from Lagos Lagoon concluded that measured values were high. The gut contained 0.03 - 0.19 ppm Hg, while in whole minced fish, it was 0.10 - 0.40 ppm Hg. Kakulu and Osibanjo (1986) found the level of Hg in fish from Niger Delta area of Nigeria to be less than 10 mg/kg – 40 mg/kg wet weight and 0.024 - 1.54 mg/kg dry weight. Oyewo (1998) found mercury to be toxic in test species (*Tilapia guineensis*, *M. cephalus* and *T. fuscatus*) by bringing about reduced weight increase or weight loss when exposed to sub-lethal concentration of Mercury over a period of 28 days.

In Nigeria, not much work had been done to investigate relative bioaccumulation potential and biomagnification of Hg on local aquatic species, but Oyewo (1998) discovered that *C. africanus* is a more efficient bioaccummulator of Hg than *T. africanus. C. africanus* exposed to highest sub-lethal concentration of Hg at 0.08 mg/l sub-lethal concentration of Hg also brought about observable

significant and consistent reduction in % wt increase of test periwinkles from Lagos lagoon. The estimated amount of mercury being introduced into the environment from industrial effluent in Lagos metropolis per industry varied between 0 - 0.47 kg of Hg for chemical and allied industry to 277.8 kg for different categories of industries within the sector (WES 1997). The concentration of Hg in bottom sediment from drainage channel (pathway) connecting effluent discharge points with Lagos lagoon in July 1989 and February 1991 showed occurrences of mercury to be between 0.001 - 0.005 mg/g and 0.0008 mg/g respectively.

Okrika in the Niger Delta is made up of many reproductive river systems that Industrial and a whole lot of other human activities depend on, for communication and discharge of effluents and wastes Over the years there has been quite a lot of ecological degradation as a result of exploration activities by companies prospecting for oil and gas in the area, a potential recipient of effluent/wastewater from the Port Harcourt Refining Company (PHRC), which is about 800 meters from Ekerekana creeks. Marine transport services are also remarkable.

The continuous discharge of refinery effluent/wastewater into the creeks from where it spreads to other areas covered by the study, may have caused the introduction and deposition into this environment trace metals and other chemical pollutants, which may have bioaccumulated in sediments, sedentary organisms, fish etc, and generally to the detriment of flora and fauna of the aquatic ecosystem and those who consume sea foods.. Marine transport services are also remarkable. These activities are sources of trace metals, among other chemical pollutants that can impact negatively on the aquatic system, hence endangering the health of those who consume aquatic sea foods. The paper reports the levels of mercury in sediment, fish and shellfish of Bonny River and creeks around Okrika in the Eastern Niger Delta, in order to identify possible sources and indicator species to monitor mercury pollution, as well as assess its possible health risk.

Study area

The studied area is in Okrika Local Government Area of Rivers State. It is a riverine and intertidal wetland which lies on the north bank of the Bonny River, about 35 miles (56 km) upstream from the Bight of Benin in the Eastern Niger Delta of Nigeria. The average elevation of Okrika is 452 meters above sea level. The area is about 905.2 sq.km, and lies on latitude 04^0 40' to 05^0 00'N and longitude 07^0 00' to 07^0 15'E. A maze of rivers and winding creeks intersect it, and within it are, stretches of marshy land having mangrove trees with thickets of tangled roots as the vegetation. The predominant vegetations include among others, the *Nypa frutcan* and *Rhizophora racemosa*. Others are *Avicennia africana, R.mangle, Leguncularia racemosa* and *Achrostichum aureumI* (Wilcox, 1985). Sampling locations and their descriptions are given in Fig. 1 and Table 1.

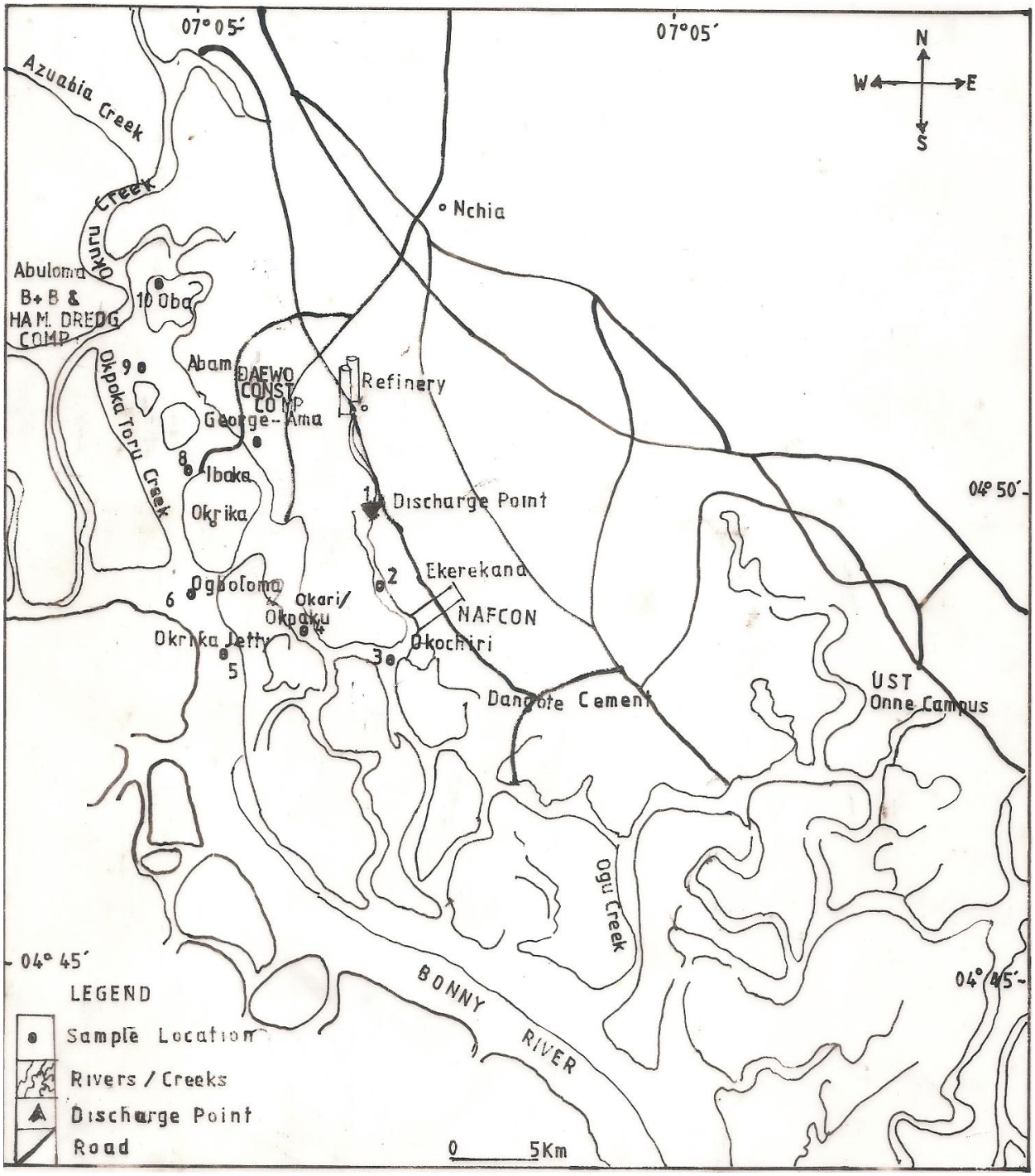

Fig.1: Map of Bonny River and Creeks around Okrika Showing Sampling Locations

Table 1: Description of sample locations and their codes

S/N	Location	Description
1	PRE	Port Harcourt Refinery Effluent/Wastewater Outfall
2	EKC	Ekerekana Creek
3	OKC	Okochiri Creek
4	OOC	Okari/Okpaku creek
5	OBR	Okrika/Bonny River
6	OGR	Ogoloma River
7	GAC	George Ama Creek
8	IBC	Ibaka Creek
9	OTR	Okpoka-Toru or Okpoka River
10	OAC	Oba Ama Creek

MATERIALS AND METHOD

Sample collection

Surface bottom sediment samples for determination of mercury were collected at low tide by the grab method using Eckman grab sampler from 3 to 4 points at each location (APHA, 1975). This was done at two-monthly intervals between December 2009 and October, 2010. The samples were put in polythene bags previously leached with dilute acid, and stored in the laboratory by freezing

Periwinkles (*Pachymalania aurita*) were hand-picked a few centimeters below the top of the sediments, while oysters (*Grassostrea rhizophorea*) were severed from mangrove trees and other hard surfaces in Ekerekana Creek (EKC) and Okpoka-Toru River (OTR), where they were found. The samples were washed with the river water and taken to the laboratory, where they were frozen after rinsing with distilled water. Three fish each of four species, namely; mudskipper (*Periophthalmus koelreuteri)*, mullet (*Mugil cephalus*), sardine (*Sardinella marderensis)* and tilapia (*Tilapia guineensis*) were caught at low tide, by means of pond nets from several locations within the studied area as shown in figure 1. They were washed with river water, rinsed again with distilled water in the laboratory and frozen in a freezer.

Sample preparation and analysis

Sediment samples were thawed and air-dried at ambient temperature and sieved through 0.5 mm sieve. The shells of the periwinkles (*Pachymalania aurita*) and oyster (*Grassostrea rhizophorea*) samples were cracked and separated to obtain their tissues. The separated tissues were rinsed with distilled water, and dehydrated to constant weight using an oven (Technicolor) at 105 ^{0}C with the individual whole tissues homogenized. Similarly frozen samples of different species of mudskipper (*Periophthalmus koelreuteri*), mullet (*Mugil cephalus*), sardine (*Sardinella marderensis*) and tilapia (*Tilapia guineensis*) were dissected and filleted to remove the edible muscle tissues alone. The muscle tissues of each of the different species were homogenized as composite. The homogenized samples were accurately weighed in porcelain crucibles and dried at 105 ^{0}C. The samples were then prepared for the determination of mercury by the cold vapour technique (McConchie *et. al.,* 1988).

Procedure

Two grams (2 g) each of sediment, shellfish and fish were placed into 250 ml Teflon bottle. 15 ml of potassium tetraoxomanganate (VII)-$KMnO_4$ solution was continuously added until a purple colour was observed. 8.0 ml of $K_2S_2O_8$ was added and the solution allowed to stand for at least 15 minutes before being heated for 2 hours in a water bath at 95 ^oC. It was allowed to cool to room temperature and hydroxylamine hydrochloride solution was added to reduce excess $KMnO_4$ until the solution became decolourised. The digested sample solution (10 ml) was then mixed with Sodium borohydride ($NaBH_4$) in a mercury kit and vapour allowed to go into the AAS instrument without flame. For water samples, after acidification with HNO_3^-, a known volume was taken straight to the mercury kit for analysis by the instrument. The instrument calculates the results automatically as sample weight and dilution volumes are entered into the sample amount column and extract volume column respectively. Manually results can also be calculated as follows:

$$\text{Mercury concentration, } \mu g/g \text{ (mg/kg)} = \frac{(A - B)C}{D}$$

Where, A = Concentration of mercury in sample, µg/ml as determined by AAS (instrument reading)

B is Concentration of mercury found in blank, µg/ml (Procedural blank)

C is Volume of extract, ml.

D is Weight of dry sample, g.

Note: Stock Quality Control (QC) solution, 1000 mg/l. NIST. Working QC solution 20.0 µg/l. 2 ml of 1 mg/l solution is usually diluted to 100 ml. This was prepared the day the analysis was to be carried out.

Accuracy of sample manipulations was checked using samples of PACS-2 (sediment) and DOLT-2 (for organisms), and for each batch of elemental analysis, an intra-run Quality Assurance Standard (1 mgL^{-1}, Multi-Element Standard Solution, Fisher Scientific) was checked for reading deviation and accuracy of every 10 samples (Cantillo and Calder, 1990).

RESULTS AND DISCUSSION

Results

Year average concentrations of mercury in the sediment are presented in Table 2 and Fig. 2

Table 2: Year average (n=6) values (ppm, dry wt.) of mercury in sediment of Bonny River and creeks around Okrika

Parameters	Sample stations										Ov.mean ±SD
	PRDC	EKC	OKC	OOC	OBR	OGR	GAC	IBC	OTR	OAC	
Hg	**0.068**	**0.018**	**0.011**	**0.036**	**0.021**	**0.015**	**0.020**	**0.034**	**0.032**	**0.023**	**0.273 ±0.016**

PRDC – Port Harcourt Refinery discharge or outfall channel

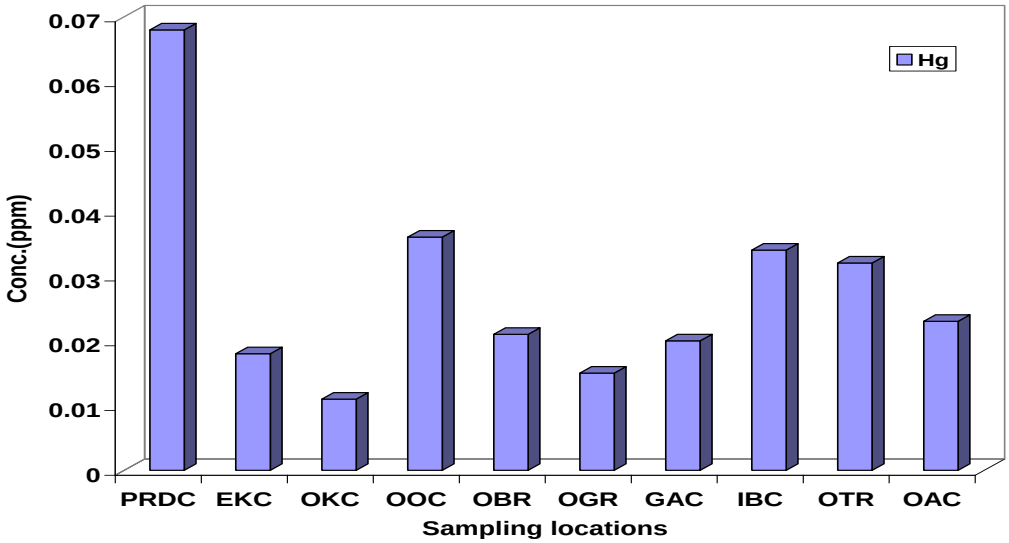

Fig. 2: Year average (n=6) values (ppm, dry wt.) of mercury in sediment of Bonny River and creeks around Okrika

Mercury level from Table 2 and Fig. 2 was highest (0.068 ppm) in the sediment taken from the refinery discharge channel, while the overall mean was 0.273±0.016. Two-way analysis of variance show no significant ($p>0.05$) difference. Seasonal variation was also insignificant ($p>0.05$).
The mean levels of mercury in shellfish, fish and their bioaccumulation factors (BF) are also presented in Table 3 and Fig. 3.

Table 3: Mean levels of mercury in shellfish, fish and their bioaccumulation factors (BF)

	Range, mean ±SD	Bioaccumulation Factors
Shellfish		
P. aurita (periwinkle)	(0.006-0.040) 0.016±0.012	80.00
G. rhizophorea (oyster)	(0.002-0.090) 0.018±0.026	90.00^{+}
Fish		
P. koelreuteri (mudskipper)	(0.003-0.050) 0.014±0.019	70.00
M. cephalus (mullet)	(0.003-0.030) 0.011±0.010	55.00
S. marderensis (sardine)	(0.003-0.040) 0.008±0.011	40.00
T. guineensis (tilapia)	(0.003-0.080) 0.026±0.032	130.00^{++}

$^{+}$: Higher accumulation in shellfish $^{++}$: Highest accumulation in fish

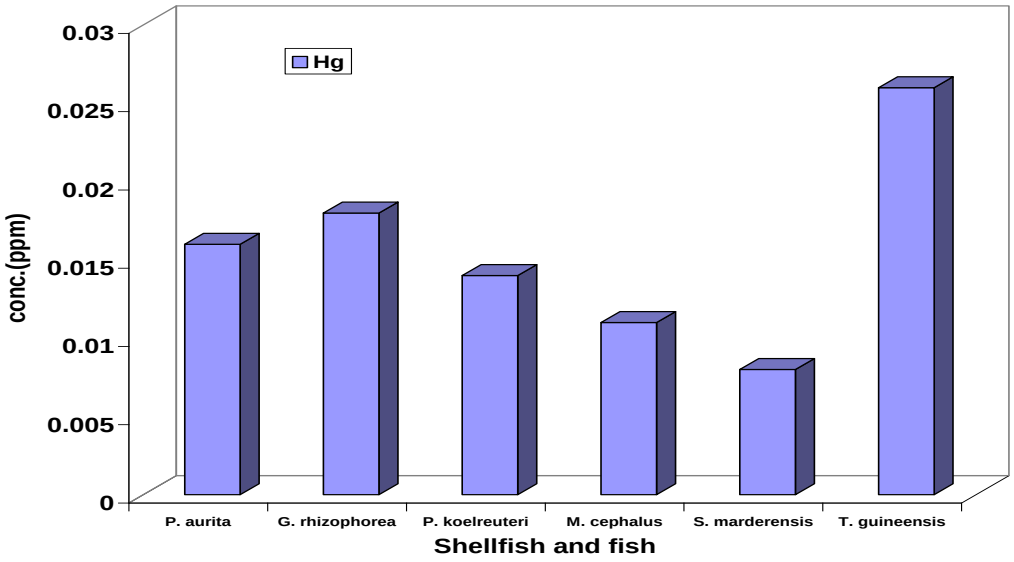

Fig. 3: Mean levels of mercury in shellfish and fish of Bonny River and creeks around Okrika

The results in table 3 and fig. 3 show that *T. guineensis* carried the highest burden with highest BF (130.00), followed by *P. koelreuteri* (70.00). The accumulation trend was generally *T. guineensis* > *P. koelreuteri* > *M. cephalus* > *S. marderensis* > G. rhizophorea > *P. aurita*.

Discussion

The sediment revealed largely anthropogenic input mainly from the refinery effluent, whose discharge channel gave the highest concentration. Other possible reasons might be anthropogenic metal inputs into the river through the use of engine and lubricating oil and corrosion of metal blades of the outboard engines.

The absence of significant seasonal differences ($p>0.05$) in the concentrations of mercury in the sediment may be explained as resulting from high flushing and dilution rates during the rains, in addition to the associated velocity of the system or "solution effect" consequent upon a process whereby ions bound in previous semi-dry land by decaying macrophytes get dissolved as water levels increased with inundation of fringing swamps and riparian zones (Welcome, 1986; King and Nkanta, 1991). On the other hand, in the dry season, the inflow of water is at minimal level, and under such condition, sedimentation would become more efficient since water is only disturbed by tidal currents. In the sediment, the concentrations of mercury were however generally low.

The levels of Hg for shellfish muscle tissues showed that accumulation in the two fish types did not depend on ecological characteristics alone, but their different ecological and physiological characteristics. *Pachymalania aurita* (periwinkle), a bottom feeder, carried lower burden of Hg than *Grassostrea rhizophorea* (oyster), a filter feeder (Table 3). Differences in ecological characteristics could not account for these observations. In the fish muscle tissues, *P. Koelreuteri* and *T. guineensis* and M. cephalus feed deeper in water than *S. Marderensis* and are expected to

pick up particulate trace metals by ingesting sediment particles, which are usually enriched with trace metals.

In order to calculate bioaccumulation factors (ratio of metal level in tissue to ratio of metal level in water), mercury in water was also determined in water, and a mean value of 0.2 ppb obtained from a few locations was converted to ppm for the calculations (Table 3). The remarkable bioaccumulation factor was only that of Hg in *T .guineensis*. This could imply that even though metal-laden particulates may be ingested while feeding, the trace metals accumulations are purely physiologically characterized as in the case of shellfish. This could be a further confirmation of a previous postulate that it is the dissolved forms of the trace metals that are effectively available to fish for bioaccumulation (Florence and Batley, 1980; Suffern *et. al*., 1981)

The rate of bioaccumulation of trace metals in these organisms however also depends on other factors such as the general physico-chemcial conditions of the water (Suffern *et. al*., 1981) as well as the levels of the metals in the water. The highest accumulation in *T. guineensis* muscles therefore could be a reflection of some intrinsic physiological characteristics of the fish. Moreover, since *T. guineensis* being biggest among the fish samples used in the study, it may have accumulated more metals than the smaller fish samples. Mercury levels in fish were generally lower than what obtained in tissues analysed from Lagos Lagoon (0.03-0.40 ppm) (Fodeke, 1979), other rivers in the Niger Delta (0.024-1.54 ppm) (Kakulu and Osibanjo, 1986).

A study conducted at University of North Carolina's Environmental Quality Institute on tested fish samples reported 0.013 ppm for oyster, 0.046 ppm for mullet, 0.050.ppm for sardine and 0.010 ppm for tilapia, which were comparable with the results of this study. The comparableness of the results of the present study with others reported imply that consumption of fish from Bonny River and creek around Okrika may not, at present portent serious danger with respect to human health, given that the permissible level reported by University of North Carolina's Environmental Quality Institute on tested fish samples was about 1.0 ppm (FDA, 2004). The values obtained in study which compared well with those reported imply However, continued discharge of industrial effluents without regular monitoring may have imminent detrimental effect on the flora and fauna and those who consume sea foods.

Conclusion

The sediments of Bonny River and creeks around Okrika are enriched with mercury especially due to direct input of industrial and domestic wastes and indirect input via tributary rivers and runoff waters. Anthropogenic metal enrichments are the major sources of this metal in the sediment. Only *T. guineensis* appeared to be good bioindicator for environmental monitoring of mercury. It is also clear from this study that metal accumulation is more often influenced by both ecological and physiological factors.

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