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## ASSESSMENT OF HEAVY METALS AND TOTAL DISSOLVED PETROLEUM HYDROCARBONS IN EDIBLE *MACTRA NITIDA* FROM THE NIGERIAN COASTLINE

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### ABSTRACT

The bivalve, *Mactra nitida* is highly abundant along Ibeno shoreline, South East Nigeria. They are largely consumed by the coastal dwellers as sea food and also serve as secondary source of income for the fishermen. They range in sizes from 1.5-2.5 cm (small size) to 2.6-4.5 cm (adult size). Chemical analyses of the soft tissues for heavy metals and total dissolved petroleum hydrocarbons (TDPHs) showed reasonable signs of contamination (max. concentration  $206.7 \pm 26.1 \mu\text{g/g}$  for Fe and min.  $1.9 \pm 1.85 \mu\text{g/g}$  for Cu). Maximum TDPH level observed was 275.4 ppm in the adult specie. There was a significant correlation between the two class sizes in relation to the metals concentration ( $P < 0.05$ ,  $r = 0.96$ ). However, Cu and Zn did not indicate early bioaccumulation in the small species when compared to the large ones. The mean concentration of all metals analyzed were above WHO maximum permissible limits for fisheries and aquatic life indicating tissue contamination of the edible bivalve. The implications of these observations and the potential health hazard with regards to the high bioaccumulative potential of *Mactra nitida* are discussed.

Key words: tissue contamination, *Mactra nitida*, heavy metals, TDPH, Ibeno shoreline, Nigeria

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### INTRODUCTION

In recent times, the occurrence of metal and hydrocarbon contaminants in aquatic systems in excess of natural loads has become a problem of increasing concern. This situation has risen as a result of rapid growth in population, increased urbanization, expansion of industrial activities, exploitation of natural resources, modern agricultural practices as well as the lack of enforcement of environmental regulations especially in the developing countries. The estuarine and coastal systems are very delicate environments since they serve as breeding and nursery grounds for most marine and sub-terrestrial species. River borne metals

entering from inland drainage tend to dissolve in coastal waters and are incorporated into living organisms, water and sediments before eventual transportation into open (FAO, 1992; UNEP, 1990; Asuquo *et al.*, 2000). Unlike physical pollutants such as tarry residues and litter which build up systematically in the environment, dissolved metals and hydrocarbons accumulate unnoticed in living tissues to abnormal levels. Apart from natural sources such as volcanic activity and continental w<sup>EKET</sup> ig, heavy metals and hydrocarbons enter the aquatic environment through diverse anthropogenic sources which include industrial and domestic effluents, urban storm water (surface) leaching of metals

from garbage and solid waste dumps, metal inputs from agricultural chemicals and pesticides, burning of fossils fuels, industrial emissions from petroleum industry activities and oil spillages among others (FAO, 1992; Henrichsen and Robey, 2000).

In Nigeria, several studies on heavy metals and total hydrocarbon concentrations in water and aquatic

resources have been carried out (Kakulu *et al.*, 1987a,b; Ibok *et al.*, 1989; Etim *et al.*, 1991; Asuquo *et al.*; 2000; Asuquo *et al.*; 2004). These studies assessed mainly the impact of the toxins on sediments, water and pelagic fishes but none on *Maetra nitida* (family:mollusca) a coastal edible specie. Out of thirty (30) species of the genus *Maetra* that are known worldwide, only three (3) species are

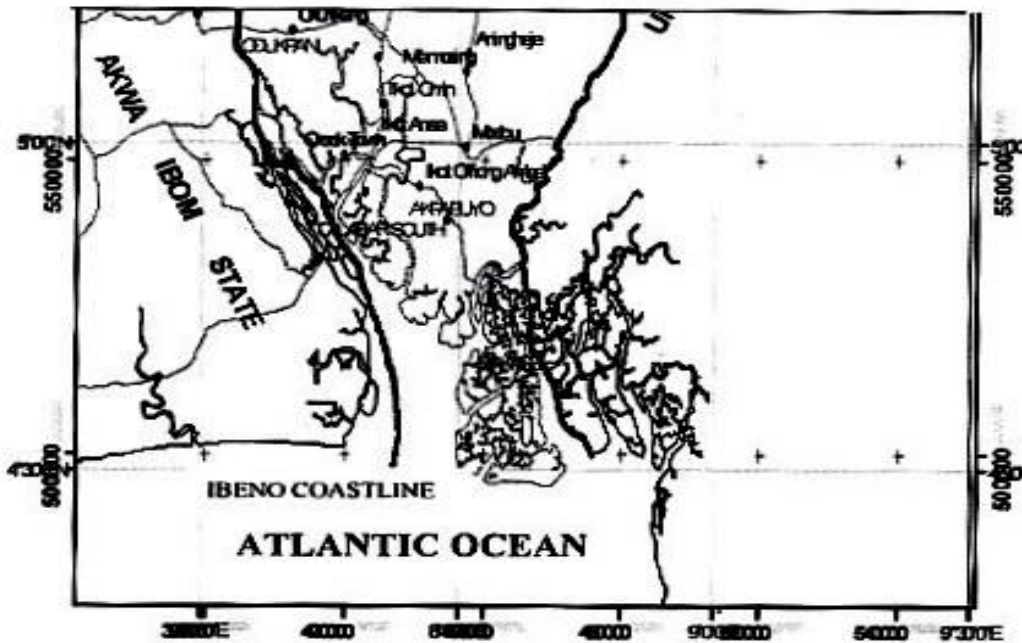


Fig. 1 Map of Akwa Ibom State showing the location of Ibeno coastline, Nigeria

available along the West African Coastline namely *M. nitida*, *M. glabrata* and *M. rostrata*. *Maetra nitida* (Mbobuk, local name), is a filter feeder and has a maximum size (length) of 4cm (Schneider, 1990). It was chosen for this study because of its availability in large quantities during all seasons, its sessile nature, feeds on detritus as well as plankton and is consumed largely by the coastal dwellers.

The Ibeno shoreline lies approximately within longitudes 7° 48' and 8° 17' E and latitude 4° 30' and 4° 35' N and stretches over 55km from Atabrikang (near Imo river) to Okposo by the Cross river estuary. It is segmented into two by the Qua Iboe river (Fig.1). The beach has a flat profile with well sorted

fine grained sand which provide a compact surface that is impenetrable to physical pollutants except dissolved components. The objective of the present study was therefore to investigate the food quality of *Maetra nitida* in recognition of its importance as one of the most edible bivalves found along the Nigerian coastline and the extent of contamination of the species arising from anthropogenic inputs of industrial sewage and petroleum production activities abounding in the study area.

## MATERIALS AND METHODS

### COLLECTION AND PRELIMINARY PREPARATION OF SAMPLES

The samples were hand picked from the fine grained sandy sediments (inter-tidal zone) of Ibeno coastline at ebb tide between November and December 2001. After pre-sorting in the field to exclude the juveniles (<1.0cm), the samples were transported in large glass jars with habitat water to the laboratory. Collected samples were separated into two classes: small size (1.5 – 2.5cm) and adult size (2.6 – 4.5cm). The soft tissues were extracted using stainless steel knives, weighed, wrapped with aluminum foil and preserved in deep freezer until analysis.

### HEAVY METAL CONTENTS

The concentration of ten metals namely Fe, Cu, Zn, Pb, Ni, V, Cr, Cd and Co were determined as reported previously (Asuquo *et al*, 2004). This involved the thawing of the soft tissues and oven drying for 4 hours. 5g of oven-dried tissue were homogenized in agate mortar and digested with a 20ml mixture of 80% Sulphuric and 40% Nitric acids (3:1v/v) in crucibles (3 cm id) in ASUBA Digestion chamber (Model 567/98) for 2-4 hours. All reagents used in the preparation of standards were of Analar Grade. Heavy metal concentrations were thereafter analysed using Atomic Absorption Spectrophotometer (Model 2380). Blanks were run simultaneously with the prepared samples. Accuracy and data reproducibility were ensured by duplicating each batch of sample and the controls. Percentage coefficient of variations were < 5.5 %.

### TOTAL DISSOLVED PETROLEUM HYDROCARBON (TDPH) CONTENTS

30gm wet weight of soft tissue for each class of organism was homogenized and refluxed in 50ml of alkaline methanol (95g of Potassium hydroxide, 75ml of Methanol) / 20% brine (20g of Sodium Chloride, 80% of deionised water) mixture for 1 – 2 hours. The resulting solution was cooled and extracted with 20ml of redistilled n-hexane (Analar). Determination of TDPH was carried out colorimetrically at 430nm using Hach Spectrophotometer Model DR/3000 after the extract (lipid) was purified using activated alumina/silica column.

## RESULTS AND DISCUSSION

Two class sizes of *M. nitida* viz: small size (1.5 – 2.5cm) and adult size (2.6 – 4.5cm) were analysed to assess the levels of ten heavy metals in the samples. Only five metals (Fe, Mn, Zn, Ni and Cu) were detected while others were below detection limit (0.001ppm) of the instrument. Fe ranged 180.6 – 232.8 µg/g, Mn, 12.6 – 16.30 µg/g, Zn, undetectable to 11.4 µg/g, Ni, ranged from 4.3 – 6.5 µg/g and Cu, from undetectable to 3.7 µg/g respectively. The mean concentrations of detectable metals in the tissues of *Macra nitida* when compared with FAO (1992) and WHO (1998) standards were all above the maximum permissible limits of these metals (Table 1).

*Macra nitida* inhabit the subsurface portion of sandy shores. It spawns during the wet season and only very few can be found close to the near surface (< 3cm depth) at this period. In the dry season, there is a multiplication of the specie and all size classes can be found. They have a life time ranging from 3-6 months in the coastal habitat.

**Table 1** Mean concentration of heavy metals in tissues of *Mactra nitida*, the maximum permissible limits and possible sources along Ibeno coastline

Specific metals	Metal concentrations $\mu\text{g/g}$	Permissible limits in aquatic life	Pollution Index	Potential industrial sources
Fe	206.7 $\pm$ 26.0	300 (0.3)	1.56	Petroleum production offshore, crude oil tank farms, discarded / dumped ships at nearshore
Mn	14.5 $\pm$ 0.06	100	0.06	Offshore/onshore production, fuel, accidental spillages
Zn	5.7 $\pm$ 2.7	50 (0.03)	0.01	Discarded /dumped ships, fuel
Ni	5.4 $\pm$ 1.0	- (0.15)	0.45	Discharges from oil tank farms, fuel
Cu	1.9 $\pm$ 1.85	0.04 (0.004)	0.06	Dumped ships, fuel, drilling platforms

\* Modified after FAO (1992), \*\* WHO (1998)

Pollution Index =  $\sum M_i \text{ org/ sed}$ ,  $i$  represents the specific metal concentration,  $M_i$  / in organism and in sediment.

Most shorelines are vulnerable to anthropogenic influences especially when there are ongoing coastal activities such as petroleum extraction/refining from where untreated sewage and effluents are released into the near shore waters. The situation can be aggravated when the morphology of the coastline is undulating and flat. Under such topographical conditions, entrained pollutants are eliminated by incorporation into the nearshore marine sediments where the organisms live. Therefore, the occurrence of Fe, Mn, and Ni in concentrations above the permissible limits for these metals suggest an absorption from petrogenic source since these metals have been found to occur in fuel/refinery effluents (FAO 1992) and also in Qua Iboe crude oils (Asuquo *et al* 1995, 1996) extracted from the area.

Figs. 2 and 3 show the trends and the variation in heavy metal concentrations between the small (juveniles) and large

(adults) sizes of *Mactra nitida* and the different locations respectively. The heavy metal trend followed the order Fe>Mn>Ni and Fe>Mn>Zn>Ni>Cu for juveniles and adults respectively. It appears there is a consistent pattern in the bioaccumulation of the contaminants by the organism. A slight decrease in contaminant concentration with class size could be detected along the coastline. This is associated with the high affinity and specificity of Fe and Mn to form organometallic complexes with polymeric organic molecules in sea water as compared to other trace elements (Morel and Hering, 1993). Furthermore, organic-organic complexation between the hydrocarbons and the lipid materials in the organisms is responsible for the enhanced concentration of TDPH than the trace metals. Concentrations of TDPH observed were generally higher than those of the trace metals. A significant correlation ( $r=0.96$ ,  $n=120$ ,  $P<0.05$ ) were observed in

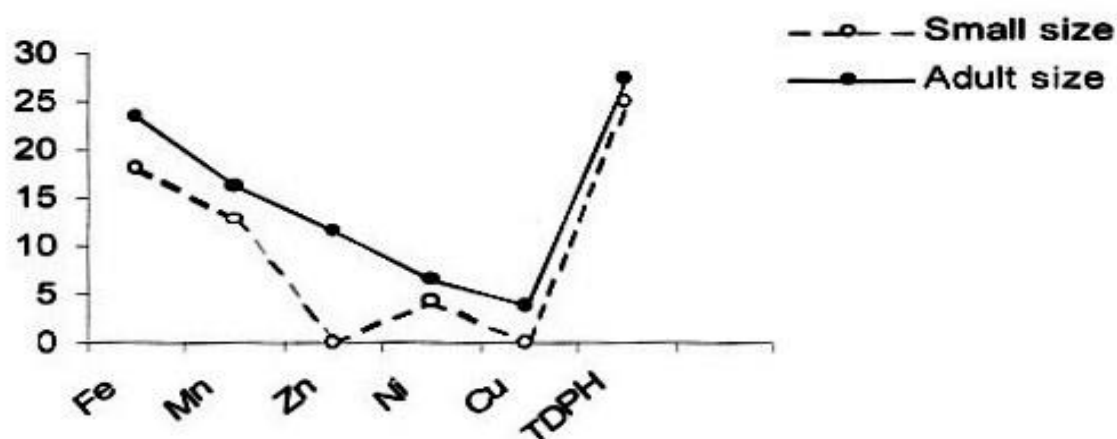


Fig. .2 Comparison of tissue concentrations of Fe,Mn, Zn, Ni and Cu in small and adult species Of *Macra nitida* (Fe concs = 10 x obs values; TDPH- total dissolved petroleum hydrocarbon)

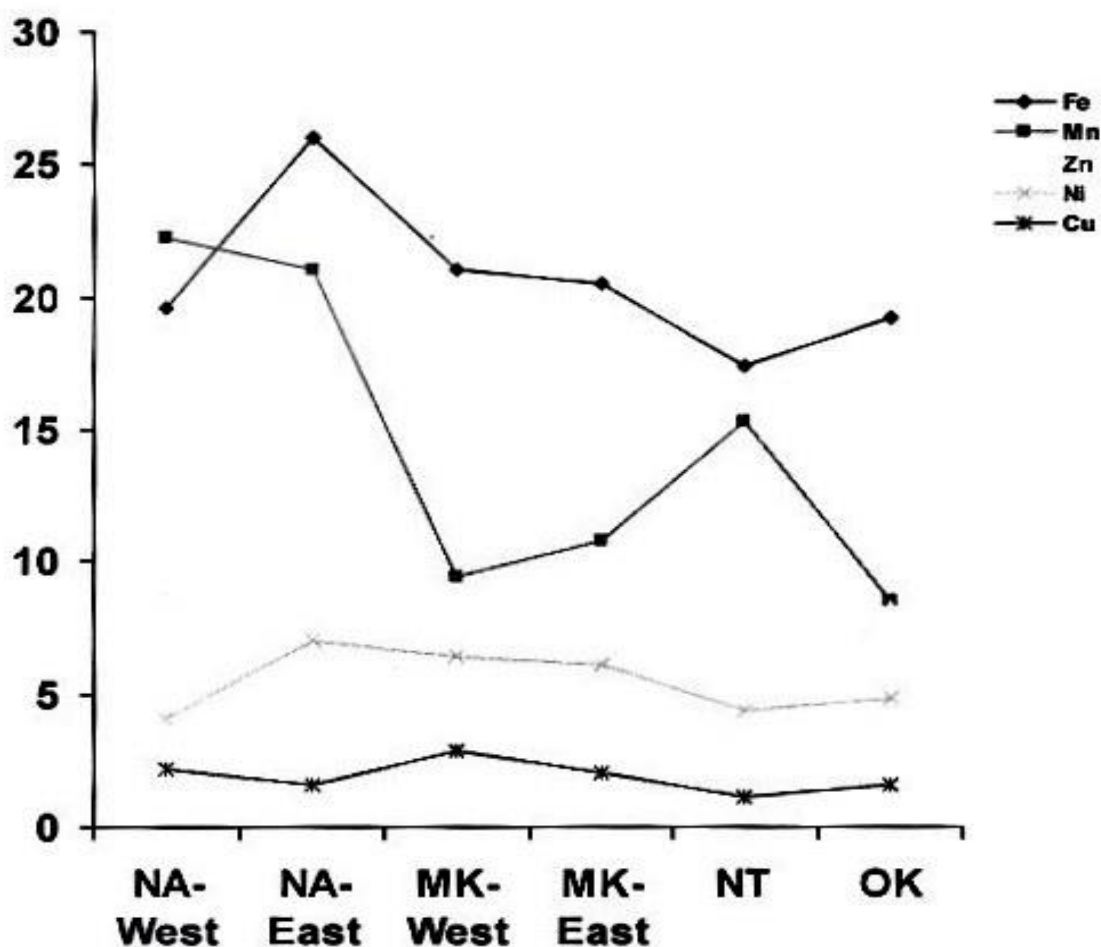


Fig. 3 . Variation of the mean concentrations of trace metals along the coastline (Fe values = 10 x obs. Value, NA- W: Ntafre West, NA-E: Ntafre East, M-West: Mkpanak West, M- East :Mkpanak East, NT-Ntaikang, OK-Okposo)

relation to the metal contents between the juveniles and the adult sizes which confirmed the observed trend in contaminant accumulation along the coastline.

In Table 1, the heavy metals pollution indices for *Macra nitida* along the coastline are presented. The observed indices indicate that the potential to accumulate toxic metals increase with increase in size of the organisms. Expectedly, the large sizes than the small size (juveniles) and the (adults) bioaccumulated more hydrocarbons concentration ranged from 235.0 –266.3ppm for juveniles and 240.2 –305.0 ppm for the adults. Fe was the most bioaccumulated metal.

The mean concentrations as shown in Fig. 2 are higher than GESAMP (1977) limit( 25ppm) for THC concentration in coastal organisms.

### Copper

Copper has been implicated in brain and bone damage (WRI, 1987) and enormously high concentrations of copper have been found in water, sediments and biota of some coastal areas (Hinrichsen and Robey, 2000). Studies of long-term change in copper content in seaweed in the coastal areas without any known direct discharge has revealed no notable changes during the last decade. There are no indications yet to a food chain magnification of Copper (FAO, 1974).

### Zinc

Zinc contamination in the open sea is not fully known, but high levels of Zinc have been found in the sediment and biota of some coastal waters associated with heavy local discharges. Data from heavily contaminated coastal areas show that \*\*\* levels generally decrease when going up the food chain (FAO, 1974).

### Cadmium

Cadmium concentrations has been noticed in some marine mammals, for example sea oyster have been reported to contain up to 500ppm of Cadmium in their kidneys; corresponding concentrations in man would cause severe kidney damage. The biological effects of these Cadmium levels in

sea oyster and other marine organisms are unknown (FAO, 1974).

### Lead

Lead is cumulative poison that inhibits enzymes and impair cell metabolism. It also reduces IQ (intelligent Quotient) in children and also causes other neurological defects (UNDP, 1998; Hinrichsen and Robey, 2000) it has the half-life in upper mixed layers of the oceans of a few years (FAO, 1974).

### Vanadium

Large amounts of Vanadium enter the atmosphere from the burning of fossils fuels. Open ocean surface water contains more Vanadium than does subsurface water; this could be due to atmosphere fallout but also to surface contamination from oil spills or to a natural accumulation process in the surface film. Some marine organisms can concentrate Vanadium from sea water to very high levels (FAO, 1974).

The extent of man's impact on Vanadium concentrations in marine organisms is unknown, as are the biological and ecological effects of Vanadium contamination (FAO, 1974).

### Manganese and Iron

As a result of mining, large amounts of Iron and Manganese are discharged to the marine environment. Compared to the natural flux, however, the amounts released and discharged by man are small. Elevated concentrations of Iron and Manganese are only found locally in coastal areas. Bioaccumulation of Iron and Manganese provides a medium for vertical transport with dead organisms or faecal pellets (FAO, 19974).

This study also revealed a significant correlations between class sizes and concentrations of heavy metals ( $r = 0.9959$ ;  $p < 0.05$ ;  $n = 10$ ); however, Zn and Cu did not show early bioaccumulation in the small class size when compared to the large class size. Murphy et al (1978) suggested that the kinetics of Zn uptake may apparently alter heavy contamination of species by Zn.

### Hydrocarbons in the aquatic environment.

Hydrocarbon contaminants have been shown to lead to the following biological

responses even at very low-level; inhibition of enzymes functions, bioconcentration in tissues, interference with growth, reproduction failures and genetic (carcinogenic, mutagenic and teratogenic) effects (NRC, 1985; Clark et al., 1997).

Polycyclic aromatic hydrocarbons (PAHs) which are the high molecular weight components of petroleum have been reported to have genetic (carcinogenic, mutagenic and teratogenic) effects (NRC, 1985; Clark et al., 1997) even at low-level contaminations in sub-tidal sediments after 18 in oil months in oil spill sites (GESAMP, 1989).

Input of contaminants into the sea associate with offshore oil drilling and production include accidental spillage, discharges of cuttings and discharges of production waters. (Kingston, 1992; OSPARCOM, 1992). The drilling discharges of oil based muds (OBM – diesel or low aromatics) turned out to have long lasting effect on the benthos detectable in a 500m radius even 8 years after cessation of drilling activities (Daan and Mulder, 1996). Water based muds (WMB) are far less toxic to the fauna than OBM (Kroncke and Bergfeld, 2001).

Addy et al., (1984) regarded the brittle star *Amphiura filiformis* and the polychaetes *Myriochele oculata* and *Owenia fusiformis* as indicator species being sensitive to oil pollution effects. Studies by Gray et al. (1990) and Olsgard and Gray (1995) partly supported these findings and added *Aonides poucibranchiata*, *Montacuta substriata* and *Ophiura affinis*. Because sensitive species varies greatly over time and between fields, Olsgard and Gray (1995) assumed that there are no "universal" indicator species sensitive to initial oil pollution effects, since there are natural differences in faunal composition even in fairly discrete geographical areas. Species react differently to the impacts of chemical toxicity, organic enrichment and physical disturbance which all co-occur in the case of oil pollution (Kroncke and Bergfeld, 2001).

Many marine and estuaries fishes and shellfishes are known to accumulate THC from water and food (Clark et al., 1997) and this poses a serious threat to public health, as

these substances tend to concentrate along the food chain.

Polyaromatic Hydrocarbons (PAHs) are found in sediments throughout the world (Hites et al, 1980) their presence is thought to be primarily anthropogenic. PAHs occur naturally in petroleum products and also are produced during combustion. They enter the environment from fuel spills, tar coating, coal and other fossils fuel usage, road dust. Concentration of detected heavy metals (Fe, Mn, Ni and Cu) in the tissues of *M. nitida* from Ibeno coastline showed a general increase in the level of bioaccumulation with increase in size, which is in agreement with the reports of Jaahkola et al. (1971) and Murphy et al. (1978) with fish and Bryan (1976) with bivalve, *Scrobicularia plana* from Gennel and Plym Estuaries; as against the reciprocal relationship reported by most authors that worked on Mussels (*Mytilus edulis*) and *Scrobicularia plana*. Etim et al., (1991) also, reported a peculiar temporal fluctuation pattern in clam (*Egeria radiata*).

*M. nitida* from Ibeno coastline showed a wide range of pollution indices for the detectable heavy metals, however there are few reported cases of metal toxicity in humans (Asuquo et al, 2004 ) arising from consumption of fish and shellfish, which is an important source of protein in Nigeria (Etim et al., 1991) , therefore, there is need for proper and regular monitoring of seafood for bioaccumulation of heavy metals in the interest of public health since mollusks are especially noted for accumulating extremely high concentrations of environmental contaminants.

The high concentration level of THC in the tissues of *M. nitida*, which are more than 10 times the GESAMP (1977) Maximum Permissible limits in Fisheries and Aquatic life can be attributed to discharges of drilling muds into the surrounding waters, residual oils from ships and motorized boats commuting between creeks (Daan and Mulder, 1996, Asuquo, 1999) and frequent oil spillages (Kingston, 1992; GESAMP, 1977, Mobil Report, 1988).

The inter-tidal zones of the coastal areas are the impacted by heavy metals and THC contamination from biogenic and



anthropogenic source (FAO, 1974; Hinrichsen and Robey, 2000), especially in oil producing areas such as Ibeno, which are exposed to frequently oil spillages and the associated hazards.

## CONCLUSION

Due to the frequencies of oil spillages along Ibeno coastline and the observed levels of concentration of heavy metals and THC in the tissues of *M. nitida* most of which were well above Maximum Permissible Limits in Fisheries and Aquatic life there is an obvious health implications due to their bioaccumulation and concentration in the food chain.

It is therefore, recommended that a more elaborate study and monitoring of the concentrations levels of heavy metals and THC in the most commonly consumed organisms, the sediment and water be conducted along the coastlines to have a more clearer picture of the extent of bioaccumulation of heavy metals and THC in seafood. So that such polluted seafood could be avoided or prohibited.

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