CONTAMINATION LEVELS OF ORGANOCHLORINE PESTICIDES IN *Tympanotonus fuscatus* AND SEDIMENT OF LAGOS LAGOON, NIGERIA

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Abstract: The wide use and application of Organochlorine pesticides (OCPs) is a menace to non-target aquatic biota. The study evaluated the levels of OCPs residues in *Tympanotonus fuscatus* and sediment within three (3) selected areas of the Lagos Lagoon, Nigeria using Gas Chromatography coupled with Electron Capture Detector (GC-ECD). The mean concentration of OCP residues detected in *T. fuscatus* and sediments were Lindane, Diedrin, Aldrin, Endosulfan (isomers alpha and beta endosulfan), and DDT (isomers orthopara and para-para DDT). Generally, the total OCP concentration was higher in *T. fuscatus* than in sediments while stations 1 had the highest concentration of ∑ OCPs in both tissue and sediment samples followed by stations 2 and 3. Endosulfan concentration was the highest followed by Dieldrin > DDT > HCH > Lindane in decending order. In sediment, the mean concentration of Lindane ranged from Not Detected (ND) to 342.0 ng g^{-1} while HCH ranged from 262 - 818 ng g^{-1}. Total Endosulfan ranged from 776 – 4849 ng g^{-1} while DDT ranged from 349 – 2211ng g^{-1}. Bioaccumulation Factor (BAF) values in descending order was as follows: Endosulfan > Beta _BHC > Endrin aldehyde with the highest BAF values recorded from Iddo (3). Additionally, concentrations of Dieldrin > Heptachlor > DDT were recorded in descending order at Unilag Lagoon front that exceeded the FEPA and USEPA Limit (BAF > 1); an indication that harmful effects are likely for aquatic species. Thus warrants proper and consistent monitoring of OCPs in the Lagos Lagoon.

Keywords: Bioaccumulation, lindane, pesticides, organochlorine, sediment, *Tympanotonus fuscatus*

Introduction

Chlorinated Organic Compounds (COCs) otherwise known as Organochlorine Pesticides (OCPs) is one of the multi-arrays of hydrophobic organic compounds which have been produced in large quantity, and used for the control of weeds, termites, mosquitoes and other insects constituting nuisance in many part of the world for years (Ssebugere *et al*., 2014). Organochlorine pesticides have been widely used in chemical and agricultural industry all over the world. Concentrations of OCPs generally is on the decline in developed countries since it was banned but levels in developing countries have shown an increasing level because there still an abuse of these chemicals in agriculture and public health purposes. The consequence is a distribution of these pesticides in the different strata of the environment. These compounds are raising a lot of dust environmentally due to their persistence, bioaccumulative ability. Organochlorine Pesticides pass through the food web with its potential negative impacts on humans and wildlife (Donaldson *et al.*, 2010). Studies have shown various levels of pesticides such as OCPs in fish (Okoumassoun *et al*., 2002; Unyimandu and Udochu, 2002; David *et al.*, 2008).

Most water bodies in Nigeria, especially Lagos serve as a sink for the disposal of waste from about 2000 medium and large scale industries located in the metropolis (Odiete, 1999) in an unregulated manner. The indiscriminate use of pesticides in Nigeria has resulted in the occurrence of the residues in biota and other abiotic compartments (Ize-Iyamu *et al*., 2007; Okoya *et al.,* 2013). The sediment is likely the largest sink in the environment for OCPs and the release of these contaminants from soils continue to be a source to other environmental compartments (Bidleman, 2008). Evidence suggested that much of this exposure to contaminants are presented as multiple mixtures of chemicals, the toxic effect of which are unknown, particularly over longer time scales (Reffstrup *et al*., 2010). OCPs accumulate in organisms and biomagnified through the food chain, so consumption of biota from contaminated areas may be a major health risk for the consumers. Most of these compounds are considered to act as environmental hormones, which disrupt reproductive cycles of wildlife and reported to be possible carcinogens and or mutagens. Considerable research has been carried out in Nigeria related to OCPs in the fish studies (Ize-Iyanu *et al*., 2007; David *et al*., 2008) but very few on benthic organisms such *Tympanotonus fuscatus.*

Tympanotonus fuscatus (prosobranch gastropod) is a widely consumed high animal protein delicacylocally known as “Periwinkle” in Nigeria. It is highly patronized because it cheap, available and nutritious. Hence, the present study was conducted to estimate the levels of OCPs in the benthic organism (*T. fuscatus*) and sediments in selected areas of the Lagos Lagoon.

Materials and Methods

Study area

Lagos Lagoon is among the major Lagoons in the Gulf of Guinea and it is located between longitude 30 10’ and 304’ SE and latitude 60 5’ and 60 36’ N (Fig. 1). Several rivers empty into the lagoon among which are Yewa, Ogun, Oshun and Ona Rivers (Ayoola, 2016). The Lagos Lagoon is the ultimate sink of a number of industrial discharge/effluents and run off from surrounding metropolis. Selection of sampled areas;Unilag Lagoon front (1), Makoko (2) and Iddo (3) was based on pollution dynamics of the Lagos Lagoon (Table 1).

Fig. 1: Study Area showing sampled stations in Lagos Lagoon

Table 1: Description of sampled locations

Sample Locations Stations	Coordinates	Description of Site
Unilag Lagoon Front (1)	N 06°31. 057' E 003° 24. 113'	Characterised by natural fish ponds built, boat transport and fishing activities.
Makoko (2)	N 06°29. 457' E 003 ° 23. 443'	Characterised by wooden residential buildings along the coast, fishing, saw mills and high boat transport density.
Iddo (3)	N 06° 28. 174' E 003° 24. 113'	Wooding/Bricks residential buildings lining the coastline, solid waste dumps in several locations along the coast, and sand mining activities.

Animal and sediment sample collection

Thirty (30) *T. fuscatus* species collected alive from their natural environment, sacrificed, de-shelled and stored in ice container before transport to the laboratory where it was kept in the refrigerator at a temperature of -20°C until ready for use. Sediment samples were collected between September and November, 2016 using a stainless steel Van Veen Grab of 0.1 m^2 in three (3) replicates, kept in aluminum foil and stored at -20°C until OCPs and stable isotopes analyses in the laboratory.

Extraction of OCPs in biota and sediment

Adopting the USEPA 8180B method 5 grams of well homogenized *T. fuscatus*, muscle tissue and sediment was ground (separately) with 5 g of activated sodium sulfate until a fine powder was obtained and extracted twice with 50 ml of n-hexane and the extract was filtered into a conical flask. The filtered extract was re-extracted with 40 ml of n-hexane/ethyl acetate (3:2) in a separating funnel. The organic layer was collected and sample was passed through anhydrous sodium sulfate, then concentrated to 5 and 20 ml of n-hexane was added to the extract, condensed to 2 ml in rotary evaporator and then purified using silica gel. The packed column was pre-rinsed with 30 ml of n-hexane. The elution was subsequently carried out using 30 ml of n-Hexane. The extract was further condensed to 2 ml for GC-ECD analysis.

Gas chromatography- electron capture detector (GC-ECD) analysis

Detection, identification and quantification of OCP congeners in cleaned-up extracts were done using a gas chromatography coupled electron capture detector (GC-ECD).

Quality control and quality assurance

The samples were analyzed in GC-ECD (Gas Chromatograph-Electron capture detector) (QP 2010 Agilent) equipped with capillary column DB-1 (30 m long, ID 0.32 mm) and 5% methyl phenyl silicone. The limit of detection (LOD) of OCPs was determined three times of the standard deviation of the blank. From stock solution of organochlorine pesticides standard containing cocktail of 17 pesticides hexachlorocyclohexane (α, β & γ-HCH), Cyclodiene (aldrin, dieldrin and endrin), heptachlor, hexachlorobenzene (HCB), trans-Chlordane, cis-Chlordane, mirex and diphenyl aliphatic (p,p'-DDE, o,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT), 200 ppb (200 ng/ml) of working standard was prepared. For the standard calibration, eight different concentrations from 5 to 200 ng/ml were prepared. All standards show a linear range from 5 ppb to 200 ppb. The coefficient (R2) values ranged from 0.9746 to 0.9985 for 8 concentrations levels. The limit of detection (LOD) as 3S varied from 0.69 to 18.23 ng/ml (3S) for OCPs.

Bioaccumulation factor (BAF)

In this study, BAF was considered as a measure of the biotic fate of OCPs and defined using the following equation:

$$BAF = \frac{Concentration\ of\ OCPs\ in\ Typanotonus\ tissue}{Concentration\ of\ OCPs\ in\ sediment}$$

Statistical analysis

Data analysis was done using Statistical Package for Social Sciences (SPSS) version 16.0 and Excel Statistical Tool pack.

Data was subjected to one way Analysis of Variance (ANOVA).

Results and Discussion

Mean concentration of Organochlorine Pesticides (OCPs) congeners detected in *T. fuscatus* and sediments were Lindane, Diedrin, Aldrin, Endosulfan (the isomers alpha and beta endosulfan), and DDT (the isomers orthopara and para-para DDT). Generally, the total OCP concentration was higher in *T. fuscatus* than in sediments while stations 1 had the highest concentration of ∑ OCPs in both tissue and sediment samples followed by stations 2 and 3 (Fig. 2). Endosulfan concentration was the highest followed by Dieldrin > DDT > HCH > Lindane in decending order. The result obtained from the assessment of OCPs in *T. fuscatus*muscle tissue was in accordance with the findings of Sankaramakrishnan *et al.* (2005). The low concentration of Lindane detected in this study should not be ignored as WHO classifies lindane as "Moderately Hazardous" pesticides. However, exposure to large or small amount of Lindane in continuous manner, can negatively affect the nervous system producing a range of symptoms from headaches, dizziness, convulsions and more rarely death (ATSDR, 2005).

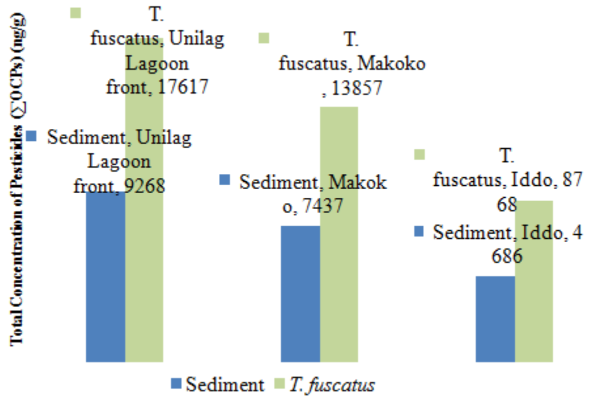

Fig. 2: Relative proportion of ∑ OCPs in Tissues of *T. fuscatus* and Sediment from Lagos lagoon

The relatively high level of Endosulfan detected in this study, is an indication that though it was banned in many countries, its occurrence in the present study depicts its persistent behavioural pattern. This might be due to extensive use of these pesticides and being an organochlorine it also has a tendency to accumulate in the sediments and bottom dwellers. The findings of the present study is in accordance with the findings of Sinha *et al*. (2001) and Falahudin and Munawir (2012) who investigated organochlorine pesticides in sediment at contaminated levels in the aquatic environment. This indicated that large quantities of these substances are still in use and are subsequently absorbed by the aquatic organisms in the water body. Endosulfan is responsible for many fatal pesticides poisoning incidents. Environmental fate and persistent behavior of Endosulfan as xenoestrogen; an endocrine disruptor, that synergises reproductive and developmental damage in animals and humans. It has been established that Endosulfan is highly toxic for aquatic organisms and has bioaccumulative effect especially in biota.

The concentration of Lindane which was detected in sediment was higher than that detected in *T. fuscatus* tissue. In sediment, Lindane ranged from ND to 342.0 ng g-1 while the mean concentration of HCH ranged from 262 to 818 ng g-1. The concentration of HCH in sediment was higher than that detected in *T. fuscatus* tissue. The order of the concentration of Lindane at different stations in the tissue was in the sediment was: station 2 > station 1> station 3. Total Endosulfan ranged from 71 to 739 ng g-1 while T-DDT ranged from 64 to 237 ng g-1 (Fig. 3). Among the isomers of the HCH, α and β -isomers were the most widely detected. The wide distribution of α - HCH isomer in the tissue and sediments samples may be explained based on the fact that γ-HCH can be easily degraded by microorganisms in soil, bottom sediments and photochemical. Other sources of HCH are known to include industrial emissions, especially from the manufacture of poly (vinyl chloride), and it has also been reported as a biotransformation product of Lindane in the environment. Its high persistence and volatility have combined to make HCH one of the most evenly distributed global pollutants, with levels of around 100 pgm~3.

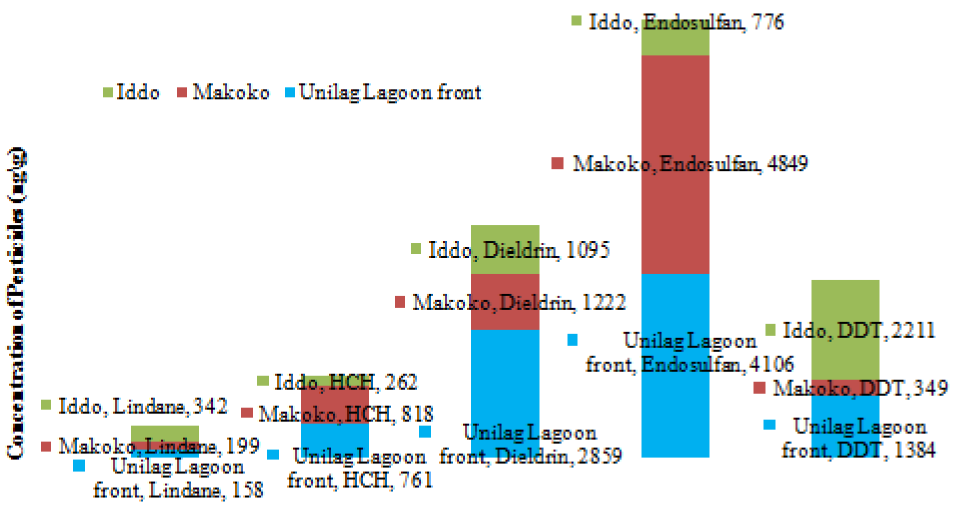

Fig. 3: Range of concentration of pesticides at various sites in sediment

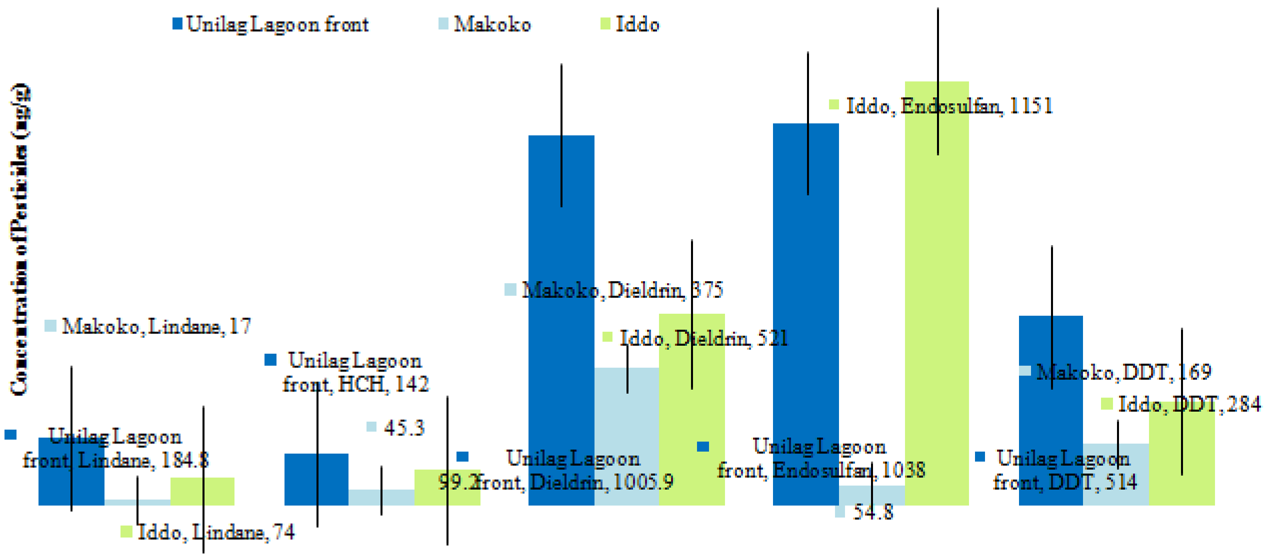

Fig. 4: Range of concentration of pesticides at various stations in tissue of *Tympanotonus fuscatus*

BAF values for most OCPs in the *T. fuscatus* samples were less than 1 (Table 2). However, Endosulfan > Beta _BHC > Endrin aldehyde was recorded to have the highest BAF values in *T. fuscatus* sampled from Iddo. Additionally, concentrations of Dieldrin >Heptachlor >DDT were recorded in descending order at Unilag Lagoon front that exceeded the FEPA Limit BAF>1, USEPA Limit BAF> 1. The highest level of Dieldrin and Aldrin were recorded in the sediment sample in station 2. A similar observation was reported by Gitahi *et al.* (1994). High level of Aldrin and Dieldrin in the aquatic environment was also recorded by David *et al.* (2008). Dieldrin is a chlorinated cyclodiene that was widely used in the Nigeria. The National Agency for Food and Drug Administration and Control (NAFDAC) banned the sale and supply of 30 different agrochemical products in the country that included Dieldrin and Aldrin. The toxicity of this persistent pesticide posed imminent danger to human health although the product is still in use because of the low cost and affordability. Dieldrin is not easily metabolized in water and has limited capacity of being digested and excreted from the body. It is, however, easily absorbed and transported throughout the blood of vertebrates and hemolymph of invertebrates.

Table 2: Bioaccumulation factor (BAF) in the sampling stations

Congeners	Unilag lagoon front (ng/g)	Makoko (ng/g)	Iddo (ng/g)
ALPHA_BHC	ND	ND	0.116
BETA-BHC	ND	0.036	1.175
GAMMA-BHC	0.595	0.020	0.01
DELTA_BHC	0.008	0.234	0.211
HEPTACHLOR	1.155	0.637	0.744
HEPTACHLOR EPOXIDE	0.581	0.557	0.213
METHACHLOR	0.194	0.825	0.362
DIELDRIN	1.970	0.517	0.28
ALDRIN	0.932	0.172	0.965
ENDRIN	0.396	0.525	0.205
ENDRIN ALDEHYDE	0.691	0.132	1.386
ENDOSULFAN I	0.104	0.289	0.333
ENDOSULFAN II	0.335	0.123	15.07
ENDOSULFAN SULPHATE	0.290	0.991	0.04
P,P'-DDE	0.367	0.265	0.236
P,P'-DDD	0.1	0.047	0.320
P,P'-DDT	1.518	0.512	0.09

DDT along with its isomer o, p' and p, p'-DDT were present in higher concentration in tissue of *T fuscatus* and in the sediment of Lagos Lagoon. However, p, p'-DDE concentration which was relatively higher in the sediment than p'-DDD in *T. fuscatus* tissue may be explained by high chemical stability, persistence, biomagnifications potential in the environment and in living organisms. This might be attributed to environmental fate of DDT to its metabolites, which are more stable and persistent than parent molecules of DDT (Bossi *et al.*, 1992). The concentration of T-DDT in *T. fuscatus* tissue and in sediment were maximum at station 1, probably due to affinity of these compounds to particulate matter and marine sediments, which is thought to be the major sinksfor the pollutants (Doong *et al.*, 2002). It also indicated different sources of contamination as well as slow degradation resulting in environmental persistence of these compounds (Kim *et al.*, 2007). The present result, with reference to sediment, is in accordance with the findings of Sikoki *et al*. (2014). The authors pointed out that residue levels of the OCPs in the environmental matrices analyzed from the sampling stations increased overtime, reflecting increase in the release of these pesticides into the environment, probably due to increase in agricultural activities with the subtle use of pesticides in various forms. Environmental fate and persistent behavioral pattern of DDT and its metabolic products magnify through the food chain and stored mainly in the body fat. DDT is highly toxic to aquatic life especially biota as it can bioaccumulates leading to long-term exposure to high concentrations. The bioaccumulation factor (BAF) was used to evaluate the environmental fate and persistent behavior of OCP residues in *T. fuscatus* samples in relation to sediment from the three sampling stations were in conformities.

The results obtained in this study indicated that human exposure to pesticides via consumption of contaminated *T. fuscatus* could lead to potential health risk. It also supports the fact that the long term accumulation of pesticide residues in the human body via dietary intake of benthic invertebrates is a source of concern. The result of this study has shown that sediment and *T. fuscatus* samples from these selected areas of the Lagos Lagoon are contaminated with some organochlorine pesticides residue when compared to the FEPA and WHO Maximum Residue Limits. This calls for proper and continuous monitoring of OCPs in order to protect aquatic life. Documentation of data from this study will create public awareness on the probable health risk associated with OCPs especially in Africa, Nigeria inclusive where awareness is relatively low.

Conclusion

The study has established the fact that Lagos Lagoon is contaminated due to continuous discharge of toxic materials such as OCps from the point and non point sources. Due to difficulty in degrading OCPs they persist in the environment and bio-accumulate in the food chain, which might pose potential hazards man on the long run.

Conflict of Interest

Authors declare that there is no conflict of interest reported in this work.

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