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Distribution of Chlorinated Pesticides in Shellfishes from Lagos Lagoon, Nigeria

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Abstract

Shellfishes namely *Ocypoda africanus*, *Penaeus notialis* and *Procambarus clarkii* were collected from Lagos Lagoon and analysed for chlorinated pesticides because they are the most abundant group of aquatic sediment macro-fauna within tropical areas and have the capability to concentrate in their tissues pesticide residues from sediments and water. Sampling was conducted between December 2008 and September 2009 during the dry and wet seasons. The shellfishes were subjected to cold extraction with petroleum ether/acetone (1:1 v/v) mixture and clean-up on silica gel adsorbents. The samples were analysed for aldrin, dieldrin, endrin, DDT, heptachlor, HCH, endosulfan, chlordane and methoxychlor. The detection and determination of the pesticide residues were performed by gas chromatography. The total detectable concentration of chlorinated pesticide residues (wet weight) of the muscle tissues of the shellfishes ranged from 6.47 ng/g to 4516.71 ng/g in *Procambarus clarkii.* The pesticide residue distribution pattern in their muscle tissues were in the order: *Procambarus clarkii* > *Ocypoda africanus* > *Penaeus notialis*. The male shellfishes accumulated higher pesticide levels than the female shellfishes. The residue levels were higher in the Lagos Lagoon than in Agboyi Creek while a higher concentration of the residues was observed during the dry season. Except for endrin and heptachlor, the estimated daily intakes of the pesticides were within the acceptable daily intakes as established by experts while the levels of residues in the shellfishes were within the permissible residue limits.

Keywords

Chlorinated pesticides; Lagos lagoon; *Ocypoda africanus*; *Penaeus notialis*; *Procambarus clarkii*

Introduction

Shellfishes consist of terrestrial and aquatic animals including lobsters, oysters, crabs, shrimps, prawns, crayfish and barnacles. The aquatic crustaceans are the majority and live in either freshwater or marine habitat while terrestrial crustaceans live in holes made on waterlogged land. Chlorinated pesticides are synthetic organochlorines which are lipophilic and hydrophobic. Their lipophilicity, hydrophobicity, stability to photo-oxidation, low vapour pressure, low chemical and biological degradation rates have led to their accumulation in biological tissues and the subsequent magnification of concentrations in organisms, progressing through to the food chain [1]. They can be recycled through food chains and produce a significant magnification of the original concentration at the end of the chain [2]. They are resistant to natural breakdown processes and are extremely stable and persistent, highly toxic and bioaccumulate in the fatty tissues of animals and humans [3].

The decline in the hitherto viable commercial artisanal shellfishery in Lagos Lagoon, points to environmental degradation and possible changes in water quality with biological consequences for biota [4]. The contamination of the environment and food by chlorinated organic pesticides has become a topical issue of considerable concern in many parts of the world, and has led many researchers to investigate their occurrence, distribution and concentrations in several ecosystems [5-7]. The toxicity of pesticides varies greatly with their intrinsic properties, the species being studied, their persistence, the partitioning of the pesticides between the particulate and aqueous phases, toxicity to aquatic organisms and the tendency to bioaccumulate. The contamination in fishes may be linked to the relative fat contents in fishes, fish size and feeding habits, as well as biogeochemical transformations in aquatic ecosystems. Nigerian fishes have been reported to contain all the commonly encountered chlorinated pesticides [8-10].

Shellfishes have been recognized as excellent bioaccumulators of organic and inorganic pollutants [11,12]. Bivalves, crabs and shrimps have been identified as standard bioindicators of aquatic pollution owing to their capability to bioaccumulate and bioconcentrate organic pollutants in their target organs at levels higher than background concentrations [13,14]. Shellfishes are used in many pollution monitoring and assessment studies because they have world-wide geographical distribution and are relatively stationary. Biological monitoring of persistent organic pollutants provides information on the extent of biotransformation and bioaccumulation processes that the contaminants have undergone during their passage through biological systems and, therefore, provides a more realistic view of the contaminant distribution in the environment site [15]. Shellfish's reflect traces of contamination better than finfishes. They are also sediment-dwelling and have a pronounced ability to concentrate persistent organic pollutants from sediments and water [16,17].

Many persistent organic pollutants, which pollute the environment, become incorporated into food webs. Humans, being the final links in the food chain, are the most affected. Consequently, the general public has become increasingly concerned about the potential risk to human health from the consumption of such polluted biota. The ill effects of pesticides may arise from short- or long-term and low- or high-level exposure through dermal absorption, inhalation and oral ingestion. Chlorinated pesticides could lead to human breast and liver cancers, testicular tumours and lower sperm counts in humans [18,19]. Some of the symptoms of pesticides poisoning include irritation, dizziness, tremour, tonic and chronic convulsion [20]. Studies have also suggested that pesticides may affect the normal function of the endocrine system of humans and wildlife [21].

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Lagos Lagoon is a depository for a large number of surface runoffs, drainage channels and important rivers flowing from the interior of Southwestern Nigeria to the Atlantic Ocean. The surrounding landmass to the lagoon is also among the most densely populated areas in the country. Deleterious materials are introduced into the lagoon and it is subjected to domestic and industrial pollution because of the poor enforcement of water pollution control laws and regulations. Given the importance of shellfishes as food and the negative health effects of chlorinated pesticides on humans, it is very important to evaluate the levels of these pollutants in edible fishes such as *Ocypoda africanus*, *Penaeus notialis* and *Procambarus clarkii*. This research was a pollution monitoring study aimed at investigating the occurrence, concentration and distribution of organochlorine pesticides in selected shellfishes from Lagos Lagoon with a view to assessing their exposure to these toxicants.

Materials and Methods

Study area

The study area for the investigation is the Lagos Lagoon, which lies between latitude 6° 26' - 6° 37' N and longitude 3° 23' – 4° 20' E in the western part of Nigeria. The lagoon consists of three main segments namely Lagos Harbour, Metropolitan End and Epe Division. It empties into the Atlantic Ocean via Lagos Harbour and is drained by Ogun, Agboyi, Majidun and Aye Rivers. Its brackish nature is a consequence of the influence of tidal sea water incursion and freshwater discharge from the adjoining rivers and creeks. Human activities associated with the lagoon are fishing, aquaculture and sand mining. The fauna is composed of fresh, marine and brackish water species and include crabs, shrimps and crayfishes.

Sampling strategy

Sampling was conducted between December 2008 and September 2009 during the dry and wet seasons to study the effects of seasonal variations on the samples.

Collection of shellfish samples

Shellfishes were harvested with the assistance of fishermen at the Lagos Harbour and Agboyi Creek in order to analyse them for OCP residues. Freshly harvested shellfishes - crab (*Ocypoda africanus*), shrimp (*Penaeus notialis*) and crayfish (*Procambarus clarkii*) - were collected from each harvesting area using nets. The harvested shellfish samples were separately wrapped in aluminium foil, stored in ice-packed coolers and transferred to the laboratory where they were frozen, thawed, cleaned in distilled water. Figure 1 and Table 1 shows the shellfishes sampled.

Determination of sex

The shellfish samples were separated into males and females by examining their gonads.

Measurement of length

The carapace lengths (cm) of the shellfishes were measured using a ruler.

Evaluation of percentage (%) dry matter

The frozen shellfish samples were thawed and cleaned in distilled water before the evaluation of their percentage dry matter. 1.0 - 2.0 g of muscle tissue of each of the fresh shellfish samples was weighed and dried in an oven maintained at 105°C for 8 hours. The dried shellfish samples were cooled in a desiccator and weighed in an analytical balance to constant weight. The percentage dry matter was calculated as follows:

$$\%\ Dry\ matter = \frac{dry\ weight}{fresh\ weight} \times 100$$

Determination of fat content

10 g of shellfish muscle tissue was homogenized with 10 g of anhydrous Na_2SO_4 using a mortar and pestle. Cold solvent extraction was carried out using 50 cm^3 petroleum ether/acetone (1:1 v/v) mixture in a reagent bottle. The mixture was well shaken and the stopper removed continuously to release the gas built up in the bottle. The mixture was allowed to stand for 30 minutes and then filtered. After evaporating the solvent extracts with the aid of a rotary evaporator, the fat content of the muscle tissue was determined gravimetrically:

$$\%\ Fat = \frac{weight\ of\ fat}{weight\ of\ tissue} \times 100$$

Extraction of shellfish samples for determination of chlorinated pesticides

The muscle tissues of the shellfishes were extracted. 10 g of fish sample was homogenized with 10 g of anhydrous granulated Na_2SO_4 using a mortar and a pestle. Cold solvent extraction was performed. 50 cm^3 of the petroleum ether/acetone (1:1 v/v) mixture was introduced into a 250 cm^3 reagent bottle containing the homogenized fish sample. The mixture was shaken and the stopper removed intermittently to release the gas built up in the bottle. The mixture was allowed to stand for 30 minutes and then filtered into a glass container using a filter paper [22].

Pre-concentration of extracts: The solvent extracts were concentrated to 1 cm^3 using a rotary evaporator and kept for clean-up procedure.

Clean-up of extracts: Column chromatography was employed to clean-up the extracts [23]. The glass separating column (20 cm) was packed with activated silica gel (90% < 45 µm) and washed down with n-hexane to remove any dirt. The extracts were demoisturized over 1 g of anhydrous granulated Na_2SO_4 and separated into two eluted fractions using mixtures of dichloromethane, hexane and acetonitrile as eluting solvents. For the first fraction, 30 cm^3 of a dichloromethane/hexane (20/80) mixture was used, while 30 cm^3 of a dichloromethane/hexane/acetonitrile (50/49.5/0.5) mixture was used for the second fraction in order to ensure that the polar acetonitrile eluted any

Figure 1: Shellfishes sampled for pesticide analysis.

Table 1: Sampled shellfishes for the determination of chlorinated pesticide residues.

	Common Name	Biological Name	Feeding Mode	No Collected		No of Males	No of Females
				AGR	LAG		
1.	Crab	*Ocypoda africanus*	Omnivorous	12	12	12	12
2.	Shrimp	*Penaeus notialis*	Omnivorous	-	12	6	6
3.	Crayfish	*Procambarus clarkii*	Omnivorous	12	12	12	12
	Total			24	36	30	30

AGR = Agboyi Creek; LAG = Lagos Lagoon

remaining residue. The fractions were combined, concentrated to 1 cm^3 using a rotary evaporator and subsequently analysed.

Identification and determination of chlorinated pesticide residues by gas chromatography: A gas chromatograph equipped with an electron capture detector (GC-ECD) was used for the analysis of the pesticide residues. The cleaned-up extracts were dried and re-dissolved in 1.0 cm^3 of analar grade isooctane for injection into the gas chromatograph [24]. Blank runs were made for background correction and performance of the system. Organochlorine Pesticides II EPA Method 8081A {Mix AB # 3, cat. #32415 (ea.)} was employed for the analyses. The detection and determination of the residues were performed by injecting 1 µL of the 1.0 cm^3 purified extract into the injection port of a gas chromatograph with a ^{63}Ni electron capture detector (GC-µECD Agilent Technology 7890A) equipped with the ChemStation software. The column consisted of a DB-5 fused silica capillary column (30 m length × 0.32 mm i.d. × 0.25 µm film thickness). The column temperature was programmed from 50°C at a rate of 25°C/min to 100°C, held for 1 min, and then at a rate of 5°C/min to 300°C, held for 5 mins. The temperatures of the injector and detector were 250°C and 300°C, respectively. The injection was carried out on a splitless injector at 250°C and the purge activation time was 30 s. The carrier gas was helium while nitrogen gas was used for the makeup flow. The run time was 17 mins. Identification of pesticide residues was accomplished using reference standards and relative retention time techniques, while the concentration of the residues was determined by comparing the peak heights of the samples with the corresponding peak heights of the reference standards of known concentrations. The concentrations (ww) of the pesticide residues were calculated directly by the gas chromatograph after inputing the weight of the samples and the blank corrections were carried out.

Quality assurance: Before analysis was performed, standards were run to check for the column performance, peak height, resolution and the detection limit. The correlation coefficients of calibration curves of the pesticides were all higher than 0.998. The quality assurance measures included strict cleaning procedures, procedural blank, recovery of spiked standards and monitoring of detector response. The stock solution of the organochlorine pesticide standards was purchased from Restek Corporation, USA. It contained 1000 ppm in n-hexane and was serially diluted to obtain the desired concentrations of 10, 20 and 40 ng/mL.

Recovery study: Recovery studies were undertaken to evaluate the efficiency of the extraction. The recovery of organochlorine pesticides was done in replicate and was determined by spiking the previously analysed samples with the pesticide standard at concentrations similar to those expected in the samples. The recovery values expressed in percentages were calculated from the chromatograms.

$$\%\text{Recovery} = \frac{CS_2 - CS}{CS} \times 100$$

where, CS_1 = concentration of pesticide residues in the sample

CS_2 = concentration of pesticide residues in the spiked sample

CS = concentration of added pesticide

Estimation of daily intakes (EDI) of chlorinated pesticide residues by humans

The daily intake of OCP residues by humans was estimated based on questionnaires and interviews conducted in 100 families. The respondents were persons who eat the types of fishes harvested and were categorized into males and females. Information on preference of the fish species, age and weight of the respondents and frequency of consumption was collated in order to estimate the daily dietary intake of the fishes. The respondents were mainly adults and a few children who reside in Lagos. Their economic activities cut across fishing, farming, teaching, public service and business. The average per capita consumption was estimated and compared with the acceptable daily intake. The dietary intake of chlorinated pesticides was calculated by multiplying concentrations measured in the muscle tissues of each fish by the per capita consumption. The estimated daily intake of the pesticides was calculated using the equation:

$$EDI = \frac{FDC}{BW} \times CC \quad [25]$$

where, FDC = Fish daily consumption (g)

CC = Contaminant concentration (ng/g)

BW = Body weight (kg)

EDI = Estimated daily intake of OCPs (ng/kg body weight/day).

US EPA recommends standard values for daily intake calculations. 70 kg is taken as average body weight, 6.5 g as daily fish consumption and 70 years as exposure for a lifetime.

Analyses of data: The shellfish extracts were analysed for aldrin, dieldrin, endrin, DDT, heptachlor, HCH, endosulfan, chlordane and methoxychlor. Concentrations of OCP residues were calculated individually and as the sum of their isomeric forms. Description of data was performed using a Statgraphics Centurion XV statistical software, with the level of significance maintained at 95% for each test. The mean and standard deviation were calculated from the detectable values, and values below the detectable limit were considered not detected (ND). The mean was calculated from triplicate determinations.

Table 2: Mean biometric data of shellfishes in Agboyi Creek during the dry season.

Shellfish species	Feeding mode	Sex	Wet weight (g)	% Dry matter	% Fat	CL (cm)
O. africanus	Omnivorous	Male	29.9 ± 0.2	19.5 ± 0.2	0.2 ± 0.1	11.0 ± 0.1
		Female	128.4 ± 0.6	19.9 ± 0.5	0.2 ± 0.2	13.0 ± 0.2
P. clarkii	Omnivorous	Male	5.9 ± 0.3	15.8 ± 0.3	0.2 ± 0.1	9.0 ± 0.3
		Female	6.0 ± 0.2	16.0 ± 0.4	0.2 ± 0.2	9 ± 0.2

CL = carapace length of wet shellfish; the mean value was calculated from 3 shellfishes of each species

Table 3: Mean biometric data of shellfishes in Agboyi Creek during the wet season.

Shellfish species	Feeding mode	Sex	Wet weight (g)	% Dry matter	% Fat	CL (cm)
O. africanus	Omnivorous	Male	63.6 ± 0.7	20.4 ± 0.5	0.2 ± 0.2	11.0 ± 0.1
		Female	205.0 ± 0.9	23.0 ± 0.8	0.3 ± 0.1	9.0 ± 0.2
P. clarkii	Omnivorous	Male	5.9 ± 0.2	16.0 ± 0.2	0.2 ± 0.3	9.0 ± 0.1
		Female	6.1 ± 0.3	16.2 ± 0.2	0.2 ± 0.1	9.0 ± 0.1

CL = carapace length of wet shellfish; the mean value was calculated from 3 shellfishes of each species

Table 4: Mean biometric data of shellfishes in Lagos Lagoon during the dry season.

Shellfish species	Feeding mode	Sex	Wet weight (g)	% Dry matter	% Fat	CL (cm)
O. africanus	Omnivorous	Male	29.9 ± 0.4	19.5 ± 0.3	0.2 ± 0.1	11.0 ± 0.2
		Female	220.0 ± 0.6	23.4 ± 0.4	0.3 ± 0.1	9.1 ± 0.2
P. notialis	Omnivorous	Male	46.7 ± 0.2	28.6 ± 0.2	0.02 ± 0.01	19.5 ± 0.1
		Female	49.6 ± 0.2	28.9 ± 0.3	0.02 ± 0.01	19.6 ± 0.2
P. clarkii	Omnivorous	Male	5.6 ± 0.1	15.8 ± 0.5	0.3 ± 0.2	11.5 ± 0.1
		Female	6.5 ± 0.2	16.1 ± 0.2	0.3 ± 0.1	11.6 ± 0.2

CL = carapace length of wet shellfish; the mean value was calculated from 3 fishes of each species

Table 5: Mean biometric data of shellfishes in Lagos Lagoon during the wet season.

Shellfish species	Feeding mode	Sex	Wet weight (g)	% Dry matter	% Fat	CL (cm)
O. africanus	Omnivorous	Male	104.1 ± 0.3	20.3 ± 0.2	0.2 ± 0.1	12.5 ± 0.3
		Female	81.1 ± 0.5	19.9 ± 0.1	0.2 ± 0.2	12.0 ± 0.2
P. notialis	Omnivorous	Male	45.3 ± 0.8	28.5 ± 0.3	0.02 ± 0.01	19.4 ± 0.2
		Female	49.0 ± 0.3	28.8 ± 0.3	0.02 ± 0.01	19.5 ± 0.3
P. clarkii	Omnivorous	Male	5.5 ± 0.2	15.7 ± 0.2	0.3 ± 0.2	11.4 ± 0.1
		Female	6.3 ± 0.1	16.0 ± 0.4	0.3 ± 0.1	11.5 ± 0.2

CL = carapace length of wet shellfish; the mean value was calculated from 3 fishes of each species

Results and Discussion

The mean biometric data of shellfishes are presented in Tables 2-5. During the dry season, shellfishes at Agboyi Creek recorded 0.20% fat. The % dry matter ranged from 16.00 to 19.95%. In the wet season, % fat was between 0.20 and 0.30% while the % dry matter was between 16.00 and 23.00%. At Lagos Lagoon, % fat was between 0.02 and 0.30% while the % dry matter ranged from 15.70 to 28.90%. Table 6 shows the percentage recoveries of chlorinated pesticides in the fish samples and the mean recoveries of the residues ranged from 88.45 to 98.42%. These recovery values indicate good accuracy of the methodology used in this study, thus validating it. The calibration curves of the analysed pesticides present a good regression line ($r>0.999$) in the range of explored concentrations.

The pesticide residue distribution pattern in muscle tissues of the shellfishes were in the following order: *Procambarus clarkii* > *Ocypoda africanus* > *Penaeus notialis* (Tables 7-9). *Procambarus clarkii* recorded the highest pesticide residue of 4516.71 ng/g in the lagoon during the dry season. The total detectable concentration of pesticide residues (wet weight) of the muscle tissues ranged from 6.47 ng/g to 4516.71 ng/g in *Procambarus clarkii.* The male shellfishes accumulated higher pesticide levels than the female shellfishes. The processes of bioaccumulation and biomagnification of persistent contaminants may be affected by the fish's physiology, age, trophic levels, habitat, structure of food web and contaminant physicochemical properties [26]. The residue levels were higher in the Lagos Lagoon than in Agboyi Creek while a higher concentration of the residues was generally observed during the dry season. This is due to the higher contamination of the Lagos Lagoon compared to the creek and dilution effect that is witnessed during the wet season. The

Table 6: Recoveries in shellfish samples.

OCPs	% Recoveries
Alpha-BHC	93.12
Beta-BHC	97.55
Lindane	97.1
Delta-BHC	98.42
Heptachlor	95.7
Aldrin	97.1
Heptachlor -epoxide (B)	95.05
Cis-Chlordane	92.21
Trans-Chlordane	92.75
Endosulfan	95.16
Dieldrin	90.37
p,p´-DDE	94.25
Endrin	88.45
Endosulfan 11	95.02
p,p´-DDD	96.31
Endrin aldehyde	90.85
Endosulfan sulphate	94.34
p,p´-DDT	94.2
Methoxychlor	90.38
Endrin ketone	89.13

levels of chlorinated residues were all within permissible limits [27-29].

The muscle tissue was used in determining the dietary intakes to human body. The estimated daily intakes (EDI) of organochlorine pesticide residues by humans are shown in Table 10. ΣBHC, Σendrin, Σchlordane, Σheptachlor, Σendosulfan and ΣDDT were used in estimating the daily intakes. The highest EDI for the shellfishes was observed in endrin for *P. notialis* (250.17 ng/kg body weight/day). The total EDI calculated was 4160.48 (ng/kg body weight/day). Except for endrin and heptachlor, the estimated daily intakes of the pesticides were within the acceptable daily intakes. The appraisal of dietary intake was based on comparison of acceptable daily intakes established by the joint FAO/WHO expert committee, Health Canada and USEPA (Table 11). Acceptable daily intake represents the daily concentration below which there is a high probability of no adverse health effect. It is an estimate of the residue that can be ingested by a person daily over an extended period of time without suffering deleterious effects. ADI is expressed by body mass per kilogram per day. Levels of chlorinated pesticides in the fish species analysed were within the permissible limits recommended by the international organizations, suggesting that the fishes were safe for consumption.

Conclusion

Results of the pesticide analyses showed that a total of twenty three pesticide residues were detected in the samples. The organochlorine pesticide residues were detected in all the samples though the frequency of detection of a few of the residues was less than 100%. The residue levels were higher in the Lagos Lagoon than in Agboyi Creek

Table 7: Mean concentrations (ng/g) of organochlorine pesticide residues in muscle tissues of male and female Crab (*Ocypoda africanus*) during the dry and wet seasons

OCPs	Agboyi Creek				Lagos Lagoon			
	Dry Season		Wet Season		Dry Season		Wet Season	
	Male	Female	Male	Female	Male	Female	Male	Female
Alpha-BHC	34.5 ± 9.3	17.9 ± 9.4	13.0 ± 3.2	2.7 ± 1.6	4.8 ± 2.5	1.9 ± 1.4	3.5 ± 2.3	1.3 ± 5.6
Beta-BHC	43.9 ± 4.4	18.8 ± 3.3	80.0 ± 8.4	3.0 ± 2.5	20.6 ± 3.3	8.5 ± 8.5	4.1 ± 1.3	6.5 ± 4.2
Lindane	39.3 ± 3.1	19.9 ± 2.8	27.0 ± 6.2	4.2 ± 2.3	2.6 ± 1.2	2.7 ± 2.3	1.9 ± 1.2	14.5 ± 5.4
Delta-BHC	37.7 ± 2.4	6.3 ± 5.2	28.9 ± 9.7	2.7 ± 2.4	7.7 ± 6.3	5.1 ± 3.2	5.0 ± 2.3	1.4 ± 1.6
ΣBHC	155.4 ± 19.2	62.9 ± 20.7	149.4 ± 27.5	12.6 ± 8.8	35.6 ± 13.3	18.1 ± 15.4	14.5 ± 7.1	23.7 ± 16.8
Heptachlor	26.9 ± 1.5	10.6 ± 7.1	9.4 ± 5.2	2.3 ± 1.6	4.0 ± 2.1	2.5 ± 1.4	2.6 ± 2.3	73.2 ± 9.6
Heptachlor-epoxide (B)	40.4 ± 6.3	4.1 ± 4.3	8.8 ± 7.1	0.8 ± 0.9	1.9 ± 1.2	0.9 ± 0.3	1.3 ± 1.5	3.3 ± 2.4
Aldrin	37.2 ± 7.2	19.3 ± 8.5	21.7 ± 5.2	4.8 ± 1.2	2.6 ± 2.3	2.0 ± 0.2	1.7 ± 1.3	13.2 ± 4.2
Dieldrin	40.2 ± 8.3	92.8 ± 6.3	5.1 ± 2.3	0.6 ± 0.1	1.3 ± 1.2	0.7 ± 0.1	0.8 ± 0.2	7.1 ± 4.5
Endrin	158.7 ± 9.4	23.0 ± 5.4	16.3 ± 5.5	0.9 ± 0.2	2.2 ± 1.8	0.4 ± 0.2	1.6 ± 0.3	5.3 ± 2.2
Endrin aldehyde	ND	ND	38.2 ± 2.3	1.1 ± 1.3	3.5 ± 2.3	0.4 ± 0.3	0.8 ± 0.4	14.3 ± 3.5
Endrin ketone	1429.2 ± 12.3	63.2 ± 9.7	ND	0	0	0.8 ± 0.6	0	5.6 ± 2.2
Cis-Chlordane	48.2 ± 4.6	20.5 ± 8.5	16.4 ± 8.3	1.2 ± 2.1	6.4 ± 3.4	0.7 ± 0.5	3.0 ± 0.3	3.3 ± 2.4
Trans-Chlordane	22.0 ± 6.3	7.4 ± 2.3	22.7 ± 5.5	1.2 ± 1.2	3.5 ± 2.5	0.9 ± 0.3	1.7 ± 0.4	5.0 ± 1.3
Endosulfan 1	43.9 ± 2.4	3.8 ± 2.7	17.1 ± 6.2	1.8 ± 2.3	4.5 ± 3.3	0.9 ± 0.6	2.4 ± 0.4	4.7 ± 1.4

Endosulfan 11	81.8 ± 7.5	ND	7.5 ± 6.6	0.9 ± 0.6	1.8 ± 1.1	ND	1.2 ± 0.3	8.7 ± 4.3
Endosulfan sulphate	332.9 ± 4.8	ND	17.5 ± 9.2	2.1 ± 2.3	1.8 ± 1.3	1.7 ± 1.4	0.8 ± 0.2	4.6 ± 1.6
Methoxychlor	105.2 ± 3.4	70.3 ± 9.5	8.1 ± 6.3	0	0	0	0	0
p,p´-DDE	47.6 ± 5.2	ND	6.2 ± 5.8	2.9 ± 1.5	1.6 ± 2.2	0.8 ± 0.5	1.0 ± 0.4	ND
p,p´-DDD	88.9 ± 3.3	43.6 ± 7.0	5.4 ± 5.3	1.8 ± 1.2	1.6 ± 1.3	1.6 ± 1.6	1.9 ± 0.7	3.9 ± 2.2
p,p´-DDT	274.3 ± 2.8	28.1 ± 5.3	ND	1.0 ± 1.3	1.4 ± 1.5	2.4 ± 1.3	0.7 ± 0.2	2.5 ± 1.4
ΣDDT	410.8 ± 11.3	71.7 ± 12.3	11.6 ± 11.1	5.7 ± 4.0	4.6 ± 5.0	4.8 ± 3.4	3.6 ± 1.3	6.4 ± 3.6
ΣOCPs	2932.8 ± 104.5	449.3 ± 97.3	349.7 ± 88.3	36.3 ± 26.6	73.8 ± 28.8	34.8 ± 24.7	35.9 ± 16.0	178.5 ± 60.0

The mean value was calculated from triplicate determinations

Table 8: Mean concentrations (ng/g) of organochlorine pesticide residues in muscle tissues of male and female Shrimp (*Penaeus notialis*) during the dry and wet seasons.

OCPs	Lagos Lagoon			
	Dry Season		Wet Season	
	Male	Female	Male	Female
Alpha-BHC	9.4 ± 2.1	2.7 ± 1.4	2.9 ± 1.6	2.3 ± 1.2
Beta-BHC	32.7 ± 4.2	2.2 ± 1.5	2.7 ± 1.5	2.2 ± 1.1
Lindane	12.9 ± 3.3	0.9 ± 0.6	1.1 ± 1.1	0.9 ± 0.3
Delta-BHC	11.1 ± 2.2	0.9 ± 0.4	0.9 ± 0.3	0.7 ± 0.2
ΣBHC	66.2 ± 11.8	6.8 ± 3.9	7.6 ± 4.5	6.2 ± 2.8
Heptachlor	28.9 ± 7.1	0.9 ± 0.4	0.9 ± 0.1	0.9 ± 0.4
Heptachlor-epoxide (B)	79.1 ± 3.2	ND	ND	ND
Aldrin	37.5 ± 8.3	1.4 ± 0.5	1.6 ± 0.3	1.2 ± 0.6
Dieldrin	ND	ND	ND	ND
Endrin	ND	0.7 ± 0.6	0.6 ± 0.4	0.5 ± 0.1
Endrin aldehyde	ND	ND	ND	ND
Endrin ketone	2694.1 ± 8.4	0	0	0
Cis-Chlordane	80.6 ± 7.6	ND	ND	ND
Trans-Chlordane	18.5 ± 4.2	0.5 ± 0.4	0.5 ± 0.5	0.5 ± 0.3
Endosulfan 1	32.7 ± 7.3	0.9 ± 0.3	0.9 ± 0.2	0.9 ± 0.2
Endosulfan 11	238.7 ± 5.8	ND	0	ND
Endosulfan sulphate	ND	0.3 ± 0.2	ND	0.3 ± 0.3
Methoxychlor	77.5 ± 6.5	ND	0	ND
p,p´-DDE	ND	ND	ND	ND
p,p´-DDD	ND	ND	ND	ND
p,p´-DDT	ND	ND	ND	ND
ΣDDT	ND	ND	ND	ND
ΣOCPs	3353.7 ± 70.2	11.6 ± 6.3	12.1 ± 6.0	10.5 ± 4.7

Table 9: Mean concentrations (ng/g) of organochlorine pesticide residues in muscle tissues of male and female Crayfish (*Procambarus clarkii*) during the dry and wet seasons.

OCPs	Agboyi Creek				Lagos Lagoon			
	Dry Season		Wet Season		Dry Season		Wet Season	
	Male	Female	Male	Female	Male	Female	Male	Female
Alpha-BHC	1.1 ± 0.4	0.9 ± 0.2	2.6 ± 1.1	0.6 ± 3.4	54.6 ± 4.3	ND	1.3 ± 0.1	1.1 ± 0.2
Beta-BHC	1.5 ± 0.6	1.2 ± 0.4	19.2 ± 4.2	0.6 ± 4.3	93.4 ± 7.2	0.4 ± 0.4	1.7 ± 0.3	1.2 ± 0.3

Lindane	0.8 ± 0.2	0.8 ± 0.3	6.7 ± 2.4	0.7 ± 3.2	58.3 ± 3.3	0.6 ± 0.2	0.9 ± 0.2	0.8 ± 0.4
Delta-BHC	0.8 ± 0.3	0.7 ± 0.2	5.1 ± 1.2	0.7 ± 2.3	76.8 ± 5.2	0.8 ± 0.2	2.3 ± 0.4	0.7 ± 0.3
ΣBHC	4.3 ± 1.5	3.6 ± 1.1	33.6 ± 8.9	2.6 ± 13.2	283.1 ± 20.0	1.8 ± 0.8	6.2 ± 1.0	3.8 ± 1.2
Heptachlor	0.9 ± 0.3	0.9 ± 0.1	4.8 ± 2.3	1.7 ± 3.2	132.4 ± 2.3	0.8 ± 0.3	0.9 ± 0.4	0.9 ± 0.1
Heptachlor-epoxide (B)		ND	ND	7.7 ± 2.4	ND	186.6 ± 6.5	ND	ND
Aldrin	0.9 ± 0.1	1.1 ± 0.2	3.8 ± 2.2	0.9 ± 2.3	70.9 ± 4.4	1.3 ± 1.4	1.1 ± 0.3	1.0 ± 0.1
Dieldrin	ND	ND	7.3 ± 2.4	ND	181.6 ± 5.6	ND	ND	ND
Endrin	0.6 ± 0.2	0.6 ± 0.1	43.9 ± 5.3	0.5 ± 3.4	405.2 ± 12.7	0.5 ± 0.3	0.6 ± 0.6	0.5 ± 0.2
Endrin aldehyde	ND	ND	86.1 ± 2.1	ND	1103.5 ± 7.3	ND	0.4 ± 0.3	ND
Endrin ketone	0	2.3 ± 0.2	ND	0	418.4 ± 42.3	0	0	0
Cis-Chlordane	ND	ND	3.3 ± 1.1	ND	ND	ND	ND	ND
Trans-Chlordane	0.5 ± 0.3	ND	10.4 ± 6.2	ND	ND	0.5 ± 0.5	0.5 ± 0.4	ND
Endosulfan 1	0.8 ± 0.4	0.8 ± 0.3	9.6 ± 3.1	0.8 ± 2.5	647.9 ± 6.6	0.8 ± 0.4	0.9 ± 0.3	0.8 ± 0.3
Endosulfan 11	ND	ND	14 ± 2.0	ND	ND	ND	ND	ND
Endosulfan sulphate	0.4 ± 0.3	2.4 ± 0.2	ND	ND	ND	ND	0.3 ± 0.1	0.6 ± 0.2
Methoxychlor	4.1 ± 2.4	3.4 ± 0.1	9.8 ± 3.2	0	451.2 ± 9.7	0	0	0
p,p´-DDE	ND	ND	13.5 ± 2.1	ND	300.2 ± 8.4	ND	ND	ND
p,p´-DDD	ND	ND	13.8 ± 1.3	ND	335.8 ± 7.3	ND	ND	ND
p,p´-DDT	ND	2.6 ± 0.2	ND	ND	ND	0.8 ± 0.4	0.6 ± 0.2	0.7 ± 0.2
ΣDDT	ND	2.6 ± 0.2	27.3 ± 3.4	ND	636.0 ± 15.7	0.8 ± 0.4	0.6 ± 0.2	0.7 ± 0.2
ΣOCPs	12.5 ± 5.5	17.7 ± 2.5	261.8 ± 41.6	6.5 ± 24.6	4516.7 ± 133.3	6.5 ± 4.1	11.4 ± 3.6	8.4 ± 2.3

Table 10: Estimated daily intake (EDI) of chlorinated pesticide residues (ng/g) by humans.

Pesticides	*Ocypoda africanus*	*Penaeus notialis*	*Procambarus clarkii*
BHC	14.43	6.14	26.27
Heptachlor	7.1	10.03	29.62
Aldrin	3.45	3.48	6.59
Dieldrin	8.61	ND	16.86
Endrin	147.46	250.17	178.94
Chlordane	6.52	9.2	1.27
Endosulfan	42.59	25.2	60.17
Methoxychlor	9.76	7.2	41.9
DDT	38.14	ND	59.06

Table 11: Acceptable daily intake (ng/kg body weight/day) of chlorinated pesticide residues in fish.

Pesticides	FAO/WHO	Health Canada	USEPA (RfD)
BHC	42000	18000	18000
Heptachlor	5000	-	-
Aldrin	7000	-	-
Dieldrin	-	-	-
Endrin	6000	-	-
Chlordane	-	3000	30000
Endosulfan	-	-	-
Methoxychlor	-	-	-
DDT	1200000	1200000	30000

Source: Oostdan et al., 1999; FAO/WHO, 2005; USEPA, 2006

while a higher concentration of the residues was generally observed during the dry season. Generally, the male shellfishes accumulated higher pesticide levels than the female shellfishes. The total detectable concentration of pesticide residues (wet weight) of the muscle tissues of the shellfishes ranged from 6.47 ng/g to 4516.71 ng/g in *P. clarkii*. The estimated daily intakes of the pesticides were largely within the acceptable daily intakes recommended by various agencies. Levels of residues in the fishes were within the permissible limits.

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