ASSESSMENT OF ORGANOCHLORINE PESTICIDE (OCP) RESIDUES IN WATER, SEDIMENTS AND FISH FROM BONNY ESTUARY, NIGERIA.

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ABSTRACT

Organochlorine pesticide (OCP) residues from water, sediment and fish in Bonny estuary were assessed quarterly from 2016 to 2017 to ascertain their concentrations in the matrices with respect to the regulatory limit by Nigeria legislation. Surface water samples were obtained directly from three locations using cleaned 1.5litres plastic vessels, while Sediment samples were collected at 10cm depth using triple sediment corer. Fish specimens: Tilapia, mullet and shrimps were obtained from fishers during the field trip. OCP in the samples were determined, using Gas Chromatography-Mass Spectrometry (GC-MS). The OCP concentration in sediment ranged from 0.7ppm (2016) to 0.59ppm (2017), biota (16ppm-Tilapia sp.,17ppm-Mullet, and 14ppm-Shrimps), and water(>10ug/l) Five pesticide residues; DDE, DDT, endosulfan sulphate, sulfan 1, endrin aldehyde occurred commonly in all the three biota. The result indicated a percentage increase in concentration of 10.3% (Tilapia), 44.5% (Mullet), and 94.06% decrease (Shrimps) from 2016 to 2017.

Keywords: Organochlorine pesticides (OCP), Bonny estuary, Persistent organic pollutants (POP)

INTRODUCTION

Organochlorine Pesticides (OCPs) is a class of pesticides commonly found in Nigeria through illegal importation of their finished pre-packed products (United Nations Environment Programme, 2011; Pesticides Action Network, 2007). Lindane (Gamma BHC). aldrin. dieldrin, dichlorodiphenyltrichloro ethane (DDT), chordane, toxaphene are some of the organochlorine pesticides used by subsistent farmers particularly those in the rural areas to protect their crops, animals and human from pests. Sixty-five per cent of the total volume of pesticides marketed in Nigeria is used on large-scale farms and plantations, while 35 per cent are used on small scale farms (Ikemefuna, 1990). The wide spread application of pesticides in Nigeria is worrisome as the bulk of food consumed in the country is produced by small scale farmers who have little or virtually no information about the handling of pesticides (Akunyili and Ivbijaro, 2012).

These pesticides find their way into the aquatic ecosystem including the Bonny estuary, through run-offs from large and small scale farms, pesticide drifts beyond pest infested areas, and discharge of expired pesticides into the ecosystem from pesticide marketing companies. , the main entry of pesticides into the aquatic ecosystem is through direct application of pesticide for industrial, domestic and agro-allied purposes (Pesticides Action Network, 2007, Okoya *et al.*, 2013). OCP residues enter aquatic environments through effluent release, discharges of domestic sewage and industrial waste water, atmospheric deposition, equipment washings, disposal of empty containers (Yang *et al.* 2005).

The pesticides in the aquatic ecosystems accumulate in the sediment, water and biota, including fish and insects (Unyimadu et al., 2018). Frequent pesticide application creates unstable environment and reduces the abundance of desirable insects such as bioindicators, biological control agents (dragonflies) and keystone species. Loss of keystone species for instance, would deprive dependant species such as fish of their food or other resources and consequently, cause ecosystem degradation (Schowalter, 2011). Furthermore, a lot of human health implications have been reported on the application of persistent organochlorine pesticides. Akunvili and Ivbijaro (2012) stated that they have effect on liver even in low doses and also stimulate the activity of microsomal enzymes in the liver cells, which may affect the metabolism of other compounds. Sosan and Oyekunle (2017) revealed that the Hazard Index values of some pesticides were above one which could pose a serious public health problem

The organochlorine pesticide residues in some rivers in the western Nigeria showed that there are varying concentrations of pesticide in Ibadan River, Lagos lagoon and River Oluwa (Nwankwoala and Osibanjo, 1992; Adeyemi *et al.*, 2011; Okoya *et al.*, 2013). Organochlorine pesticides in biota obtained from Lagos lagoon showed a range of 0.02 - 54.6ppb (Osibanjo and Bagbose, 1990) and 0.01 - 54.6ppm (Adeyemi *et al.*, 2008) and in sediments $0.06-119\mu g/g$ (Ezemonye *et al.*, 2008; Ezemonye *et al.*, 2010), and 20-313 $\mu g/g$ (Olatunbosun *et al.*, 2011). The authors attributed the increase in concentration of organochlorine pesticides over the period of 1990 – 2008 in fish (biota) and 2008 – 2011 in sediments to increase in agricultural activities in the area of study.

Following these developments in Lagos, Ibadan and environs, it became pertinent to monitor the level of organochlorines in the Bonny estuary which is the route of many imported products including pesticides. According to Ivbijaro (1998), in many fishing communities, Lindane is poured into rivers and streams to kill fish, and the Bonny estuary may not be an exemption. OCPs could distribute to water and sediments, and accumulate in the biota (Unyimadu, 2018). Since the sediment serves as a sink from which water and biota are continuously polluted, the quality of sediments is essential in assessing the pollution status of the water ecosystem (Doong et al., 2002).

Organochlorine pesticide residues in three matrices; sediment, water and biota (fish) were monitored in Bonny estuary during 2016 and 2017 to ascertain their concentrations. Monitoring OCPs in water, sediment and biota has the advantage of producing an immediate, geographically localized measure of contamination (Williams 2013). especially, as the indiscriminate use of pesticides in Nigeria has resulted in the occurrence of OCP residues in biota and other components (Okoya et al., 2013; Ize-Iyamu et al., 2007; Adeyemi et al., 2008).

MATERIALS AND METHODS

Study area

Bonny Estuary in Port Harcourt is located in the Niger Delta region of Nigeria. The study area was divided into three locations marked 1, 2, and 3(Fig. 1). stattions 1 and 2 are located at the wharf of the Nigerian Ports Authority and have the coordinates; 46'33.73"E 4°44'12.21"N, and 7°00'01.15"N and 7°00'18 85"E respectively. station 3 was the dock and compound of a cement bagging factory with the co-ordinates $4^0 45' 04.03"$ N and $7^000'$ 14.08"E. Samples were collected quarterly from the three locations on 3 sampling points from 2016 to 2017: station 1 - NPA, station 2 - Cement Factory, and station 3 -River Creek, separated by 100m from each other (Fig 1). Surface water samples were obtained directly using cleaned plastic 1.5liters vessels. Water temperature was

measured in the field at the point of sampling. Water samples were transported in cool boxes to the laboratory for further analysis.

Sediment samples were collected from the three points in each sample station, using the triple sediment corer, Uwitec fitted with Plexiglass tubes of 50cm height. Sediment samples were collected at 10m depth. Generally, sediments and overlying water of up to approximately 40cm were recovered. Samples were transported to the laboratory the same day for further preparations for analysis. Sediment cores were sliced at 2cm intervals, weighed, dried at 50oC until constant dry weight of samples was obtained. Samples were then homogenized using Agatha mortar and pestle and sieved with 0.5mm mesh size sieves.

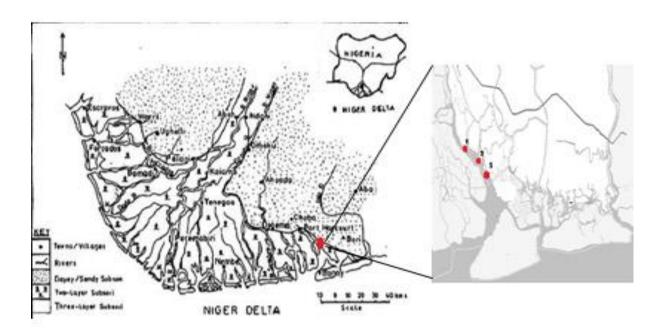


Fig 1: Map of the study area

Tilapia, Mullet and Shrimps were obtained directly from fishers during the field work. Fish samples were transported in ice boxes to the laboratory where they were dried in an electric oven (Grenlab oven model; Ninco 130) at 100°C. The dried samples were ground with ceramic mortar and glass pestle.

Organochlorine pesticides in the samples were determined in accordance with the United States Environmental Protection Agency (USEPA) analytical protocol. Seventeen organchlorine residues were analysed for in the three matrices; sediment, water and biota in both 2016 and 2017. The fish samples were saponified with alcoholic KOH to break down esters. Thereafter, both dried and saponified samples were cleaned Quantitative up using 1% H_2SO_4 . determination of the organochlorine pesticides was done by injecting the aliquots of the final extracts into a gas chromatography-mass spectrometry (GC-MS, Agilent 7890A[®]) with auto-injector and 5975 mass selective detector) equipped column of HP-55% phenyl-methyl-siloxane bonded fused silica of 30m, 0.25µm thickness and 0.25µm internal diameter. The carrier gas was helium gas at 1.1ml/min constant flow.

Statistical Analysis:

The data were analysed using descriptive statistics (mean and standard error) and analysis of variance (ANOVA) was used to obtain differences in OCP concentration between the locations. Thereafter, T-test was conducted to see if the differences between (i) sampling locations and (ii) biota were significant.

RESULTS

In the sediment, a total concentration of 1.29 ppm organochlorine pesticide were obtained, out of which 0.7ppm and 0.59ppm occurred in 2016 and 2017, respectively (Table 1). A total of 17 OCP residues occurred in the sediment in 2016, and 15 OCP residues occurred in 2017. The two OCP residues which were absent in 2017. but occurred in low concentrations in 2016 were gamma hexachlorocyclohexane (g-BHC; lindane) and heptachlor. Three OCP levels were obtained from the sediment within the period of study (2016-2017): eight residues; methoxychlor, α -, β , d and g hexachlorocyclohexane (BHC), dieldrin and aldrin (0.02 - 0.05ppm), 4 residues; endosulfan II, endrin aldahyde, 4'4' DDE and 4'4' DDD (0.06-0.10ppm) and 3 residues; endosulfan sulflate, 4'4' DDT, endosulfan I (0.11-0.37ppm)(Table I). The highest concentration of organochlorine pesticide residues in the sediment was recorded in 4'4' DDT with 0.24ppm in 2016 and endosulfan I with 0.35pmm in 2017. The residues levels of endosulfan sulphate and endosulfan I, which occurred at a concentration range between 0.02 to 0.05 ppm in 2016 increased to a range of 0.07 to 0.35 ppm in 2017.

Concentration (ppm)						
S/N	OCP	2016	2017	Mean ±SE		
1	Aldrin	0.04 ± 0.01	0.01±0.01	0.03		
2	a – BHC	0.03 ± 0.01	0.01 ± 0.01	0.02 ± 0.01		
3	b–BHC	0.02 ± 0.01	$< 0.01 \pm 0.00$	0.01 ± 0.01		
4	d –BHC	0.02 ± 0.01	$< 0.01 \pm 0.00$	0.01 ± 0.01		
5	g-BHC (Lindane)	$< 0.01 \pm 0.00$	ND	0.00		
6	4, 4' DDD	0.07 ± 0.03	0.02 ± 0.01	0.05 ± 0.03		
7	4,4' DDE	0.06 ± 0.02	0.02 ± 0.01	0.04 ± 0.02		
8	4,4' DDT	$0.24{\pm}0.07$	0.04 ± 0.03	0.01 ± 0.1		
9	Dieldrin	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01		
10	Endosulfan I	0.02 ± 0.05	0.35 ± 0.08	0.19 ± 0.17		
11	Endosulfan II	0.05 ± 0.02	0.02 ± 0.01	0.04 ± 0.02		
12	Endosulfan sulphate	0.05 ± 0.03	0.07 ± 0.01	0.06 ± 0.01		
13	Endrin	<0.01±0.01	0.01 ± 0.01	0.01 ± 0.01		
14	Endrin aldehyde	0.05 ± 0.02	0.03 ± 0.01	$0.04{\pm}0.01$		
15	Heptachlor	0.01 ± 0.01	ND	0.01 ± 0.01		
16	Heptachlor epoxide (iso	<0.01±0.01	< 0.01	0.00		
17	Methoxychlor	0.02 ± 0.01	$<\!0.01\pm\!0.00$	0.01 ± 0.01		
	TOTAL 0.7 0.59					

Table 1: Total Concentration (ppm) of Organochlorine Pesticides in Sediment Samples at 3 Stations on the Bonny Estuary in 2016 and 2017.

The percentage and total mean concentration of pesticides distributed in the sediments along the three sampled station, indicated that the cement factory station recorded the highest (49.6%; 0.32ppm mean concentration), and river creek recorded the lowest (10.8%; 0.07ppm mean concentration) (Table 2). There is a non-significant statistical difference in pesticide levels between the different locations during the period of study (P=0.729).

Table 2: Mean Total Concentrations (ppm) of OCP in Sediment of Bonny Estuary in 2016 and	
2017	

S/N	STATIONS	2016	2017	TOTAL	%	MEAN ± SE
1	NPA	0.34 ^a	0.17 ^a	0.51	39.50%	$0.26 \pm \ 0.09$
2	Cement Factory	0.25 ^a	0.39 ^a	0.64	49.60%	$0.32 \pm \ 0.07$
3	River Creek	0.11 ^a	0.03 ^a	0.14	10.80%	$0.07 \pm \ 0.04$
	Mean ± SE	0.23 ± 0.07	0.20 ± 0.10			

Note: Values in each row with the same superscript are not significantly different at P > 0.05

Table 3, shows the level of each organochlorine pesticide residues in the biota, with a percentage increase in concentration of 10.3% (Tilapia sp.), 44.5% (Mullet) and percentage decrease of 94.06% (Shrimps) from 2016 to 2017 (Table 3). In mullet, the increase occurred in twelve pesticide residues; α -BHC, β ,-BHC, DDD, DDE, DDT, dieldrin, endosulfan I and II, endosulfan sulphate, endrin aldehyde, heptachlor, methoxychlor. In shrimp, a decrease in concentration of

pesticide residues occurred from 2016 to 2017. Among the biota, the residue level of lindane (g-BHC) was non-detectable in Tilapia, and Mullet in 2017 and Shrimps (2016 and 2017). The residue level of dieldrin and endosulfan II which occurred in Tilapia sp. in 2016 and 2017 was not detectable in Mullet in 2016, though occurred in 2017 (Table 3). The total level of OCP residues in the biota in 2017 was 16 (Tilapia), 17 (Mullet) and 14 (Shrimps).

Five pesticide residues; DDE, DDT, endosulfan sulphate, endosulfan 1, endrin aldehyde occurred commonly either at or above 0.02ppm concentration in all the three biota. Heptachlor residues were found in all the biota in 2016 and 2017 except in shrimps in 2017. The residue of endosulfan II did not also occur in shrimps in 2017.

Table 3: Concentrations of organochlorine	pesticides in	biota	(Tilapia,	Mullet,	and
Shrimp) at 3 Stations in 2016-2017 (ppm).					

S/N	ОСР	TIL/ 2016		MULLET MEAN±SE 2016-2017 N		SHRIMP MEAN±SE 2016-2017		MEAN±SE		
1	Aldrin	0.04	0.06	0.05±0.01	0.19	0.14	0.165±0.025	0.02	<0.01	0.01±0.01
2	a – BHC	0.06	0.02	0.04±0.02	0.06	0.16	0.11±0.05	0.01	0.01	0.01
3	b –BHC	0.04	0.01	0.025±0.015	0.02	0.40	0.21±0.19	0.02	0.01	0.015±0.005
4	d –BHC	0.02	0.01	0.015±0.005	0.05	0.01	0.03±0.02	0.01	< 0.01	0.005 ± 0.005
5	g –BHC	0.02	< 0.01	0.01±0.01	0.01	< 0.01	0.005 ± 0.005	< 0.01	< 0.01	0
6	4, 4' DDD	0.02	0.01	0.015±0.005	0.05	0.06	0.055 ± 0.005	0.02	0.01	0.015 ± 0.005
7	4,4' DDE	0.14	0.35	0.245 ± 0.105	0.03	0.23	0.13±0.1	0.14	0.08	0.11±0.03
8	4,4' DDT	0.03	0.08	0.055 ± 0.025	0.01	0.08	0.045 ± 0.035	0.03	0.02	0.025 ± 0.005
9	Dieldrin	0.03	0.04	0.035 ± 0.005	< 0.01	0.05	0.025 ± 0.025	0.04	< 0.01	0.02 ± 0.02
10	Endosulfan I	0.03	0.02	0.025 ± 0.005	0.01	0.07	0.04 ± 0.03	6.10	0.02	3.06±3.04
11	Endosulfan II	0.01	0.01	0.01	< 0.01	0.02	0.01 ± 0.01	0.01	< 0.01	0.005 ± 0.005
12	Endosulfan sulfate	0.04	0.04	0.04	0.04	0.09	0.065 ± 0.025	0.06	0.02	0.04 ± 0.02
13	Endrin	< 0.01	0.01	0.005 ± 0.005	0.02	0.01	0.015 ± 0.005	0.02	0.01	0.015 ± 0.005
14	Endrin aldehyde	0.05	0.08	0.065 ± 0.015	0.05	0.09	0.07 ± 0.02	0.65	0.05	0.35±0.3
15	Heptachlor	0.05	0.01	0.03 ± 0.02	0.01	0.02	0.015 ± 0.005	0.03	< 0.01	0.015 ± 0.015
16	Heptachlor epoxide	0.02	< 0.01	0.01 ± 0.01	0.01	0.01	0.01	< 0.01	0.01	0.005 ± 0.005
17	Methoxychlor	0.01	< 0.01	0.005 ± 0.005	< 0.01	0.02	0.01±0.01	0.01	0.01	0.01
	TOTAL	0.61	0.75		0.56	1.46		7.17	0.25	

The mean concentrations of the 17 organochlorine pesticide residues were compared for each of the biota between 2016 and 2017. The results are presented on Figs 2, 3 and 4. The statistical analysis indicated that in Tilapia- 4'4'DDE was significantly different (P<0.05; Pvalue=0.000) in concentration within the period of study (Fig.1). In Mullet, aldrin, b-BHC, a-BHC,4'4'DDE differ significantly (p<0.05; pvalue=0.001,0.000,0.028 and 0.000, respectively) (Fig.2), and while in Shrimp, differences exist in endosulfan 1(p<0.05; pvalue=0.000) (Fig.3). The t-test analysis showed that Tilapia was significantly different from shrimp, and Mullet from Shrimp.

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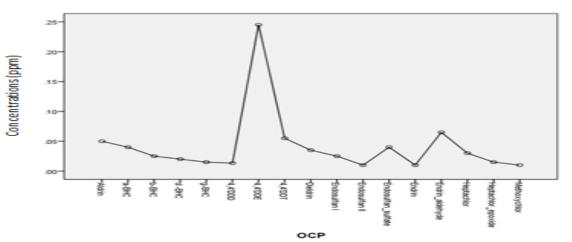


Fig. 2: The plot of mean concentrations of the 17 Organochlorine pesticide residues in Tilapia within the period of study (2016/2017)

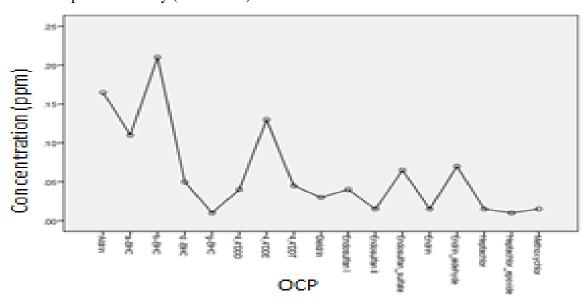


Fig. 3: The plot of mean concentrations of the 17 Organochlorine pesticide residues in Mullet within the period of study (2016/2017)

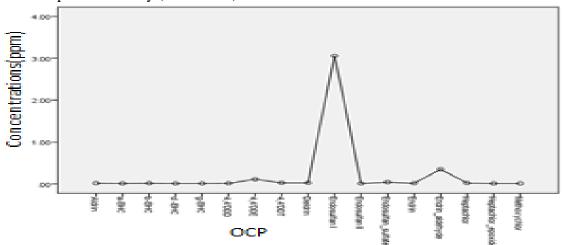


Fig. 4: The plot of mean concentrations of the 17 Organochlorine pesticide residues in Shrimps within the period of study (2016/2017)

In the water samples, the level of organochlorine pesticide residues were either non-detectable or below 10µg/L in all sampled the three stations. Ten organochlorine pesticide residues were absent and non-detectable in 2017 water samples, though DDT and endosulfan sulphate out of these were contained at very low concentration in 2016 (Table 4). Both aldrin and its metabolite dieldrin were nondetectable in the water samples. The three hexachlorocyclohexane (HCH) and lindane were also non-detectable in 2016 and 2017 water samples (Table 4). Seven pesticide residues recorded in 2017 were below 10µg/L (Methoxychlor, Endosulfan I, DDE, DDD, and Heptachlor epoxide and endrin aldehyde (Table 4).

The result showed that out of the 12 chemical substances defined under the Stockholm 2009 convention on persistent organic pollutants (POPS), eight, aldrin, α -BHC, β -BHC, g-BCH, DDT, deldrin,

endrin, and heptachlor with a total concentration of 0.37ppm, representing 28.68% residues occurred in the sediment. Out of these eight, lindane and heptachlor were non-detectable in 2017 sediment samples, with a 0.02ppm reduction in total concentration leaving 0.35ppm of all POPS in the 2017 sediment.

In biota, the concentration of the 8 POPS was 0.24 ppm (*Tilapia sp*); 0.87ppm (Mullet) and 6 POPS excluding heptachlor, g-BHC (lindane) was 0.5 ppm (Shrimps). Lindane was non-detectable in 2017 samples of *Tilapia sp*, Mullet and Shrimps, while heptachlor occurred in all the 2016 and 2017 except in 2017 samples of shrimps. In the water samples, seven of the POPS (aldrin, α -BHC, β -BHC, dieldrin, DDT, Heptachlor) were non-detectable; while endrin occurs at lower than 10µg/L. Endosulfan I occurred in all the matrices, with the highest concentration in 2017 sediment samples.

S/N	Organochlorine Pesticides (µg/L)	2016	2017
1	Aldrin	ND	ND
2	$\alpha - BHC$	ND	ND
3	b – BHC	ND	ND
4	d – BHC	ND	ND
5	g – BHC (Lindane)	ND	ND
5	4'4' – DDD	<10	<10
7	4'4' – DDE	<10	<10
8	4'4' – DDT	<10	ND
Ð	Dieldrin	ND	ND
10	Endosulfan I	<10	<10
11	Endosulfan II	<10	ND
12	Endosulfan Sulphate	<10	ND
13	Endrin	<10	<10

Table 4: Concentrations of Organochlorine Pesticides in Water Sample of Bonny Estuaryin 2016 and 2017.

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14	Endrin Aldehyde	<10	<10
15	Heptachlor	ND	ND
16	Heptachlor epoxide	<10	<10
17	Methoxychlor	<10	<10
	TOTAL	<10	<10

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DISCUSSION

The Bonny estuary is impacted by organochlorine pesticide residues following the amount and number of pesticides recorded in the present study. The high amounts of organochlorine pesticides and individual concentrations of DDT, DDE, Heptachlor and endosulfan in sediments and biota (Tilapia sp; Mullet) indicate that the aquatic ecosystem is impacted and could affect biodiversity of aquatic species. The impact is caused by the characteristics of the detected OCPs; persistent, lipophilic properties, and ability to bioaccumulate in organisms as they are known to have endocrine (estrogenic) disruption properties in fish, lowered haematological values and induce oxidative stress in rat (Soto et al., 1994; Kanu et al., 2016). Statistical results supports this concept of bioaccumulation as the following OCPs; 4'4'DDE, aldrin, a-BHC, b-BHC and endosulfan were significantly different in the biota indicating their high level of accumulation. However, the non -significant difference between the concentrations in biota in the stations indicates that all the stations were impacted.

The water samples among the three matrices, contained lower or virtually no amounts of OCPs residues. The high number (15) and concentration (0.59ppm)of OCPs residues recorded in the sediments. in this present study is attributable to their accumulation. In the sediments, it is caused by accumulation of residues which resulted in the high concentration of DDT and endosulfan I indicating that they have been used for a long period of time in the Bonny estuary. The lower amount in the water samples is caused by turbulence which resulted to mixing, particularly during high tides. This agrees with the work of Ize-Iyamu *et al*; (2007); Williams, (2013) that tidal flows causes water turbulence which leads to a mixing of water, and consequently a difference in concentration of residues between water and sediment samples.

The detection of certain pesticide residues in the sediment and biota showed that chemical substances defined under the Stockholm 2009 convention on persistent organic pollutants (POPs) exist in Bonny estuary. The occurrence of POPs in the sediment and biota samples is caused by a long time accumulation over the years, while their absence in water samples is attributed to the thorough mixing of the water. This may have informed Olayinka, et al, (2015) to report that organochlorine pesticide molecules were sparingly soluble in water (hydrophobic) and therefore adsorb on the sediment particles of Ogbese River in Nigeria. Turbulence in this situation contributes to the low level of pesticides residues in the water samples which are Federal Environmental below the Protection Agency (FEPA) allowable level of $10\mu g/L$.

The higher levels of OCP residues recorded in the biota than the water samples indicated that OCPs accumulated more in the biota which contain fatty tissues, because pesticides are lipophilic and accumulate more in species that have fatty tissues. However, the accumulation of OCP residues was higher in shrimps than in Tilapia sp. because Tilapia sp. as fin fishes metabolize OCPs, preventing their accumulation in edible fatty tissues, while shrimps which are shellfishes do not have the ability to metabolize OCPs (UNEP, 2011). This must have accounted for the finfish that unlike shellfish report metabolize Polyaromatic Hydrocarbons (PAHs) (UNEP, 2011). This agrees with the report that residues which enter fishes through ingestion, dermal absorption and respiration reside in their fatty tissues (Ize-Iyamu, et al; 2007).

The concentrations of three OCP residues in the sediment samples in this present study were higher than their metabolites. They are DDT (0.28ppm), aldrin (0.05ppm) and endosulfan I (9.37ppm), while their respective metabolites; DDD and DDE (0.17ppm), dieldrin (0.03PPm)and endosulfan sulphate (0.12ppm). This shows that decomposition of these OCPs is occurring at a slower rate and it is on-going in the sediment.

The results also show an increase in the concentration of endosulfan I in 2017 and decrease in DDT and aldrin, indicating a continuous use of endosulfan I and a discontinuation of the use of DDT and aldrin in agriculture. This is attributable to the low level of agricultural practices in Rivers State following the absence of intensive farming activities in the State. The absence of g-BHC (Lindane) in the three matrices, indicates that the use of gammalin 20 (Lindane) may have drastically reduced in fishing activities in the Bonny estuary.

Higher concentration of OCP occurred at the station with cement factory than the other two stations. This may be due to high impact human activities and lower mixing of water at this station. The station is highly polluted with a percentage mean concentration of 49.6% while the least station was river creek (10.8%).

The levels of OCP residues detected in the sediment and biota from the present study were relatively lower than those obtained from Lagos Lagoon and Ibadan River. In this study, aldrin and dieldrin are nondetectable in water samples whereas in Lagos lagoon, it was 0.04µg/L and 0.311µg/L respectively and in Ibadan River $0.375 \mu g/L$ and $0.657 \mu g/L$ respectively (Nwankwoala and Osibanjo, 1992: Adeyemi et al., 2011). Ezemonye et al., (2010) stated that OCP residues in sediments in Lagos lagoon are between 0.6-11.9ug/g but in the present study it ranged between 0.02-0.37ppm. In the biota it ranged from <0.01 to 0.35ppm in the present study, while at Lagos lagoon; 0.01-8.92ppm (Adeyemi et al. 2008).

The low levels of OCPs recorded in this study are due to low level of agricultural activities in the Rivers State as compared to large scale agriculture in Lagos and Ibadan (Olatunbosun *et al.*, 2011; Adeyemi *et al.*, 2011). In addition, there are many pesticide manufacturing companies in Lagos and Ibadan which could be discharging expired pesticides directly into the rivers.

CONCLUSION

OCPs residues monitored in Bonny estuary between 2016 and 2017 indicate that the sediment and biota samples contained more residues than water samples, due to long time accumulation of residues in sediment

and continued turbulence and biota. resulting in thorough mixing of water which affect water samples. Scarcity of Large scale agricultural activities which involve the use of pesticides is lacking in rivers state and this could be said to account for the low level of pesticide residues in the three matrices as compared to other rivers in Nigeria. The presence of OCPs residues in water samples and shrimps is still below the allowable limit of Federal Ministry Environment, Nigeria. Gamalin 20, a lindane was non-detectable in the three matrices, and thus no longer used for fishing in the estuary. The study pointed out a reduction in the use of DDT and aldrin, an increase in the use of endosulfan I, and that POPs are contained in the Bonny estuary and accumulate in *Tilapia* sp and Mullet.

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