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Evaluation and risk assessment of organochlorine pesticide residues in some fish species in south-south Nigeria

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Abstract

This study reports the presence, distribution pattern, concentration levels and health risk assessment of organochlorine pesticide residues in fresh and cured fish species in South-South Nigeria. The concentrations of organochlorine pesticides in fresh and cured fish were analysed with Gas Chromatography/ Mass Spectrophotometry (GC-MS) after Soxhlet extraction of the fish species. The study revealed that no organochlorine pesticide was present in fresh fish. However, cured fish species from all the markets sampled had at least two organochlorine pesticide residues which ranged from endosulfan (0.252±0.0022–748±0.004ug/g), lindane (0.386±0.010–0.443±0.009 ug/g), heptachlor-epoxide (0.328±0.005–3.162±0.010ug/g), ortho-para-dichloro-diphenyl-trichloro-ethane (o,p'-DDT) (0.021±0.001–0.180±0.030ug/g) and aldrin (0.140±0.040–2.770±0.020ug/g). These levels are far higher than the maximum residual limit and allowable daily intake values recommended by World Health Organization (WHO) and Food and Agricultural Organization (FAO). There were no pesticide residues in fresh fish probably because the fisher folks in the study area may have abolished the use of obnoxious fishing methods due to the awareness of threats to the aquatic ecosystem. The high percentage occurrences, amounts and distribution of organochlorine pesticides in cured-fish from markets sampled could be as a result of the fact that these organochlorine pesticides were consistently used in the study area by fish processors, distributors and sellers. Human risk assessment of this study revealed a potential danger in the consumption of cured-fish containing the organochlorine pesticides seen in the study.

Keywords: Organochlorine pesticides, Fresh fish, Cured fish, GC-MS, South-South, Nigeria

Introduction

Fish is of great importance in the diet of Nigerians (Akinrotimi *et al.*, 2007). It is made up of nutrients needed for complementing infants, adults and even animal diets (Abdullahi *et al.*, 2001). Fish is very perishable because it provides support for the multiplication and growth of microorganism after death (Aliya *et al.*, 2012; Oparaku and Mgbenka, 2012).

Once spoilage starts in fish, its original nutritional value, odour, flavour, texture, colour and composition change. Spoilage starts the moment fish is caught. In a tropical country like Nigeria, the deterioration sets in earlier (Adebayo-Tayo *et al.*, 2008). An estimated post-harvest loss of 40% of all the fish caught has been reported (Akande, 1996).

According to Eyo (2001) marketing plays a vital role in agro-ventures because it acts as a link between producers and consumers but it is normally a long distribution channel from the capturing and culturing areas to the consumers.

It has been observed that about 60-70% of fresh fish harvested in Nigerian waters is further processed into cured and smoke-dried products. Preservation, packaging, transportation, and storage methods place the practitioners in the cured fish trade in desperate positions as a result of its deteriorative changes caused by insect attacks and spoilage. Some fishmongers and processors resort to the use of some unapproved chemicals such as lindane (Gammalin 20^{R}), Gardona, Malathion and "a locally-mixed pesticide" to prevent insect and mould infestation (Abolagba, 2014).

A field survey conducted by Abolagba (2014) revealed that pesticides are still in cured fish, particularly in the North-East and North-Central zones of Nigeria. The study observed that an average quantity of 3.25 kg of cured fish was consumed weekly per person in the study area while each trader sold 31-40 kg of cured fish per day in some parts of the middle belt of Nigeria.

Thus, the present study was intended at determining the presence, concentrations, distributions and assessing health risk associated with the consumption of organochlorine pesticides in some fresh and dried fish species in South-South Nigeria.

Materials and Methods

Collection of fresh fish samples

Fresh and cured fish samples were purchased from fishermen and fish processors in fishing and processing sites around water bodies and nearby markets in Ekehuan, Illushin, Agenebode and Uselu in Edo State; Koko, Ogbe-Ijoh in Delta State; Choba in Rivers State, Inbikiri in Bayelsa State; and Mkpana and Oron in Akwa-Ibom State. The samples were washed in flowing water to get rid of adhering dirt, after which they were sorted, identified and packed according to species into previously cleaned, nitric acid-treated plastic bags. The samples were stored in ice packs prior to preparation for analysis. Each fish sample was pulverized, 20g of the pulverized sample was used for extraction (Shinggu *et al.*, 2015; Farshid 2015).

Collection of cured fish samples

Cured fish samples were also obtained from fish processors in markets, fishing and processing sites and nearby markets in the study area of South-South, Nigeria. The cured samples were sorted, identified and packed according to species into previously cleaned and nitric acid-treated plastic bags. Each fish sample was blotted with filter paper and oven-dried at 105 ± 2°C. After drying to constant weight, each of the fish samples was ground separately and 5g was used for each extraction (Hassan *et al.*, 2013).

Broad-spectrum screening of fish samples

This experiment was conducted to assess whether trace(s) of pesticides could be recovered from fish, soil and water samples obtained from the processing and marketing sites visited during the study.

Extraction and clean-up procedure for fresh and cured-fish samples

Each sample was ground and 5g was extracted with 150ml dichloromethane for 3 hours using a Soxhlet apparatus according to Darko *et al.* (2008).

The extract from the fish sample was cleaned-up (solid phase extraction) using a short column (15cm) diameter silica gel of 200-400 µm particles mesh size with CH_2Cl_2 as the mobile phase. The sample was then eluted thrice with 5 ml of CH_2Cl_2.

The filtrate was dried and the extract was reconstituted with CH_2Cl_2 and pipetted into sample vials for gas chromatography-mass spectrophotometry (GC-MS) (EPA, 1984).

Gas chromatography-Mass spectrophotometry (GC-MS)

GC-MS was used to identify and quantify the organochlorine residues in the extracts replicated from the cured fish samples. A Shimadzu GC-MS (P-2010) was used to detect organochlorine pesticide compounds. The GC-MS used for this study was Restek Stx-Cl. It was equipped with split and splitless injectors as well as a pesticide column. Electron ionization mass spectra were generated at 70 eV, monitoring for ions m/z 50 to 450 in full-scan and selected ion recording mode. Injection volume and temperature were 1µL and 250˚C, respectively. Interface and ion source temperatures were 250˚C and 200˚C respectively, injection temperature and detection temperature were set at 250˚C.

The column temperature was set at 60˚C and increased immediately at the rate of 10˚C /min to 180˚C where it was held for 2 mins, after which, it was increased at the rate of 15 ^{0}C /min, to 280˚C, and was held finally for 4 mins.

Estimation of health risk

The guidelines for potential risk assessment by the United States Environmental Protection Agency (USEPA), were used to assess the health risk of the consumption pesticide-laden cured fish. Estimated Average Daily Intake (EADI) was calculated as equation 2 (WHO, 1997). The Food and Agricultural Organization (FAO, 2017) projected that the per capita consumption of fishes in Nigeria is 13 kg per year. The Health Quotient (HQ) was calculated as shown in equation 1 (Fianko *et al.*, 2011).

$$EADI = \frac{\text{Conc. (µg/g) x Consumption Rate in Nigeria}}{\text{Body Weight (kg)}} \quad \ldots\ldots (1)$$

$$HQ = \frac{EADI}{\text{Reference dose}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Statistical analysis

The data obtained from the field survey was analyzed using Statistical Package for Social Sciences (SPSS) Version 15 (2015). Analysis of variance was used to compare the means at 5% level of significance. Data were presented using descriptive statistics such as frequency distribution tables, percentages and bar-charts.

Results

Results of *Organochlorine pesticides levels in fresh fish*

No organochlorine pesticide was detected in fresh fish samples from South-South Nigeria as shown in Table 1.

Organochlorine pesticides levels in cured fish

The highest weight (180g) of smoked-fish was recorded for *Heterobranchus bidorsalis* from Jigawa State but the point of purchase was Agenebode in Edo State, while the lowest was 7g recorded for *Ilisha africana* from Oron in Akwa-Ibom State.

The weight of the different extracts from 5g of the samples ranged from 0.25g (*Heterotis niloticus* from Koko in Delta) to 1.60g (*Clarias gariepinus* from Yenegoa).

Percentage occurrence of pesticides in cured fish

The organochlorine pesticide residues found in smoked fish from South-South Nigeria were endosulfan, DDT, aldrin, lindane and heptachlor-epoxide. The five pesticides were evaluated because of their relevance to public health.

Endosulfan had the highest percentage occurrence (38%) of all the pesticide residues in cured fish, followed by DDT which was 26% and then, aldrin residue (22%). Lindane and heptachlor-epoxide had the least % occurrence (7%). These results are presented in Figure 1.

Percentage occurrence of pesticides in some markets in south-south Nigeria

Figure 2 showed that aldrin residues were present in fish from Koko (9.1%), Uselu (9.1%), Choba (9.1%), Yenegoa (9.1%), Oron (18.2%), Mkpana (18%) and Ogbe-Ijoh (18%). In addition, DDT residues occurred 7.7% each in Koko, Agenebode and Uselu, while it had 15.4% occurrence each in Yenegoa, Oron, Mkpana and Ogbe-Ijoh Lindane had the same percentage occurrence (33%) in Koko, Ekehuan and Choba Markets.

Endosulfan was detected in all markets sampled in South-South. It had 5.6% frequency occurrence in Ibeno; Ogbe-Ijoh and endosulfan had 10.5% occurrence each in Koko, Ekehuan, Agenebode, Uselu, Choba, Yenegoa and Oron. The least (5.3%) was found in Illushin.

Heptachlor Epoxide also had equal percentage occurrence (33.3%) in Ekehuan, Illushin and Agenebode.

Percentage occurrence of pesticides in various species of dried-fish from south-south zone of Nigeria

Figure 3 shows that *E. fimbriata* (Bonga Fish) collected from South-South had 9.1%, 7.7% and 10.5% of the total residues of aldrin, DDT and endosulfan respectively. *Xenomystus nigri* had lindane (33.3%), heptachlor-epoxide (33.3%) and endosulfan (5.3%); 33.5% of total lindane residues and 5.3% of total heptachlor-epoxide residues were found in *O. niloticus* and *H. bidorsalis*, respectively. *Clarias gariepinus* contained 18.2%, 23.1% and 26.3% of total aldrin, DDT and endosulfan residues in all the cured fish species, respectively. *Heterotis niloticus* and *C. senegalensis* had the highest number (4) of pesticides residues but at different levels; *H. niloticus* had 18.2% of total aldrin residues found in all the fish species, DDT (23.1%), lindane (33.3%) and endosulfan (15.8%) while *C. senegalensis* had aldrin (9.1%), DDT (7.7%), lindane (33.3%) and endosulfan (53.1%).

The percentage occurrences of aldrin, DDT, endosulfan in *P. senegalensis* were 27.3%, 23.1% and 15.8%, respectively. The percentage occurrences of aldrin, DDT and endosulfan in *I. africana* were 18.2%, 15.4% and 10.5%.

Table 1: Organochlorine pesticide levels of fresh fish samples from some water bodies in south-south Nigeria

S/No	Water body	Sampling Stations	Sample Name	Average wt of whole Fish (g)	Wt of Ext. Analyzed with GC-MS (g)	Pesticides/Conc. Found (ug/g)
1.	Ekehuan	1	*C. gariepinus*	365	0.44	ND
		2	*P. obscura*	459	0.65	ND
		3	*S. clarias*	320	0.52	ND
2.	Illushin	1	*C. gariepinus*	600	0.80	ND
		2	*E. fimbriata*	250	0.76	ND
		3	*P. obscura*	355	0.52	ND
3.	Agenebode	1	*P. obscura*	420	0.56	ND
		2	*S. clarias*	463	0.64	ND
		3	*C. senegalensis*	250	0.51	ND
4.	Old NPA (Warri)	1	*S. clarias*	405	0.98	ND
		2	*H. niloticus*	900	0.46	ND
		3	*P.senegalensis*	400	0.66	ND
5.	Koko	1	*C. senegalensis*	310	0.57	ND
		2	*P.senegalensis*	290	0.76	ND
		3	*E. fimbriata*	320	0.86	ND
6.	Oron	1	*E. fimbriata*	450	0.68	ND
		2	*C. senegalensis*	290	0.50	ND
		3	*P.senegalensis*	195	0.70	ND
7.	Choba	1	*H. niloticus*	545	0.85	ND
		2	*C. gariepinus*	654	0.80	ND
		3	*S. clarias*	343	0.45	ND
8.	Mkpana (Ibeno LGA)	1	*P.senegalensis*	255	0.76	ND
		2	*C. senegalensis*	321	0.65	ND
		3	*E. fimbriata*	254	0.56	ND
9.	Brass (Yenegoa)	1	*C. gariepinus*	250	0.78	ND
		2	*S. clarias*	435	0.50	ND
		3	*H. niloticus*	565	0.60	ND

* ND – Not Detected

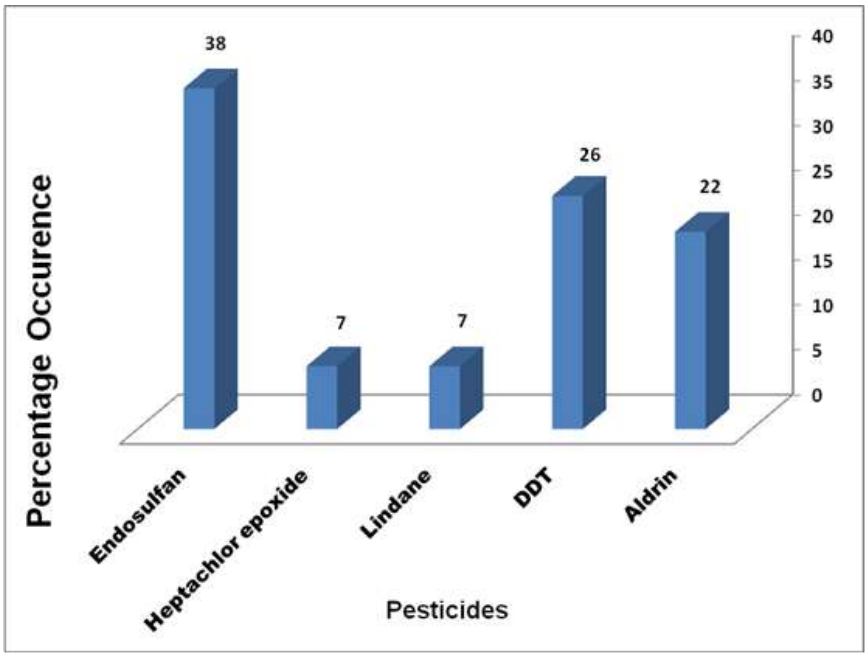

Figure 1: Percentage occurrence of pesticides in south-south

POP = The total number of samples with a particular pesticide X 100

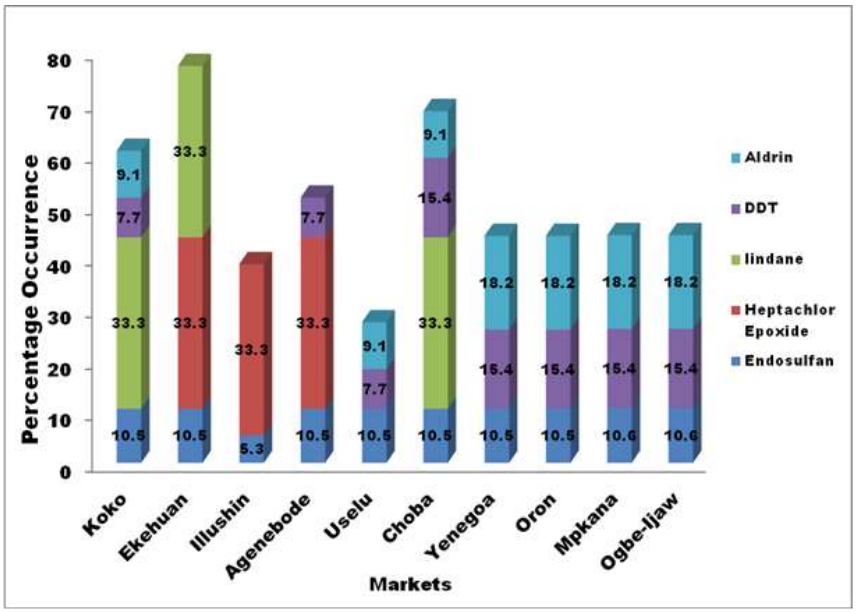

Figure 2: Percentage occurrence of pesticides in the various markets studied

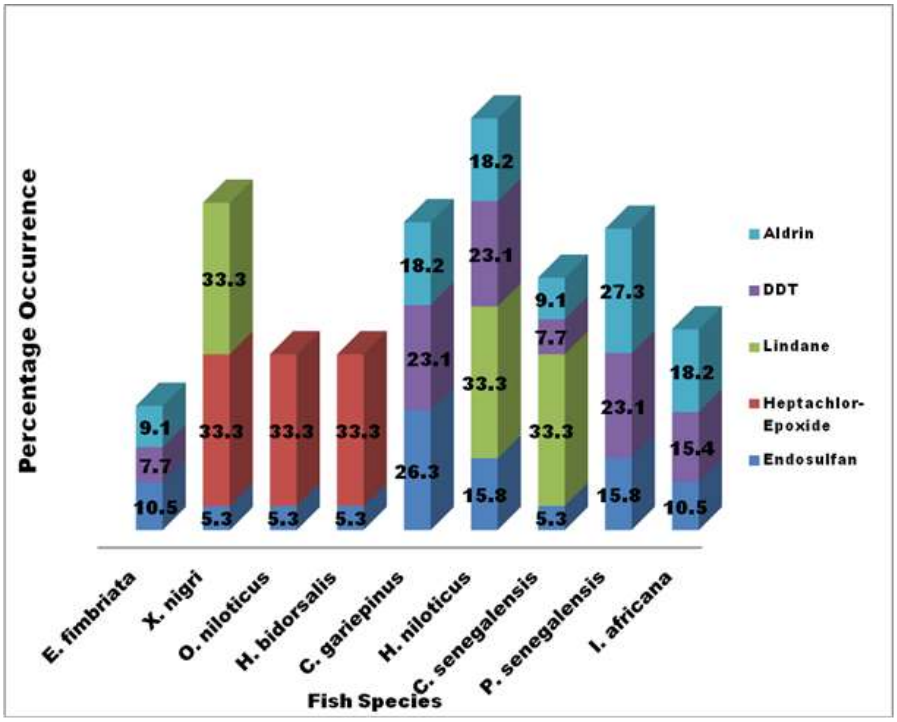

Figure 3: Percentage occurrence of pesticides in cured-fish species

Distribution and concentrations of organochlorine pesticides in cured fish

Endosulfan

Endosulfan was found in cured fish from Ogbe-Ijoh and Koko markets in Delta State; Ekenhuan, Illushin, Agenebode and Uselu markets in Edo State; Choba market in Rivers State; Inbikiri Market in Yenegoa (Bayelsa State) as well as Mkpana beach and Oron markets in Ibeno and Oron L.G.As respectively which are both in Akwa-Ibom State (Table 3). The highest amount of endosulfan residues (2.748±0.004µg/g of fish), was found in *H. bidorsalis* (Agenebode Market), while the least (0.252±0.002 µg/g), was in *C. gariepinus* from Ekehuan.

Lindane

Lindane residues were found in *H. niloticus, X. nigri* and *C. senegalensis* fish species obtained from Koko, Ekehuan and Choba markets, respectively (Table 3). The highest (0.443±0.009µg/g) amount of lindane residues was found in *H. niloticus* from Koko Market. The least (0.386±0.010µg/g) amount was recorded in *X. nigri* procured from Ekehuan.

Table 2: Weight parameters of dried-fish samples taken before GC-MS analysis

S/N	Sample Name	Market	Average Wt. of whole fish (g)	Wt. before clean up (g)	Wt. after clean up (g)	Wt. analysed with GC-MS (g)
1.	*Ethmalosa fimbriata*	Koko	65	0.45	0.36	0.10
2.	*Heterotis niloticus*	Koko	74	0.65	0.45	0.10
3.	*Xynomistus nigri*	Ekehuan	8	1.00	0.54	0.14
4.	*Clarias gariepinus*	Ekehuan	10	0.50	0.30	0.12
5.	*Oreochromis niloticus*	Illushin	30	0.74	0.60	0.10
6.	*Ethmalosa fimbriata*	Illushin	23	1.03	0.52	0.10
7.	*Heterobranchus bidorsalis*	Agenebode (Jigawa)	180	1.23	0.97	0.49
8.	*Clarias gariepinus*	Agenebode	70	0.99	0.78	0.10
9.	*Clarias gariepinus*	(Lokoja) Uselu	90	1.23	0.70	0.20
10.	*Ethmalosa fimbriata*	Uselu	56	1.44	0.96	0.07
11.	*Heterotis niloticus*	Choba	30	0.45	0.28	0.10
12.	*Cynoglosus senegalensis*	Choba	56	0.29	0.19	0.05
13.	*Clarias gariepinus*	Yenegoa	173	1.60	0.83	0.08
14.	*Heterotis niloticus*	Yenegoa	42	0.46	0.19	0.05
15.	*Pseudotolitis senegalensis*	Oron	10	0.46	0.31	0.05
16.	*Ilisha Africana*	Oron	7	1.03	0.51	0.07
17.	*Clarias gariepinus*	Mkpana Beach	34	0.81	0.20	0.01
18.	*Pseudolotis senegalensis*	Mkpana Beach	23	0.36	0.23	0.05
19.	*Pseudolitis senegalensis*	Ogbe-Ijoh	140	0.90	0.33	0.03
20.	*Clarias gariepinus*	Ogbe-Ijoh	34	1.54	0.64	0.05

* 5g of fish was taken from each fish species for extraction

Heptachlor-epoxide

Heptachlor-epoxide residues were found only in cured *O. niloticus, X. nigri* and *H. bidorsalis* obtained from Illushin, Ekehuan and Agenebode, respectively.

The highest (3.162±0.010µg/g) concentration of heptachlor-epoxide residues was recorded in *X. nigri* collected from Ekehuan, while the least (0.328±0.005µg/g) was in *O. niloticus* from Illushin (Table 3).

DDT

D.D.T residues were found in different fish species in South-South Nigeria as shown in Table 4.

The highest (0.180±0.003µg/g) concentrationt of DDT residues was detected in *I. africana* from Oron while the least (0.021±0.001µg/g) was found in *C. gariepinus* from Agenebode.

Aldrin

Aldrin residues were found in *H. niloticus* from Koko (Delta State); *Ethmalosa fimbriata* from Uselu market (Edo State); *C. senegalensis* from Choba (Port- Harcourt); *C. gariepinus* and *H. niloticus* from Inbikiri market (Bayelsa State); *I. africana* and *P. senegalensis* from Mkpana beach and Oron (Akwa- Ibom State); *P. senegalensis* and *C. gariepinus* from Ogbe-Ijoh market (Delta State).

The highest amount of Aldrin residues (2.770±0.020µg/g) was found in *I. africana* from Oron Market. The least amount (0.140±0.040µg/g) was detected in *E. fimbriata* obtained from Uselu Market (Table 4).

Mean concentrations of pesticides in cured fish from south-south Nigeria

Of the various pesticides analyzed, heptachlor-epoxide had the highest mean concentration (2.081 µg/g) cured fish from South-South. DDT had the least (0.269 µg/g) mean concentration (Figure 4).

Human health risk associated with consumption of pesticide-laden cured-fish from south-south, Nigeria

Table 5 shows the Estimated Average Daily Intake (EADI) and the hazard quotient (HQ) for each pesticide. Three population groups: 10kg - baby, 30kg - child and 70kg - adult were used for this study.

Hazard Quotient was greater than 1 for the mean concentrations of endosulfan, lindane, heptachlor-epoxide and Aldrin residues in cured-fish from Edo, Delta, Bayelsa, Rivers and Akwa-Ibom States for all weight groups. For DDT residues, HQ was greater than 1 in cured-fish from Edo, Delta, Bayelsa and Akwa-Ibom States while in Rivers state it was less than 1 for baby weight group. For 30kg child weight group, the HQs for all the states sampled in south-south was all less than 1 except for Akwa-Ibom State. For 70kg adult weight group, the HQs were less than 1.

Table 3: Distribution and mean concentrations of endosulfan, lindane and heptachlor-epoxide residues in dried-fish species from south-south zone of Nigeria

Pesticide	Market	Fish species	Wt. of fish (g)	Wt Extracted (g)	Conc. of pesticides in fish (µg/g)	Amount in whole fish (µg)
Endosulfan	Koko	*E. fimbriata*	65	0..36	0.733±0.070^{d}	68.640±0.002^{g}
		H. niloticus	74	1.80	0.560±0.010^{i}	298.368±0.0003^{c}
	Ekehuan	*X. nigri*	8	0.54	1.017±0.004^{e}	12.552±0.010^{j}
		C. gariepinus	10	0.30	0.685±0.005^{f}	6.850±0.002^{k}
	Illushin	*O. niloticus*	30	0.60	0.665±0.005^{g}	47.880±0.003^{h}
	Agenebode	*H. bidorsalis*	180	0.97	2.748±0.004^{a}	391.680±0.020^{a}
		C. gariepinus	70	0.78	0.276±0.002^{m}	60.270±0.003^{g}
	Uselu	*E. fimbriata*	56	0.96	0.466±0.003^{j}	143.314±0.020^{e}
		C. gariepinus	90	0.70	0.252±0.002^{n}	31.770±0.001^{i}
	Choba	*H. niloticus*	30	0.28	0.252±0.010^{n}	8.460±0.001^{k}
		C. senegalensis	56	0.19	0.462±0.004^{j}	39.312±0.002^{i}
	Yenegoa	*C. gariepinus*	173	0.83	0.428±0.003^{k}	307.248±0.002^{b}
		H. niloticus	42	0.19	1.268±0.008^{b}	80.934±0.004^{f}
	Oron	*P. senegalensis*	10	0.31	0.710±0.020^{e}	17.610±0.003^{j}
		I. Africana	7	0.51	1.003±0.003^{c}	20.461±0.001^{j}
	Ibeno Mpkana Beach	*I. Africana*	34	0.2	0.745±0.002^{d}	202.640±0.003^{d}
	Ogbe-Ijoh (Warri)	*P. senegalensis*	140	0.33	0.597±0.002^{h}	367.780±0.003^{a}
	Mpkana	*P. senegalensis*	23	0.20	0.360±0.030^{i}	13.248±0.002^{j}
	Ogbe-ijoh (Warri)	*C. gariepinus*	34	0.64	0.267±0.002^{mn}	46.478±0.001^{h}
Lindane	Koko	*H. niloticus*	74	1.80	0.443±0.009^{a}	236.060±0.002^{a}
	Ekehuan	*X. nigri*	8	0.54	0.386±0.010^{c}	4.768±0.002^{c}
	Choba	*C. senegalensis*	56	0.19	0.427±0.003^{b}	36.344±0.001^{b}
Heptachlor - epoxide	Illushin	*O. niloticus*	30	0.60	0.328±0.005^{c}	23.610±0.020^{c}
	Ekehuan	*X. nigri*	8	0.54	3.162±0.010^{a}	39.032±0.010^{b}
	Agenebode	*H. bidorsalis*	180	0.97	0.490±0.020^{b}	69.840±0.003^{a}

*Values with the same superscripts in the same column are significantly different (P<0.05).

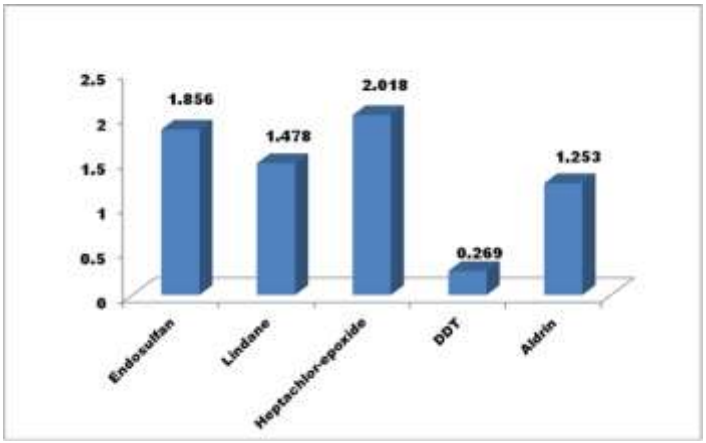

Figure 4: Mean concentrations of pesticides in cured fish from south-south Nigeria

Table 4: Distribution and Mean Concentrations of DDT and Aldrin Residues in Dried-fish Species from South-South

Pesticide	Market	Fish species	Wt. of whole fish (g)	Wt. of Extract (g)	Conc. of pesticides in fish (µg/g)	Amount in whole fish (µg)
DDT	Koko	*H. niloticus*	74	1.80	0.069 ± 0.004^{c}	36.778 ± 0.001^{b}
	Agenebode	*C. gariepinus*	70	0.78	0.021 ± 0.001^{f}	4.620 ± 0.002^{e}
	Uselu	*E. fimbriata*	56	0.96	0.070 ± 0.020^{c}	21.504 ± 0.004^{c}
	Choba	*H. niloticus*	30	0.28	0.030 ± 0.020^{ef}	1.020 ± 0.002^{e}
		C. senegalensis	56	0.19	0.066 ± 0.001^{cd}	5.600 ± 0.001^{e}
	Yenegoa	*C. gariepinus*	173	0.83	0.051 ± 0.002^{cd}	36.676 ± 0.002^{b}
		H. niloticus	42	0.19	0.173 ± 0.003^{a}	11.046 ± 0.010^{d}
	Oron	*P. senegalensis*	10	0.31	0.105 ± 0.005^{b}	2.600 ± 0.002^{e}
		I. Africana	7	0.51	0.180 ± 0.030^{a}	3.675 ± 0.003^{e}
	Mpkana Beach	*I. Africana*	34	0.20	0.095 ± 0.003^{b}	25.840 ± 0.002^{c}
	Ogbe-Ijoh (Warri)	*P. senegalensis*	140	0.33	0.094 ± 0.002^{b}	57.960 ± 0.004^{a}
	Mpkana	*P. senegalensis*	23	0.23	0.057 ± 0.002^{cd}	2.415 ± 0.030^{e}
	Ogbe-Ijoh	*C. gariepinus*	34	0.64	0.047 ± 0.002^{de}	8.194 ± 0.004^{d}
Aldrin	Koko	*H. niloticus*	74	1.80	0.252 ± 0.002^{d}	134.236 ± 0.002^{b}
	Uselu	*E. fimbriata*	56	0.96	0.140 ± 0.040^{g}	43.008 ± 0.002^{d}
	Choba	*C. senegalensis*	56	0.19	0.326 ± 0.003^{b}	27.776 ± 0.001^{e}
	Yenegoa	*C. gariepinus*	173	0.83	0.301 ± 0.001^{c}	216.077 ± 0.002^{a}
		H. niloticus	42	0.19	0.295 ± 0.003^{c}	18.816 ± 0.003^{f}
	Oron	*P. senegalensis*	10	0.31	0.282 ± 0.002^{c}	6.990 ± 0.004^{g}
		I. Africana	7	0.51	2.770 ± 0.020^{a}	56.511 ± 0.001^{c}
	Mkpana Beach	*I. Africana*	34	0.31	0.307 ± 0.004^{bc}	129.434 ± 0.002^{b}
		P. senegalensis	23	0.23	0.177 ± 0.004^{f}	7.475 ± 0.100^{g}
	Ogbe-Ijoh	*P. senegalensis*	140	0.33	0.226 ± 0.003^{e}	139.160 ± 0.004^{b}
	Ogbe-Ijoh	*C. gariepinus*	34	0.64	0.168 ± 0.004^{f}	29.240 ± 0.002^{e}

*Values with the same superscripts in the same column are significantly different ($P<0.05$).

Discussion

Analysis of fresh fish samples from water bodies in south-south

The results of the analyses of fresh fish samples from water bodies in South-South Nigeria revealed that no pesticide traces were found in the fresh fish samples. The results of this study are not in line with Ezemonye *et al.* (2015) who analysed *Clarias gariepinus* and *Tilapia zilli* from Ogbesse River in Edo State and detected residues of aldrin, heptachlor- epoxide, endosulfan and DDT pesticides. The concentrations of pesticides detected, ranged from 0.22±0.22 to 2.34±0.68 µg/g. The results are in line with the report of Alani *et al.* (2013) who detected a concentration range of 0.023 to 0.069 µg/g of dichlorodiphenyltrichloroethane, dichlorodiphenyl-dichloroethane (DDD), dichloro-diphenyl-dichloro ethylene (DDE) in *Chrysichthys nigrodigitatus*, *Tilapia guinenses*, *Mugil cephalus*, crayfish (*Penaeus* sp.), African red snapper (*Latjanus agennes*) from Lagos lagoon in Nigeria.

The absence of organochlorine pesticides in fresh fish in this study showed that people in the South-South zone may have discontinued the use of obnoxious fishing methods (pesticides) in fishing, maybe as a result of the awareness of threats to the aquatic ecosystem and man.

Pesticide residues in cured fish

The high percentage occurrences and even distribution of D.D.T, aldrin, lindane and heptachlor-epoxide in cured fish obtained from the markets sampled in south-south Nigeria indicate that they were used consistently during and after drying of marketable fish species. This is indicative of the fact that fish processors and sellers preserve their dried fish with pesticides during or after drying to prevent spoilage until they are sold. Their intention may be to maximize profit, despite the danger associated with the consumption of pesticides.

Endosulfan residues in cured fish from south south zone

Endosulfan is a xenoestrogen and endocrine disruptor, causing developmental damage in humans and animals. It is neurotoxic in mammals and insects. Endosulfan is extremely deadly to aquatic organisms and it has bioaccumulating consequences on fish (Singh, 2012).

In south-south Nigeria, endosulfan residue concentration in cured fish ranged from 0.11±0.20 to 5.96±0.03 µg/g. This is lower than those reported by Farshid (2015) on some fish from Lake Tashk in Iran. The results from this study are in agreement with those of Afful *et al.* (2010) who reported high amount of endosulfan residues in fish. However, lower levels of endosulfan residues were reported in Lagos lagoon by Adeyemi *et al.*, (2008) when compared to the levels seen in this study. The concentrations of endosulfan in all the cured fish from South-South and South-East were far higher than the 0.0001 µg/g maximum residue limit (MRL) set by WHO and 0.6 × 10^{-5} µg/g Acceptable Daily Intake value (ADI) established by FAO (2009).

Lindane residues in cured fish from south-south zone

Lindane is used majorly in the treatments of seeds and soils for the transplanting of tobacco, applications on foliage of nut, fruits, vegetables and trees, as well as protection of wood. It is used as a therapeutic ectoparasiticide, pediculicide, scabicide, and for animals and humans (Merck, 1989). WHO (2015) classified lindane as carcinogenic. The USEPA (2005) has determined that high lindane exposure negatively affects the nervous system, resulting in symptoms such as convulsion, dizziness, headaches, convulsions and sometimes death (Agency for Toxic Substances and Disease Registry, ASDR 2005).

The concentrations of lindane residue found in cured-fish from South-South ranged from 0.596±0.004 to 3.190±0.001 µg/g. The pesticide concentrations in all the fish samples were similar to those obtained by Akan *et al.* (2013) on fish samples from Alau Dam, Borno State, lower than the value reported by Farshid (2015) on fish from Lake Tashk in Iran but were much higher than 0.01 µg/kg MRLs for α-BHC and γ-BHC level set by WHO and FAO (2009). The high concentrations of lindane in cured-fish in this study could be as a result of the fact that pesticides are being used to preserve fish during or after curing.

Aldrin residues in cured fish from south-south zone

The National Agency for Food and Drug Administration and Control (NAFDAC in Nigeria) proscribed the sale and supply of aldrin in 2008 because it posed a looming health hazard to humans. Nevertheless, Aldrin is still in use because it is cheap and affordable.

The concentrations of aldrin residue in cured fish from South-south ranged from 0.325±0.002 to 8.073±0.010 µg/g. Some of the concentrations of aldrin residue in South-South and South-East were higher than those reported by Akan *et al.* (2013) in the liver of *Oreochromis niloticus* and flesh of *Heterotis niloticus* (Gitahi *et al.*, 1994) from Lake Naivasha in Kenya. The concentrations of aldrin in all fish samples were much higher than the WHO and FAO (2009) approved MRL of 0.0002 µg/g and the ADIs of 0.6 × 10^{6} µg/g. The high concentrations of aldrin in cured-fish from South-South Nigeria may be due to the fact that pesticides are used to preserve fish by a majority of processors, retailers and processors after curing.

DDT residues in cured fish from south-south zone

The concentrations of DDT residues in cured-fish from South-South ranged from 1.020±0.002 to 57.960±0.004 µg/g. The results from this study is not in line with Alani *et al.,* (2013) who reported a higher DDT range of 1.29 to 13.33 ng/g in fish. The results of this study corroborate those of Adeyemi *et al.* (2008) who reported 0.14 to 0.18 mg/g for Tilapia; 0.02 to 0.15 mg/g for Bonga shad and 0.02 to 0.05 mg/g for catfish from Lagos Lagoon. The results are in the range reported by Musa *et al.* (2010) who detected 4.220±0.599 µg/g for *Gymnarchus niloticus*, 3.323±0.395 µg/g for Catfish and 2.844±0.68 µg/g for Tilapia from South-East Nigeria. The high concentration and even distribution of DDT are suggestive of the fact that DDT is used for preservation in all the nooks and crannies of South-South Nigeria by fish processors during and after curing.

Heptachlor-epoxide residues in cured fish from south-south zone

Heptachlor-epoxide residues in cured fish from South-South were lower than 0.037–0.049 parts per billion (ppb) in fish obtained by Kafilzadeh (2005) from water, sediments and fish from Lake Tashk. The results from this study were similar to those obtained by Oso (2015) who reported 3.2062±0.0348 µg/g, 3.1476±0.0529 µg/g, 2.6926±0.0354 µg/g, 1.5324±0.1389 µg/g and 3.1086±0.0503 µg/g in Nile Tilapia, African Catfish, Atlantic horse mackerel, Sardine and Chub Mackerel, respectively.

The concentrations from this study were much higher than the EU set MRL of 0.2 µg/g. This confirms that high concentration heptachlor-epoxide is used for preservation by fish processors during and after curing.

Health risk associated with the consumption of pesticide-laden cured-fish obtained from south-south zone

All pesticides with HQ above 1 indicate possible health risk when the pesticide-laden cured fish is consumed? (Tsakiris *et al.*, 2011).

Estimated Average Daily Intake for endosulfan, heptachlor-epoxide and aldrin were far greater than the reference dose for all weight groups.

This means that the extrapolated HQs were greater than 1. Health Quotients (HQs) was greater than 1 for mean concentrations of DDT residues in cured-fish from Edo, Delta, Bayelsa and Akwa-Ibom States while Rivers state was less than 1 for 10kg baby weight group, 30kg child while 70kg adult weight were all less than 1 except for Akwa-Ibom State.

The Estimated Average Daily Intake for only lindane exceeded the reference dose for Baby (10kg) weight groups. For lindane, only the 10kg group may have potential health risk if they consumed cured-fish containing this pesticide.

These results are in line with Fianko *et al.* (2011) and Ezemonye *et al.* (2015) who established the potential danger of the consumption of pesticide-laden fish by humans.

Conclusion

This study has provided baseline information on the concentration and distribution of organochlorine pesticides in fresh and cured-fish from South-South zone of Nigeria. The study revealed that no organochlorine pesticide was found in fresh fish but was detected in all cured fish species from the markets sampled. At least two organochlorine pesticides residues such as aldrin, endosulfan, DDT and heptachlor-epoxide were detected in each cured fish species. The levels of the organochlorine pesticide residues were far higher than the maximum residual limit and allowable daily intake values recommended by WHO, FAO and USEPA.

The results from this study revealed that the people of South-South of Nigeria have discontinued the use of obnoxious fishing methods (pesticides) in fishing, probably as a result of the awareness of threats to the aquatic ecosystem. The results from this study revealed high percentage occurrences, even distribution, of endosulfan, lindane, D.D.T, aldrin, and heptachlor-epoxide in cured fish from South-South zone. This could mean that these organochlorine pesticides are consistently used in the nooks and crannies of the study area by processors, distributors and sellers during and after processing of marketable fish species. Their ultimate intention may be to prevent spoilage and maximize profit despite the inherent dangers in the consumption of pesticides-laden fish.

Health risk assessment of this study revealed that there is a potential danger associated with the consumption of cured fish containing evaluated concentrations of endosulfan, heptachlor-epoxide, aldrin and lindane but no risk may be involved in the consumption of cured fish with concentrations of DDT residues.

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