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Incidence of organochlorine pesticide residues in smoke-dried fish species marketed in South-West Nigeria

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Abstract
Organochlorine pesticides (OCPs) have been used extensively in fish preservation due to their low cost and efficacy to halt insect infestation. There is paucity of information on OCP residues in smoke-dried fish samples in the South-West zone of Nigeria and this necessitated the screening, elucidation and quantification of OCP in smoke-dried fish samples in this study. Fish samples were randomly obtained from markets in Lagos, Oyo, Ogun and Ondo States. These were extracted and analyzed for OCPs using GC-MS. The data obtained was subjected to Multivariate Analysis of variance (MANOVA) and the arising means separated using LSD test. The detected OCPs were DDT (0.001-0.077µg/ml), endosulfan (0.138-0.720 µg/ml), heptachlor epoxide (0.016-1.244 µg/ml), lindane (0.508µg/ml) and aldrin (0.030-0.491 µg/ml). Lagos State was significantly higher ($P < 0.05$) in DDT, endosulfan and heptachlor epoxide concentrations while Ogun State had higher aldrin concentrations. The estimated average daily intake (EADI) and hazard quotient (HQ), on the consumption of OCPs laden fish shows that heptachlor epoxide and aldrin concentrations exceeded the reference dose. The consumption of OCPs laden fish samples may result in adverse health complications due to OCPs toxicity. There is the need for the continuous sensitization of fishmongers to shun OCPs usage in fish preservation in the South-West.

Keywords: Organochlorine; Pesticides; Smoke-dried; Fishmongers; Fish marketers

INTRODUCTION

In Nigeria, over 80 % of fish harvested is preserved by various methods of curing to prolong shelf life; but even when fish is processed, it is still subjected to losses and spoilage due to inadequate preservation and storage practices which consequently result in economic loss [1]. Combined effects of insects and other biological agents that flourish under tropical hot and humid conditions lead to substantial losses in cured fish and to enhance shelf life especially during storage, distribution and retailing, cured fish processors/mongers often use varieties of persistent organic pollutants (POP) especially the organochlorine pesticides to prevent and halt insect infestation.

Organochlorine pesticides due to their high efficacy and low cost are among the agrochemicals and fumigants that have been used extensively in Nigeria, for weed and pest control as well as in the health sector for control of mosquitoes and tsetse fly.

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Organochlorine pesticides are characterized by low polarity, low aqueous solubility and high lipid solubility (lipophillicity). Many organochlorine pesticides as well as their metabolites have been implicated in a wide range of adverse human and environmental effects such as reproduction, birth defects, immune system dysfunction, endocrine disruptions and cancer [2] due to their potential to bio-accumulate and bio-magnify. Studies have revealed the use of OCPs in fish preservation [3,4]. However, there is the paucity of information on the possible use of organochlorine pesticide in smoke-dried fish preservation in South-West Nigeria, hence this study was designed to screen smoke-dried fish samples obtained from selected markets within South-West States, elucidate and quantify the concentrations of OCPs residues detected.

EXPERIMENTAL

The study was carried out in four (4) states namely Lagos, Oyo, Ogun and Ondo in South-West part of Nigeria and smoke-dried fish samples were purchased from sampling markets that were purposively selected based on popularity for commercial smoke-dried fish sales.

Extraction of fish samples. The smoke-dried fish samples were weighed, chopped into bits and placed into an electric blender for 10 minutes at medium speed to pulverize. 20g of the grounded samples were exhaustively extracted with Soxhlet apparatus for five (5) hours using dichloromethane as solvent. The extracts were dried over anhydrous sodium sulphate and concentrated to about 2 mL under a pure stream of nitrogen gas.

Clean-up procedure. Extract clean-up was carried out using a column (15 cm length x 1 cm internal diameter) and this was packed with 10 g activated silica gel prepared slurry form and 10 g of anhydrous sodium sulphate placed on top the column to absorb any water in the sample or the solvent. The extracts were introduced into the column and eluted with 20 mL of dichloromethane and the eluates collected, placed in plastic vials and then evaporated to dryness under stream of analytical grade nitrogen in readiness for GC-MS analysis.

GC-MS analysis. GC-MS (QP2010 SE Shimadzu, Japan instrument) was used to identify and quantify the organochlorine pesticide residues contained in the smoke-dried fish samples purchased from selected markets in South West States, Nigeria.
The pesticide analytical conditions were**:**
GC column: Stx-CL Pesticides (by Restek) Length 30m, I.D 0.32mm, thickness 0.5µm. Gas: Helium. Initial temperature: 120^{o}C; Injection Temperature: 250^{o}C; Injection Volume: 8µL; Mode: Splitless; Oven Program: 120^{o}C (0.00 min) → 200^{o}C @ 45^{o}C/min (0.00) 230^{o}C @ 12.5^{o}C/min → (0.00min) → 325^{o}C/min (2.00 min).
MS: Ion source 230^{o}C; Interface 250^{o}C; Ionization mode: EI.

Calibration and recovery. Five cured fish samples were spiked with mixture of standard pesticides and these were extracted then analyzed under the same conditions as described above to automatically obtain pesticide standards and calibration curves. The mean recovery range was between 90-95% and RSD ± 13 %.

Health risk estimation. Human health risk estimation in this study was calculated based on integration of pesticide analysis data and exposure assumption adopted by U.S. Environmental Protection Agency [5]. The human health risk posed by the smoke-dried fish samples laden with organochlorine pesticide on exposure was assessed with the reference dose (RFD) that are likely to be without an appreciable risk of deleterious effect. Based on the Estimated Average Daily Intake (EADI) and Hazard Quotient (HQ) each pesticide non-deleterious exposure was calculated thus:

$$\text{Estimated Average Daily Intake (µg/kg/day)} = \frac{\text{Residual concentration x fish consumption}}{\text{Body weight}}$$

$$\text{Hazard Quotient} = \frac{\text{Estimated average daily intake}}{\text{RFD}}$$

Ezemonye et al. [6] reported that Food and Agricultural Organization [7] quoted per capita consumption of fish in Nigeria as 9 kg and body weight was set at 70 kg and 10 kg respectively for adult and children population.

Statistical analysis. GCMS pesticide residual concentrations were analyzed by Multivariate Analysis of Variance (MANOVA) and data presented in Mean ± SD. The means were separated using LSD post hoc test ($P < 0.05$) using SPSS version 16.

RESULTS

Table 1 shows that DDT residual concentration (0.001-0.077µg/ml) was present in the smoke-dried fish samples except in samples obtained from Agege, Asejere and Bodija markets. The residual concentrations in Ikotun and Suin markets were higher and significantly different compared to the other markets. Endosulfan residual concentration (0.138-0.720 µg/ml) except in Suin and Eleweran markets was detected in smoke-dried fish obtained from markets samples and the mean concentrations in Oyingbo market was higher and significantly different compared to the other markets. Heptachlor epoxide residual concentration (0.016 - 1.244 µg/ml) was detected in smoke-dried fish samples obtained from Oyingbo, Agege, Ikotun, Epe, Eleyele and Bodija markets and samples obtained from Oyingbo market were higher and significantly different. Lindane pesticide residual concentration 0.508 µg/ml was detected in Oyingbo market. While Aldrin mean residual concentration (0.030-0.491 µg/ml) was detected in smoke-dried fish samples obtain from Iwo, Asejire, Iseyin, Suin, Eleweran, Alara and Alayinka markets and the concentrations were significantly different in Suin market, Alara and Alayinka markets.

Pesticide mean residual concentrations between states in Table 2 indicates that DDT residues in smoke-dried fish samples obtained from markets in Ogun state were higher and significantly different compared to the other states. Endosulfan residues were higher and significantly different in Lagos state. Heptachlor epoxides residues were detected in Lagos and Oyo states with concentrations that were not significantly different. Lindane residues were detected in samples obtained from markets in Lagos State. Aldrin residues were detected in samples from the respective states except Lagos and were significantly different.

Table 3 shows the health risk assessment associated with pesticide residues in smoke-dried fish samples. The estimated average daily intake (EADI) and hazard quotient (HQ) for the respective organochlorine pesticides were within the permissible reference dose except for heptachlor epoxide in Lagos State and adrin in Ogun and Ondo states that were relatively higher than the recommended reference dose and hazard quotient (HQ) greater than one (1).

DISCUSSION

States in South-West zone of Nigeria although bounded by coastal environments where fishing, fish processing and marketing activities takes place on commercial scale. Processed smoke-dried fish species is a much-cherished delicacy with relatively high demand especially in the cosmopolitan cities. To meet consumers' satisfaction, fishmongers and merchant engage in the trading of smoke-dried fish species from other parts of the country with major fish processing centers especially in the northern axis, such as Lake Chad, Kainji, Shiroro, Yauri, Jebba and Tatabu down to designated markets in the South-West States.

Table 1: Organochlorine pesticide residues mean comparison between markets

State	Markets	Pesticide residue concentrations (µg/ml)				
		DDT	Endosulfan	Heptachlor epoxide	Lindane	Aldrin
Lagos	Oyingbo	0.024±0.002^{ab}	1.529±2.088^{b}	1.244±1.526^{b}	0.508±0.090^{a}	ND
	Agege	ND	0.660±0.230^{ab}	0.036±0.030^{a}	ND	ND
	Epe	0.001±0.001^{a}	0.720±0.002^{ab}	0.033±0.003^{a}	ND	ND
	Ikotun	0.077±0.123^{b}	0.586±0.038^{ab}	0.396±0.082^{a}	ND	ND
Oyo	Iwo	0.016±0.028^{ab}	0.251±0.180^{a}	ND	ND	0.035±0.061^{a}
	Eleyele	0.001±0.001^{a}	0.525±0.041^{ab}	0.030±0.011^{a}	ND	ND
	Asejere	ND	0.138±0.037^{a}	ND	ND	0.030±0.052^{a}
	Bodija	ND	0.228±0.395^{a}	0.016±0.028^{a}	ND	ND
	Iseyin	0.019±0.033^{ab}	0.321±0.275^{a}	ND	ND	0.055±0.095^{a}
Ogun	Suin	0.072±0.024^{b}	ND	ND	ND	0.491±0.116^{c}
	Eleweran	0.012±0.021^{ab}	ND	ND	ND	0.033±0.058^{a}
Ondo	Alara	0.004±0.003^{a}	0.255±0.127^{a}	ND	ND	0.176±0.020^{b}
	Alayinka	0.013±0.001^{ab}	0.284±0.078^{a}	ND	ND	0.168±0.031^{b}

a, b - superscripts indicate mean significant differences. Columns with similar superscripts are not significantly different ND- Not detected

Table 2: Organochlorine pesticide residues mean comparison between States.

State	Pesticide residue concentrations (µg/ml)				
	DDT	Endosulfan	Heptachlor epoxide	Lindane	Aldrin
Lagos	0.026±0.062^{ab}	0.874±0.980^{b}	0.427±0.831^{a}	0.127±0.233^{a}	ND
Oyo	0.007±0.019^{a}	0.293±0.237^{a}	0.009±0.017^{a}	ND	0.024±0.052^{a}
Ogun	0.050±0.036^{b}	ND	ND	ND	0.315±0.026^{c}
Ondo	0.007±0.006^{a}	0.231±0.134^{a}	ND	ND	0.147±0.068^{b}

a, b - superscripts indicate mean significant differences. Columns with similar superscripts are not significantly different ND- Not detected

Table 3: Health risk assessment of mean residues

State	Pesticides	Mean residual concentration (µg/ml)	RfD	EADI		HQ	
				Adult	Children	Adult	Children
Lagos	DDT	0.026	0.5	0.003	0.023	0.006	0.005
	Endosulfan	0.814	6	0.105	0.733	0.018	0.122
	Heptachlor epoxide	0.427	0.013	0.055	0.384	4.231	29.538
	Lindane	0.127	0.3	0.016	0.114	0.053	0.380
Oyo	DDT	0.007	0.5	0.001	0.006	0.002	0.012
	Endosulfan	0.293	6	0.038	0.264	0.006	0.044
	Heptachlor epoxide	0.009	0.013	0.012	0.008	0.923	0.615
	Aldrin	0.024	0.03	0.003	0.022	0.100	0.733
Ogun	DDT	0.050	0.5	0.006	0.045	0.012	0.090
	Aldrin	0.315	0.03	0.040	0.283	1.350	9.430
Ondo	DDT	0.007	0.5	0.001	0.006	0.002	0.012
	Endosulfan	0.231	6	0.030	0.208	0.005	0.035
	Aldrin	0.147	0.03	0.020	0.132	0.667	4.400

RfD = Reference dose; HQ= Hazard Quotient; EADI = Estimated Average Daily intake; Bold figures indicates level above the thresh hold limit.

The marketing of smoke-dried fish samples is a very delicate business that often results in economic loss to the fishmongers due to insect infestation often as a result of long distances away from processing centers, storage period, transportation, distribution and retailing. This prompts fishmongers to device strategies such as the use of chemicals,

especially the organochlorine pesticides, to reduce post-harvest losses [8].

In samples of smoke-dried fish purchased and analyzed more than one form of organochlorine pesticides were detected and this confirms the finding of [9] as well as [3] on the presence of organochlorine pesticide residues DDT, DDE and lindane in a smoke-dried fish sample analyzed. Thus, the number of fishmongers engaged in a batch of smoke-dried fish from processing, transportation, distribution and marketing has direct influence on the forms and concentration of pesticides applied to preserve fish quality against insect infestation. In addition, the ability of insects ravaging smoke-dried fish to develop resistances on applied OCPs may prompt the fishmongers to resort to indiscriminate use of several forms of organochlorine pesticides at higher concentrations on a particular smoke-dried fish sample or batch in agreement with [10].

Exposure to organochlorine pesticides and their metabolites have possibly identified array of adverse effects on human health and these epidemiological evidences according to [11] and [12] include cancer, neurological damage, reproductive system deformities, birth defect and damage to the immune system. Thus, the assessment of human health risk on the consumption of pesticide-laden fish is essential towards public health safety by estimating the negative and non-carcinogenic impacts. From the study, the high value of heptachlor epoxide and aldrin indicates they are the most utilized OCPs in the localities and the effect of these OCPs have adverse health implications.

Conclusion. The desire by some fishmongers and marketers to use organochlorine pesticides to preserve smoke-dried fish species during storage, transportation and marketing remains a serious socio-economic problem considering the adverse health implications. In order to combat the menace on the use of OCPs in smoke-dried fish preservation, there is the need for continuous sensitization of fishmongers and marketers on the eminent dangers of organochlorine pesticides. Relevant health agencies within the states in the South-West zone should intensify efforts to assess the quality of smoke-dried fish species sold in the markets against OCPs especially those packaged in cartons and transported from other zones to designated markets in the South-West distributed in the markets. Finally, the government through its agencies should intensify efforts to check, monitor and control the importation, trade and use of banned organochlorine pesticides.

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