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Original Research Article

Organochlorine Pesticide Concentrations in Selected Rivers in South-West Nigeria

Nuntah, J. N[1*], Abolagba[1], O. J, Igene, J. O[2], Usifoh, S. F[3], Omoti, C. E[4], Usifoh, C. O[5]

[1]Department of Aquaculture and Fisheries Management, University of Benin, Benin City, Nigeria
[2]Department of Food Science Technology, University of Benin, Benin City, Nigeria
[3]Department of Clinical Pharmacy and Pharmacy Practice, University of Benin, Benin City, Nigeria
[4]Department of Haematology, University of Benin, Benin City, Nigeria
[5]Department of Pharmaceutical Chemistry, University of Benin, Benin City, Nigeria

***Corresponding Author**
Nuntah Joseph Nkem

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Abstract: Organochlorine pesticides (OCPs) are toxic environmental pollutants of worldwide concern, distributed in trace quantities within the aquatic ecosystem components (water, sediments and fish) and can possibly bio-concentrate, bio-accumulate, bio-transform and/or bio-magnify through the food web and constitute serious environmental and human health hazards. Hence, the need to determine and quantify the concentrations of OCPs in selected water bodies in some states in South-West Nigeria to ascertain the safety of the aquatic components especially the fishes which are for consumption. The study was carried out in Lagos, Oyo, Ogun and Ondo States, where two (2) water bodies in each of the State were purposively selected based on their popularity for fishing activities and other anthropogenic activities. The aquatic components (water, sediment and fish) samples were obtained, extracted and examined for OCPs forms (Dichlorodiphenyltrichloroethane [DDT], endosulfan and aldrin). The water samples retained mean concentrations (DDT [0.001 - 0.023 µg/ml], endosulfan [0.001 - 0.080 µg/ml] and aldrin [0.001 - 0.003 µg/ml]), sediment samples (DDT [0.003 - 0.028µg/g], endosulfan [0.002 - 0.355µg/g] and aldrin [0.002 - 0.013 µg/g]) and fish samples (DDT [0.001 - 0.016 µg/g], endosulfan [0.001 - 0.111 µg/g] and aldrin [0.004 - 0.123 µg/g]). The detected OCPs concentrations except for endosulfan in the water and sediment components were within WHO set maximum residual limit (MRLs) while in fish samples, the residual concentrations except for aldrin were within set MRLs. DDT, endosulfan and aldrin are persistent in the environment and have been classified by NAFDAC as likely human carcinogens or carcinogenic agent, hence their prolong exposures in the aquatic environment may result in environmental degradation, loss of aquatic biodiversity and human health hazards.

Keywords: Organochlorine, Sediments, Fish, Aquatic, Bioaccumulate.

INTRODUCTION

Pesticides have been misused in Nigeria due to dearth in relevant regulatory control and management of the production, trade, control and usage [1]. In Nigeria, Organochlorine pesticides (OCPs) were the most detected because they are major constituents in most agricultural fumigants used widely by farmers due to their effectiveness, broad-spectrum activities and cheap cost for effective vector control [2]. OCPs are banned or restricted substances under the Stockholm Convention (2001) and Nigerian is a part of this agreement but OCPs remain quite in use indiscriminately due to their low cost, availability, multifaceted nature and weak enforcement programs [3]. Organochlorines pesticides remain among the most toxic environmental pollutants of worldwide concern because they are lipophilic, hydrophobic and ubiquitous persistent contaminants that are possibly transported from the origin of application into the aquatic ecosystem via atmospheric exchange, water currents, debris, soil run-off, leaching and other anthropogenic pathways [4]. In aquatic ecosystems, OCPs are distributed within the aquatic components (water, sediments and fish) in trace quantities and their prolong exposures provide the tendency for bio-concentration, bio-accumulation, bio-transformation and/or bio-magnification especially through food web thereby posing serious environmental and health hazards [5].

The anthropogenic activities in the South-West states are relatively high, considering high levels of urbanization and industrialization in these localities and the resultant generated immense agricultural runoffs, municipal waste and industrial effluents often discharged into waterways and eventually passes into surrounding water bodies. Consequently, there are increasing OCPs pollution rates within the water bodies, hence the need to determine forms and concentrations of OCPs retained within aquatic components in selected water bodies in the study location, to ascertain the safety of the aquatic components especially fish for consumption to ensure healthy living.

MATERIALS AND METHODS

The study was executed in four states (Lagos, Oyo, Ogun and Ondo) in South-West Nigeria and two rivers in each state were purposively selected based on high levels of involvement in fishing and other anthropogenic activities. The water, sediments and fresh fish samples were obtained from three (3) locations across the width of the river and then taken to the University of Benin Pesticide Research Laboratory (UBPRL). The water samples were obtained using a 2 L pre-cleaned stained glass bottles and pulled together forming a composite sample, then acidified with concentrated HNO_3 to pH 2 to avert modification of the organic matter. The sediment samples were collected using a pre-cleaned Ekman grab sampler from depths of 2 and 4 cm, these were mixed thoroughly forming a composite sample and placed in sterile polythene bags. While the obtained fish samples were washed in distilled water and placed in ice packs.

The water samples were pre-filtered through 0.45m Whatman filter paper to take off suspended materials and the liquid-liquid extraction method as described by [6] with little modifications was undertaken (500 mL water samples were placed into a 1-litre separating funnel and extracted using 20 mL of dichloromethane [DCM] in 3 portions; the mixtures were vigorously shaken for 20 minutes each and the dichloromethane extracts collected). The sediment samples were dried in the oven at 40 ^{o}C to constant weight and homogenized with Agatha mortar and pestle then sieved with 0.5 mm mesh size to obtain fine particles. The fine sediments were extracted according to methods of [7] with slight moderation (5 g of the sediment sample was put into an extraction thimble pre-washed in n-hexane and acetone, then extraction was carried for 5 hours using dichloromethane solvent in a Soxhlet extractor). The composite whole fish samples were homogenized using Agatha mortar and pestle and 20 g of the properly mashed fish samples mixed with 10 g of anhydrous sodium sulphate was placed in extraction thimble and extracted for five (5) hours using dichloromethane solvent in a Soxhlet apparatus. The extracts were dried with anhydrous sodium sulphate (Na_2SO_4), then concentrated to about 2 mL under stream nitrogen in readiness for clean-up procedure.

The concentrated extracts were cleaned up to eliminate impurities by passing through a column (15 cm length and 1 cm internal diameter) packed with 5 g of activated silica gel prepared in slurry form in n-hexane and 5 g anhydrous sodium sulphate. Elution was carried out with 20 ml dichloromethane and the elutes were stored in plastic vials and evaporated under stream analytical grade nitrogen at 40°C [8, 9]. The concentrated eluents were reconstituted to 1 ml in dichloromethane for GC-MS analysis. GCMS- QP2010 SE SHIMADZU, Japan instrument fitted with an electron capture detector used for OCPs identification and quantification analysis based on retention values using the external standard method. The GC column used was Restek Stx -CL column of length, internal and thickness (30 m, 0.32mm and 0.5µm) and the operational GC conditions were in the splitless injection mode with helium (carrier gas) flow rate at 1 ml/min at a maintained injection temperature 250°C and injected volume 8 µl, the programmed column temperatures were 120 ^{o}C (0:00min) to 200 ^{o}C at 45 ^{o}C min^{-1} (0:00 min) to 230 ^{o}C at 12.5^{o}C min^{-1} (0:00min) to 325^{o}C min^{-1} and held for 2 minutes at 30 ^{o}C min-^{1}. The samples were injected automatically by split-less mode into the MS at an interface temperature of 250^{o}C using ion source at 230^{o}C with ionization mode of election impact ionization (EI) of 70 eV. The pesticide standards and calibration curves were prepared automatically while the concentrations of each detected OCP in the analyzed samples were determined to compare the sample peak areas against the standard calibration curves.

The GCMS detected and quantified pesticide residual concentrations were presented in Mean ± SD and statistically analyzed for significances ($P < 0.05$) with Multivariate Analysis of Variance (MANOVA) and LSD post hoc test, using SPSS version 16.

RESULTS

OCPs (DDT, endosulfan and aldrin) were detected in water samples (Figure-1), DDT concentrations were significantly higher ($P<0.05$) in Ondo State (0.023 µg/ml) compared to Lagos (0.017 µg/ml), Ogun (0.001 µg/ml) and Oyo (0.000 µg/ml) States. Endosulfan concentrations were significantly higher ($P<0.05$) in Lagos State (0.080 µg/ml) compared to Ondo (0.002 µg/ml) and Ogun (0.001 µg/ml) States. While aldrin concentrations in Lagos State (0.003 µg/ml) was highest but not significantly different ($P>0.05$) when compared to the States of Ondo (0.002 µg/ml), Ogun (0.001 µg/ml) and Oyo (0.001 µg/ml).

In the sediment samples (Figure-2), Lagos State had the highest detected concentrations (DDT = 0.028µg/g, endosulfan = 0.355µg/g and aldrin = 0.013 µg/g) and these were significantly different (P<0.05) compared to the concentrations detected in Ogun State (DDT = 0.003 µg/g, endosulfan = 0.002 µg/g, aldrin 0.003 µg/g); Oyo State (DDT = 0.005 µg/g, endosulfan = 0.003 µg/g, aldrin 0.002 µg/g) and Ondo State (endosulfan = 0.024µg/g, aldrin = 0.002 µg/g).

In the fresh fish samples (Figure-3), Lagos State had significantly higher (P<0.05) detected concentrations of DDT (0.016 µg/g) and endosulfan (0.111 µg/g) compared to Ogun State (DDT = 0.001 µg/g, endosulfan = 0.002 µg/g) and Oyo State (endosulfan = 0.001 µg/g). Aldrin concentrations (0.123 µg/g) in Ogun State were significantly higher (P<0.05) than those detected in the States of Oyo (0.016 µg/g) and Ondo (0.004 µg/g).

The validation method in this study maintained an RSD ± 13 % and percentage recoveries ranged 85-105%.

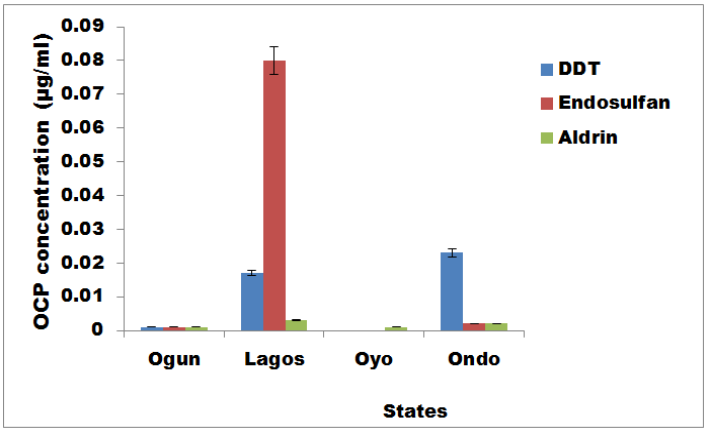

Fig-1: OCPs concentration (µg/ml) in water samples in the South-West zone

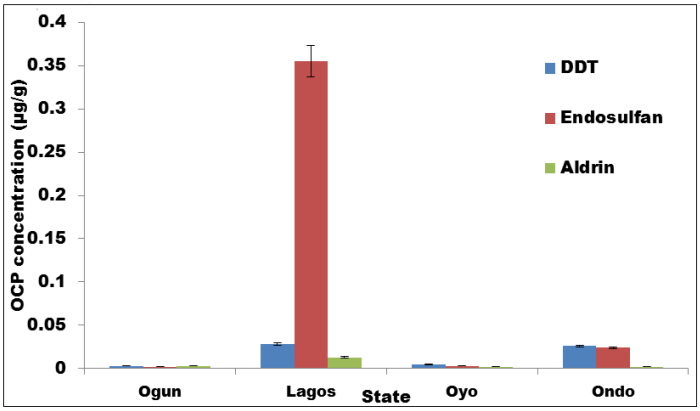

Fig-2: OCPs Concentrations (µg/g) in Sediment Samples in the South-West zone

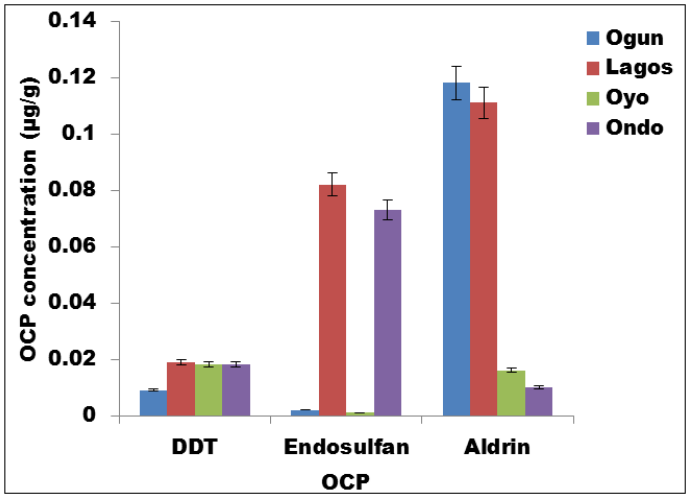

Fig-3: OCPs Concentrations (µg/g) in fresh fish Samples in South-West

DISCUSSION

The South-West states in Nigeria are bound by inland and coastal waters and play host to a great number of fisher folks engaged in fishing, fish processing, fish distribution and marketing activities. Most of the water bodies are polluted with OCPs due to anthropogenic pursuits such as the use of OCPs in fishing, agricultural run-offs, and discharges from municipal waste, sewage and industrial effluents [10]. DDT, endosulfan and aldrin were the main detected OCPs at varying concentrations in the aquatic ecosystem components (water, sediment and fish samples) and this agrees with [11, 12]that aquatic environments are major repositories for persistent pollutants. The water samples retained the least residual concentrations (DDT = 0.010; endosulfan = 0.021 and aldrin 0.002) compared to the sediment samples (DDT = 0.016; endosulfan = 0.096 and aldrin 0.005) and fish samples (DDT = 0.010; endosulfan = 0.043 and aldrin 0.049). This agrees with [13] that OCPs, when discharged into water bodies, tend to accumulate the most in aquatic sediments and fish samples but least in the water samples. The least residual concentrations were possibly due to the less solubility of OCPs in water (hydrophobicity) and in line with [6], OCPs and their sulfates are difficult to breakdown in water.

The aquatic sediment retained higher OCPs concentrations because of the sediment solubility and strong affinity for suspended particulate matter [14] According to [6] aquatic sediment serves as ultimate sinks and principal reservoirs for environmental pesticides from which residues are released to the atmosphere, groundwater and living organisms. Olutona, G. O *et al*., [15] stated that the retained OCPs concentrations in sediment samples could be attributed to the hydrophobic character along with OCPs possibility of being in the organic phase. The fish samples retained residual OCPs concentrations due to their ability to absorb OCPs directly from water and sediments during feeding, respiration and metabolic activities [16]. In line with [17], the detected retained OCPs residual concentrations in fish samples could be ascribed to OCPs lipophilic characteristics to absorb and retain in fatty tissues of the fish.

The detected OCPs (DDT, endosulfan and aldrin) concentrations in water and sediment samples were below WHO set reference standard of 0.1 µg/L in individual and 0.5 µg/L in total concentrations for OCPs residues in water bodies [18]. This implies that the water bodies sampled in the study locations although polluted with OCPs concentrations are relatively safe for the survival of the aquatic biota. While in the fish samples, in line with [18] the OCPs (DDT, endosulfan and aldrin) detected were found to retain concentrations that were above WHO set maximum residual limits (DDT = 0.001 µg/g, endosulfan = 0.0001 µg/g, aldrin = 0.0002 µg/g) for OCPs concentrations in fish samples. The OCPs concentrations detected in the fish tissues and organs indicates the extent of pollution in the water bodies and this agrees with [19] that fishes are suitable indicators for monitoring environmental pollution. Thus the ingestion of OCPs laden fish and their bioaccumulation in human may lead to a possible adverse health complication.

CONCLUSION

OCPs are still available as a major chemical constituent in most insecticides used in Nigeria despite their ban and these through different pathways settle in the aquatic components. DDT, endosulfan and aldrin are persistent in the environment and have been classified as probable carcinogens or carcinogenic agent by NAFDAC, hence prolonged exposures in the aquatic environment may result in environmental degradation, loss of aquatic biodiversity and human health hazards. Therefore relevant governmental agencies should engage in sensitizing the populace on the dangers of OCPs exposure in the environment and human health. Also, efforts should be put in place to ensure that various effluent discharges are treated from the source of contamination to limit their potency before release into waterways and water bodies.

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