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ECOLOGICAL RISK ASSESSMENT OF PESTICIDE RESIDUES IN FISH SAMPLES FROM RIVER DONGA IN DONGA, TARABA STATE, NIGERIA

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ABSTRACT: *Organochlorine pesticides are a class of toxic compounds that are characterized by their relative chemical and biological stability, which is why they are persistent in the environment. As a result of this, organochlorine pesticides are listed as the highest level on the list of potential environmental hazards In this study, the levels of the pesticide residues (DDT, DDD, Dieldrin, Aldrin, dicofol, methoxychlor, endosulfan, chlordane, heptachlor, pentachlorobenzene, mirex, toxaphene, hexachlorobenzene, α-HCH, β-HCH, and γ-HCH) in river Donga, Taraba State, Nigeria were assessed using fish samples as a case study. Five fish species (Synodotismembranaceus, Protopterusannectens, Clariasgariepinus, Heterotisniloticus and Tilapiazilli) were purchased from the fishermen at bank of River Donga and was packaged into different labeled polyethylene bags. The fish samples were transported to the Biochemistry Laboratory Federal University Wukari in a Cold box with ice on the same day. All fish samples were kept in the freezer at 0-4°C. The fish samples were then washed with de-ionized water and were allowed to thaw at room temperature. The fish samples were dissected and filleted to obtain the fish flesh. The fillets were dried at ambient room temperature.50 g of the dried samples were each homogenized using a house-hold mill. An Agilent HPLC system was used for the LC analysis.The result showed that α-HCH, β-HCH, and γ-HCH were the most abundant pesticide residues in the fish samples. The result also showed that levels of α-HCH, β-HCH, and γ-HCH in Synodotismembranaceuscupside were above the maximum residue limits (MRLs). In conclusion, Pesticides are hazardous to human health and exposure to them could result to a number of illnesses ranging from dizziness, abdominal pain to cancers, still birth and hormonal imbalance.*

KEYWORDS: maximum residue limits, residue concentration, pesticides, pesticide residues, risk assessment.

INTRODUCTION

Persistent Organochlorine Pesticides (POPs) has been used worldwide for decades **[1]**. Although many have been banned, some countries in Africa still use them, which are mainly used to stop malaria in the form of insecticides, rodenticides and herbicides **[1]**. Organochlorine compounds are synthetic organic pesticides that contain carbon, hydrogen, chlorine, and sometimes oxygen **[2]**. Organochlorine pesticides are a class of toxic compounds that are characterized by their relative chemical and biological stability, which is why they are persistent in the environment **[3].**

Therefore, organochlorine pesticides are listed as the highest level on the list of potential environmental hazards **[4]**. To increase agricultural productivity, the use of pesticides has been increased **[5]**. Modern agriculture relies to a great extent on pesticides application to feed the ever-growing large populations around the world **[6].** Pesticides include insecticides, herbicides, rodenticides, and fungicides **[5].**The use of pesticides in agricultural lands to control pests brings about bumper harvest to farmers whiles producing toxics to non-target organisms **[6].** Most pesticides are very persistent and will persist in the environment for a long time **[5].** Due to their stable structure and lipophilicity, pesticides, especially organochlorine pesticides (OCPs), tend to be bioconcentrated and amplified in the food chain, especially those related to adipose tissue, leading to non-target organisms and even non-target organisms in vertebrates and invertebrate toxicity to humans **[5].**

Organochlorine compounds have many toxic effects on human health, such as hormone-related disorders (endometriosis, infertility), male and female reproductive system cancer, developmental toxicity, neurotoxicity and immunotoxicity **[4].** Most of these effects may also be due to the ability of organochlorine to change the number of certain hormones, enzymes, growth factors, and neurotransmitters **[4].** The use of pesticides has multiple effects on the environment, which raises concerns about potentially toxic or carcinogenic residues that remain in the food chain **[7].** The widespread use of pesticides for agricultural and non-agricultural purposes has resulted in the presence of pesticide residues in various environmental matrices, especially in food **[7],** demonstrating that these chemicals they are harmful to human health and the environment **[7].** Therefore, the general population is continuously exposed to low doses of these chemicals through food, water, and soil **[7].** Due to long-term accumulation in the human body, these can cause chronic toxicity **[7].**

Aquatic habitats usually collect large amounts of natural hazardous wastes and pollutants from households, agricultural, and industries, point sources, and diffuse **[4-7].** Due to the accompanying harmful effects, the pollution of aquatic habitats by persistent organic pollutant residues has always been a concern. The pathways for these chemicals to enter the aquatic environment include leaks from agricultural uses, sewer overflows, sewage treatment plants or non-point sources (such as runoff and atmospheric extraction) **[4-7],** thereby increasing the absorption and accumulation of POPs in the food chain through re-absorption **[7].** This promotes fish pollution through ingestion, skin absorption and respiration [**4].**

Therefore, this study aims to determine the presence of organochlorine pesticides (POPs) in five different fish species of *Synodontis membranaceus, Protopterus annectens, Clarias gariepinus, Heterotis niloticus and Tilapia zilli* from River Donga, in Donga town of Taraba State.

MATERIALS AND METHODS

Study area

This study was carried outin Donga town the headquarters in Donga local government area of Taraba State northeastern region of Nigeria. It lies between latitude 7º43’00’’N and longitude 10º03’00’’E of the equator. River Donga, arises from the Mambilla Plateau of Taraba state, which is the northern continuation of the Bamenda Highlands of Cameroon. The river forms part of the international border between Nigeria and Cameroon. It flows northwest to eventually merge with river Benue in Nigeria.

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Sample collection and treatment

Five different samples of fishes; *Synodontismembranaceus, Protopterusannectens, Clariasgariepinus, Heterotisniloticus and Tilapia zilli*were purchased from the fishermen at bank of River Donga and was packaged into different labeled polyethylene bags. The fish samples were transported to the Biochemistry Laboratory Federal University Wukari in a Cold box with ice on the same day. All fish samples were kept in the freezer at 0-4^oC until analysis.The fish samples were then washed with de-ionized water and were allowed to thaw at room temperature. The fish samples were dissected and filleted to obtain the fish flesh. The fillets were dried at ambient room temperature. 50 g of the dried samples were each homogenized using a house-hold mill. 15 g of each of the sample's homogenates were weighed into 50 ml polytetrafluoro ethylene (PTFE) tubes and 100ml of 50 mg/ml triphenyl phosphate (TPP) surrogate standard solution in acetonitrile was added to each tube followed by addition of 15 ml of acetonitrile containing 1% acetic acid (v/v not accounting for purity). Then 6 g $MgSO_4$ and 2.5 g sodium acetate trihydrate (equivalent to 1.5 g of anhydrous form) were added to each tube. The samples were shaken forcefully for 4 min. After which the samples were centrifuged at 4000 rpm for 5 min and 5 ml of the supernatants were each transferred to 15 ml PTFE tubes to which 750 mg $MgSO_4$ and 250 mg PSA (primary secondary amine) were added. The extracts were shaken using vortex mixer for 20 secs and then centrifuged at 4000 rpm again for 5 min. Approximately 3 ml of the supernatants were filtered through a 0.45 mm PTFE filter (13 mm diameter), and 80 ml portions of filtrates were transferred to auto-sampler vials. The extracts were evaporated to dryness under stream of argon and reconstituted in 800 ml acetonitrile/water (20/80) for LC-MS/MS analysis. For the matrix-matched and standard addition calibrations, 4-8 ml of reconstituted samples were transferred into, auto-sampler glasses inserts and 20 ml portions of 0, 250, 500 and 1250 ng/ml standard mix solutions containing pesticides in 25/75 acetonitrile/water (v/v) were added to reach the final additional concentrations of 0, 50, 100 and 250 ng/g equivalents, respectively.

LC-MS analysis

An Agilent HPLC system was used for the LC analysis. It contained a binary pump, a degasser, column thermostat and an auto-sampler. A reverse-phase C8 analytical column of 150mm x 4.6mm internal diameter (i.d) and 5 µm particle size and a guard column of 125 x 4.6- and 5-mm particle size were coupled to the LC system. De-ionized water containing 0.1% formic acid (mobile phase component A) and acetonitrile (component B) were employed for the gradient programme, which started with 20% component B for 3 min and linearly increased to 100% B in 27 min (held for 3 min). The column was then re-equilibrated for 12 min back to 20 % B.Thus, the total run time took 45 min. the flow rate was constant at 0.6 ml/min and injection volume was 10 µl.For MS/MS analysis, an Applied Bio-systems 3200 QTRAP system was used. Applied Biosystems Analyst 1.4.2 software was used for instrument control and data processing. For the determination of pesticides, the commercial method of Applied Bio-system (2005) and its library was used.

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Statistical analysis

Statistical analysis of the results was carried out using SPSS (Statistical Package for Social Sciences) statistical software (version 21). The results were analyzed through T-test. The Means and standard deviations were calculated.

RESULTS

The result of pesticide analysis of the fishes harvested from river Donga is presented in **Table 1**. The mean concentrations of the pesticide's residue were; DDT 0.008±0.001, DDD 0.006±0.001, Dicofol 0.005±0.001, Methoxychlor 0.005±0.001, Aldrin 0.006±0.001, Dieldrin 0.008±0.010, Heptachlor 0.006±0.002, Chlordane 0.007±0.002, Endosulfan 0.007±0.011, HCB 0.005±0.010, Pentachlorbenzene 0.008±0.001, Mirex 0.006±0.001, Toxaphene 0.005±0.001, α-HCH 0.008±0.002, β-HCH 0.009±0.002, γ-HCH 0.090±0.002, cyclodigenes 0.007 ± 0.002, cyclohexane 0.004 ± 0.002, perthane 0.008 ± 0.002. The result show that there is no significance between DDD, Aldrin, Heptachlor, and Mirex. Also between cyclodigenes, chlordane, and endosulfan there is no significant difference. The result also showed that there is no significant difference between dicofol, methoxychlor, HCB and toxaphene. The result showed that *Heterotisniloticus*has the highest concentration of cyclodigenes (**Figure1**) while *Synodontismembranaceus*has the highest concentration of DDT (**Figure 1**). Concentrations of γ-HCH, β-HCH, α-HCH, toxaphene, pentachlorbenzene, chlordane, and dieldrin are highest (**Figure 2**) in *Synodontismembranaceus***.**

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Chlordane	Endosulfan	Hexachlorobenzene	Pentachlorobenzene	Mirex	Toxaphene	α-HCH	β-HCH	ɤ-HCH
0.006	0.004	0.007	0.008	0.007	0.005	0.006	0.007	0.006
0.007	0.005	0.003	0.009	0.004	0.003	0.01	0.011	0.011
0.012	0.009	0.007	0.012	0.007	0.009	0.013	0.014	0.015
0.003	0.008	0.007	0.004	0.009	0.004	0.005	0.008	0.007
0.006	0.009	0.003	0.005	0.001	0.003	0.007	0.005	0.004
0.007 ± 0.002	0.007 ± 0.011	0.005 ± 0.010	0.008 ± 0.001	0.006 ± 0.001	0.005 ± 0.001	0.008 ± 0.002	0.009 ± 0.002	0.090 ± 0.002

Table 1: Result of pesticide residue analysis (µg/kg)

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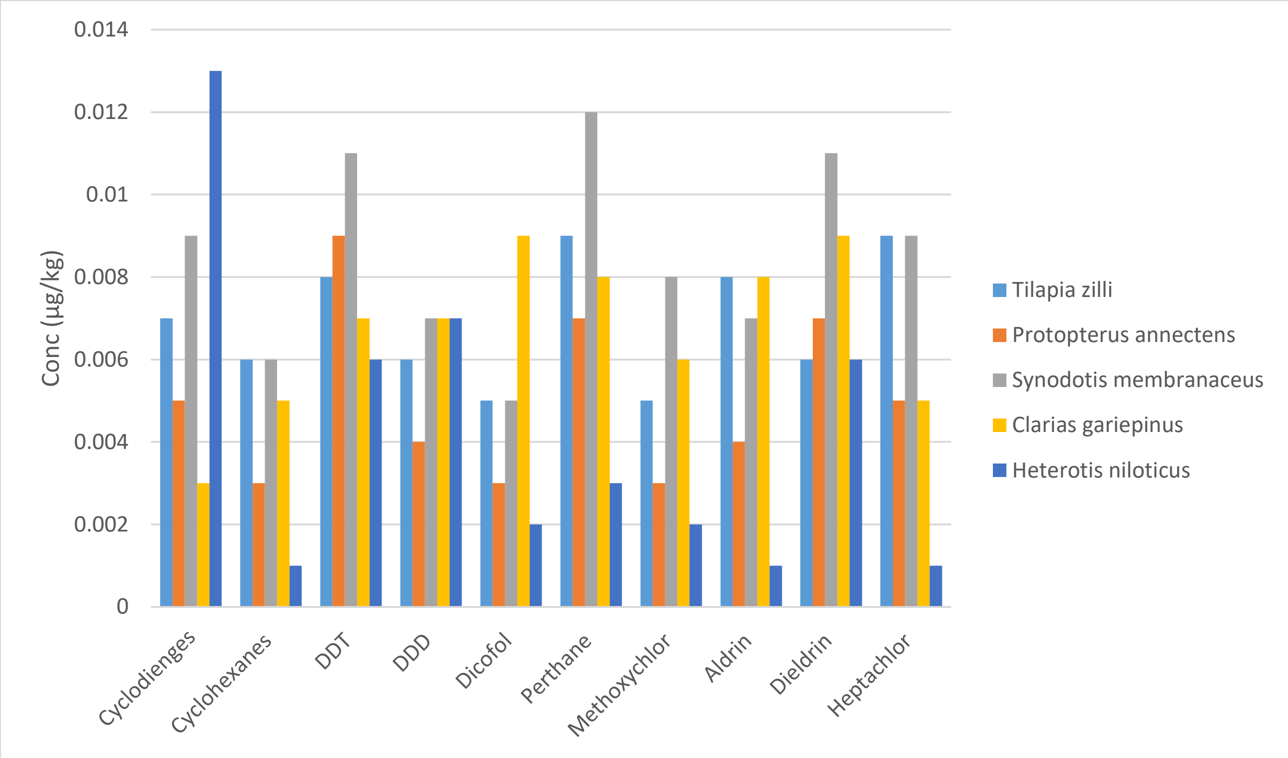

Figure 1: Comparison of pesticide residues in the fish samples

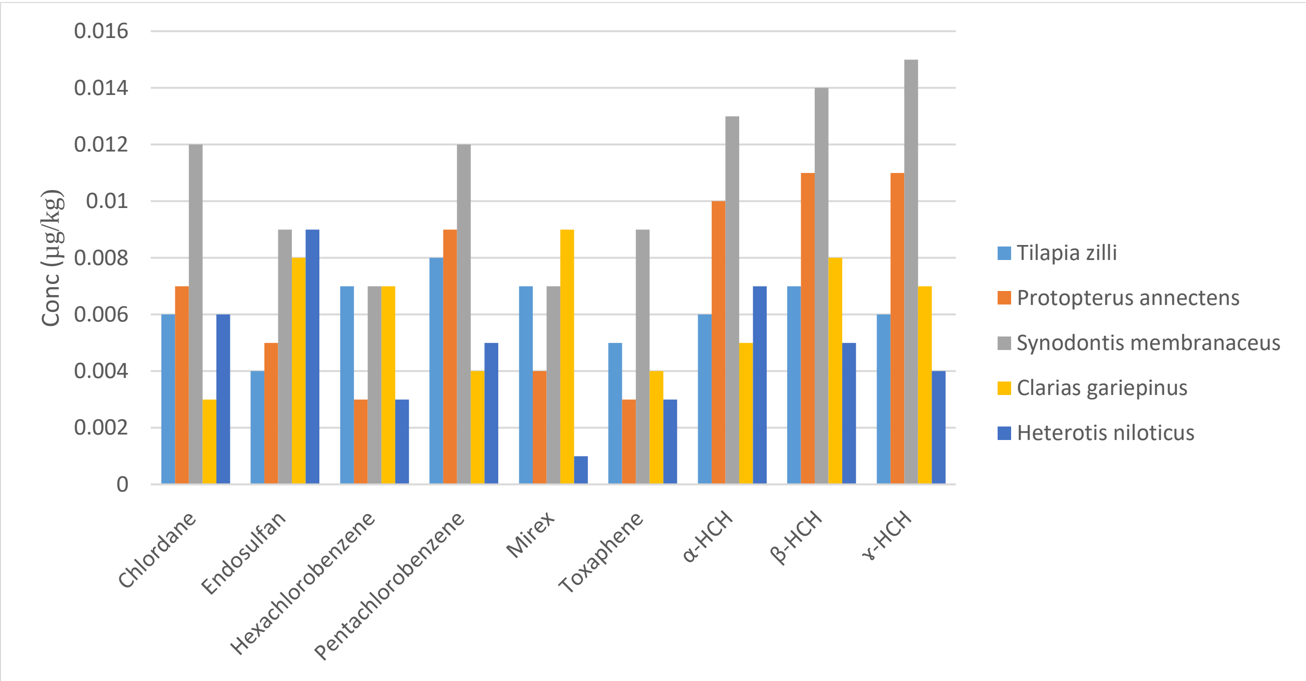

Figure 2: Comparison of pesticide residues in the fish sample

DISCUSSION

The result obtained from this study indicated presence of all pesticide residues analyzed for (cyclodienges, cyclohexane, DDT, DDD, dicofol, perthane, methoxychlor, Aldrin, dieldrin, heptachlor, chlordane, endosulfan, hexachlorobenzene, pentachlorobenzene, mirex, toxaphene, α-HCH, β-HCH and γ-HCH). Most of the pesticide residues occur in concentrations below the WHO and FAO set maximum residue limit (MRL).

In this study, the concentrations endosulfan in all the fish samples were much below the WHO and FAO (2009) set maximum residue limit (MRL) 0.1 µg/kg. This implies that consumption of these fishes may not pose any health problem related to endosulfan. In comparison, this result is not in line with the reports of Akan *et al* (2013) in which the concentration of endosulfan was above the WHO and FAO set maximum residue in fishes from Alau Dam, Borno State, North Eastern Nigeria.

The concentrations of DDT and its metabolite (DDD) in all the fish samples range from 0.006-0.011 µg/kg and 0.004-0.007 µg/kg respectively. These values are lower than the WHO and FAO (2009) set maximum residue limit (MRL) of 1.0 µg/kg. This also differed from the report of Akan *et al* (2013) in which the concentrations of DDT and its metabolites are above the WHO and FAO maximum residue limit in fishes from Alau Dam, Borno State, North Eastern Nigeria.

Dieldrin and Aldrin are widely used in agricultural areas throughout the world. The both chemicals are highly persistent in the environment, toxic and bio-accumulative. Because the toxicity of this persistent pesticide posed an imminent danger to human health, NAFDAC banned the most major uses of dieldrin and aldrin in 2008, but the product is still in used because the low cost and affordability. The concentrations of aldrin and dieldrin in all fish samples were below the WHO and FAO (2009) set maximum residue limit (MRL) of 0.2 µg/kg.

The concentrations of α-HCH, β-HCH and γ-HCH in almost all the fish samples analyzed were lower than the WHO and FAO set maximum residue limit (MRL) of 0.01 µg/kg for α-HCH, β-HCH and γ-HCH. However, the concentrations of γ-HCH in *P. annectens*and *Synodontismembranaceus,* β-HCH in *P. annectens*and *Synodontismembranaceus,* and α-HCH in *C. gariepinus* are slightly above the WHO and FAO maximum residue limit. This implies that consumption of *P. annectens, Synodontismembranaceus*and *C. gariepinus*could predispose the consumers to health problems related to α-HCH, β-HCH and γ-HCH.

CONCLUSION

This study has showed that DDT, chlordane, α-HCH, β-HCH, and γ-HCH are the most abundant pesticide residues in the studied fish species. The highest levels of these organochlorine pesticides were observed in *Synodontismembranaceus* compared to other fish species. This study also revealed that α-HCH, β-HCH, and γ-HCH levels in *Synodontismembranaceus* were above the maximum residue limits (MRLs). This could be a source of dietary exposure of humans to pesticides. To the human health pesticides are hazardous and exposure to them could result to a number of illnesses ranging from dizziness, abdominal pain to cancers, still birth and hormonal imbalance.

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