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Organochlorine Pesticide Residues in Fish Samples from Alau Dam, Borno State, North Eastern Nigeria

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Abstract

In this study, the levels of organochlorine (gamma-BCH, Alpha-BCH, aldrin, o,p'-DDE, endosulfan, dieldrin, p,p'-DDT, lindane, p,p'-DDD, o,p'-DDD and methoxychlor) pesticide residues in Alau Dam from Konduga Local Government, Borno State, Nigeria, was investigated using fish samples as a case study. Four fish species (*Clarias gariepinus, Heterotis niloticus, Oreochromis niloticus* and *Tilapia zilli*) were collected for this analysis. Fish samples of uniform size were collected in order to avoid possible error due to size differences. The fish samples were labeled with a unique identification number. Samples of fishes were transported to the laboratory on the same day and later dissected to remove the flesh, liver, stomach and Gills of each species of fish and store using 4% formalin pending extraction and analysis. The extraction, clean up and de-fattening of the fishes organs were carried out using standard procedures. The levels of all the pesticide residues were determined using GC/MS SHIMADZU (GC – 17A) equipped with electron capture detector (ECD). Eleven organochlorine pesticides were detected in all the fish samples studied. Endosulfan was the most abundant pesticide residue in the studied tissues of all the fish species with a value of 8.98 ± 0.02 µg/g in the liver of *Oreochromis niloticus.* This study also revealed that, all the pesticide residues in the fish samples studied were above the maximum residues limits (MRLs) and dietary intake (ADI) and could be an important process of transferring pesticides to humans. It also indicated the extensive presence and usage of these pesticides in the study environment, which include recent use of this pesticide for agricultural purposes. Thus, the use of these pesticides to control pest by farmers within the study area with little or no knowledge must be checked through adequate control of the trade and use of pesticides and the enforcement of appropriate sanctions.

Keywords: Organochlorine; Pesticide; Residues; Alau Dam; North Eastern; Nigeria

Introduction

Various activities such as farming, fishing, forestry, construction, mining, urban development and land pollution occurring in or near the watershed of a reservoir could bring about water quality problems and disruption in fish [1]. Chlorinated organic pesticides are very stable in both fresh and salt water and are resistant to photo degradation [2]. They will disappear from the water with secondary mechanisms such as, absorption on sediment, biological breakdown by microflora and fauna, and absorption by fish through gills, skin and feeding. They are poorly hydrolyzed and slowly biodegrades in environment. Therefore, these compounds are persistent in food chains and are readily accumulated in animal tissues. Fish absorb these compounds directly by water or by ingesting contaminated food. In particular, Organochlorine insecticides are highly stable under different environmental conditions and persistent nature and chronic adverse effects on wildlife and humans [3].

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) or pesticides including dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorobenzene (HCB) or isomers of hexachlorocyclohexane (HCHs) have been known as global contaminants of the environment for decades. Pesticide is a general classification that includes insecticides, rodenticides, fungicides, herbicides and fumigants. Although pesticides may be selectively toxic to these forms of life, they may still be toxic to man if food contaminated by them is ingested. Pesticides are known to be toxic to man [4]. Some of the symptoms of pesticides poisoning include irritation, dizziness, tremor, tonic and chronic convulsion [5]. DDT in particular can block potassium influx across the membranes of nerve fibres and causes increase negative after potentials. DDT also induces the mixed function oxidize system thereby altering the metabolism of xenobiotics and steroid hormones [4]. Organochlorine pesticides are among the first set of pesticides in use and still in use in Nigeria despite their ban in developed countries due to the associated problems of indiscriminate potency and persistency. The chemical stability of these compounds, their high lipid solubility and toxicity to human and animals [6,7], has led government and researchers to be concerned with their presence in the environment. Many ignorant farmers, fishermen and some other users have abused their use for agricultural and fishing purposes. Being persistent and toxic, they pose serious environmental and health hazards, not only in the areas of applications, but up the food chain as the receiving water body contains other edible zooplanktons apart from fish that ingest these toxic chemicals which reside mostly in the fatty parts of their bodies. Consequently, bioaccumulation and biomagnifications takes place up the food chain [8].

The presence of pesticides in water (particularly organics that is aromatic chlorinated hydrocarbons) impacts objectionable and offensive taste, odours and colors to fish and aquatic plants even when they are present in low concentrations [9]. The organochlorine (OC) pesticides are among the major types of pesticides, notorious for their high toxicity, their persistence in the physical environment and their ability to enter the food chain [10]. Although the production and use of many types of OCs and organophosphorus (OPs) have been severely

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limited in many countries including Nigeria, they are, nevertheless, still being used unofficially in large quantities in many parts of Nigeria, and in other developing countries because of their effectiveness as pesticides and their relatively low cost [10].

Pesticide residues problems in the fish tissues are serious, as reflected by the high pesticides concentrations recorded in the water and sediments [11]. The gills are directly in contact with water. Therefore, the concentration of pesticides in gills reflects their concentration in water where the fish live, whereas the concentrations in liver represent storage of pesticides in the water [12]. Sediments are important sinks for various pollutants like pesticides and also play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions and in interactions between water and sediment. Fish samples can be considered as one of the most significant indicators in fresh water systems for the estimation of pesticides pollution level [10]. The region of accumulation of pesticides within fish varies with the route of uptake. Their potential use as biomonitors is therefore significant in the assessment of bioaccumulation and biomagnifications of contaminants within the ecosystem [12].Many dangerous chemical elements, if released into the environment, accumulate in the soil and sediments of water bodies. The lower aquatic organisms absorb and transfer them through the food chain to higher trophic levels, including fish. Under acidic conditions, the free divalent ions of many metals may be absorbed by fish gills directly from the water [12]. Hence, concentrations of pesticides in the organs of fish are determined primarily by the level of pollution of the water and food under certain conditions, chemical elements accumulated in the silt and bottom sediments of water bodies can migrate back into the water.

Alau Dam is located in Maiduguri, Borno state, Nigeria (Figure 1). The Dam is nine meter high with a square reservoir area of about 50 square kilometer. The maximum storage capacity is 112 million meter cube. Alau Dam received water from River Yedzram and River Gombole which meet at a confluent at Sambisha and flow as River Ngada into Alau Dam. Alau Dam received a wide variety of waste from agricultural land. This waste generated contaminates Alau Dam with a variety of pesticides acting as point sources. The Dam is also use for commercial fishing and also received a wide variety of waste from agricultural activity within the area. Most farmers within the Alau dam area used synthetic chemical pesticides to control pests on vegetables including a number of highly persistent organochlorine pesticides. Pesticides are extensively used in agricultural production to check or control pests, diseases weeds and other plant pathogens in an effort to reduce or eliminate yield losses and preserve high product quality. Lack of knowledge of the use and the effects of these pesticides among small and large scale farmers has resulted in their misuse and consequently the waste generated flows into Alau Dam and may contaminates the river with a variety of pesticides acting as point sources. Such contaminations might accumulation in the various organs of fishes; such accumulation may affect humans and other species that depend on such fish as food.

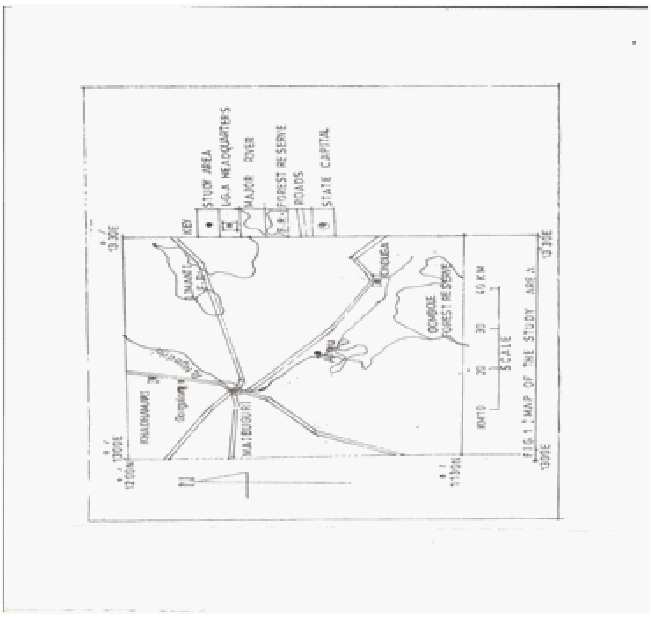

Figure 1: Map of Study Area.

Materials and Methods

Sample collection

Fish samples (*Clarias gariepinus, Heterotis niloticus, Oreochromis niloticus and Tilapia zilli)* were caught using gill nets from Alau Dam, Konduga Local Government Area, Borno State, Nigeria. Fish samples of uniform size were collected in order to avoid the possible error due to size differences. The fish were labeled with an identification number. Samples of fishes were transported to the laboratory on the same day, identified by an expert in the department of Fisheries, University of Maiduguri, and later dissected to remove the flesh, liver, stomach and gills of each species of fish and stored using 4% formalin, pending extraction and analysis.

Extraction of pesticides from fish samples

The fish samples (20 g) were weighed into a 150 mL conical flask followed by the addition of 20 g and 5 g of anhydrous sodium sulfate and sodium hydrogen carbonate, respectively. 100 mL of 1:1 (v/v) ethyl acetate/dichloromethane mixture were transferred into the 20 g fish samples and thoroughly mixed by shaking the conical flask while corked. Another 20 g of anhydrous sodium sulfate were then added to the content of the conical flask followed by 20 g of sodium hydrogen carbonate. The conical flask were corked tightly and the mixture shaken thoroughly for 10 min. The content was allowed to stand for 3h. The organic layer were decanted into a 200mL round bottom flask and evaporated using the rotary evaporator at 40°C. The pesticide in the rotary flask were dissolved and collected with 2 mL of ethyl acetate and transferred into a 2 mL vial and ready for the clean-up.

Silica gel clean-up of sample extracts

Silica gel clean-up was carried out by measuring Ten gram (10g) portion of deactivated silica gel into a 10 mm glass chromatographic column followed by addition of 3 g of anhydrous sodium sulfate. 10 ml of the 1:1 (v/v) ethyl acetate/dichloromethane mixture were used to wet and rinse the column. The extract residue that is water and fish in 2 ml ethyl acetate were transferred into the column and the extract vial rinsed (three times) with 2 ml ethyl acetate. The column were eluted with 80 ml portion of ethyl acetate/dichloromethane at a rate of 5 ml/min into a conical flask as fraction one. The column were eluted again with 50 ml portion of ethyl acetate/dichloromethane for the second elution and added to the first extract. All the fractions of each sample were concentrated to dryness using a rotary evaporator at 40 °C. Each residue were dissolved and collected in 2 ml ethyl acetate for gas chromatograph analysis.

De-fattening of the fish sample extracts

The process of de-fattening was conducted by measuring Fifty (50) ml of 1:1 (v/v) hexane/acetonitrile solution were added to 2 ml pesticide extracted from the fish samples in a 100 ml separator funnel. The separator funnels were shaken gently for 3 min while releasing the gas pressure. The separator funnels were allowed to stand for 20 min to allow for phase separation of the organic solvents. The acetonitrile fractions containing the pesticides were collected into a 50 ml beaker while the fat containing hexane solvent phase was discarded. The acetonitrile solvent extract obtained were further cleaned-up using 25 ml of the pure hexane. The acetonitrile fraction were concentrated with rotary evaporator at 40 °C and the content of the flask dissolve and collected with 2 ml of ethyl acetate into a 2 ml vial. The vial containing the pesticides extracts were stored in the refrigerator at 4 °C for GCMS analysis.

Determination of pesticide residues

The SHIMADZU GC/MS (GC – 17A), equipped with fluorescence detector were use for the chromatographic separation and were achieve by using a 35% diphenyl/65% dimethyl polysiloxane column. The oven were programmed as follows: initial temperature 40°C, 1.5 min, to 150°C, 15.0 min, 5°C/min to 200°C, 7.5 min, 25°C/min to 290°C with a final hold time of 12 min and a constant column flow rate of 1 ml/min. The detection of pesticides were perform using the GC-ion trap MS with optional MSn mode. The scanning mode offer enhances selectivity over either full scan or selected ion monitoring (SIM). In SIM at the elution time of each pesticide, the ration of the intensity of matrix ions increase exponentially versus that of the pesticide ions as the concentration of the pesticide approach the detection limit, decrease the accuracy at lower levels. The GC-ion trap MS were operate in MSn mode and perform tandem MS function by injecting ions into the ion trap and destabilizing matrix ions, isolating only the pesticide ions. The retention time, peak area and peak height of the sample were compared with those of the standards for quantization.

Data handling

Data collected were subjected to one-way analysis of variance (ANOVA) were used to assess whether pesticide residues varied significantly between fish and tissues samples, possibilities less than 0.05 ($p<0.05$) were considered statistically significant. All statistical calculations were performed with SPSS 9.0 for Windows.

Results

Concentrations of organochlorine pesticide residues

The mean concentrations of some organochlorine pesticides (dichlorodiphenyldichloroethylene, (o,p'-DDE), 4,4-dichlorodiphenyldichloroethan (p,p'-DDD), 2,4-dichlorodiphenyldichloroethan (o,p'-DDD), 4,4- dichlorodiphenyltrichloroethane (p,p'-DDT), Alpha BHC, Gamma BHC, metoxichlor, lindane, Endosulfansulphate, dieldrin and aldrin) residues in the liver, gills, stomach and flesh of *Tilapia zilli* from Alau Dam are presented in Table1. The concentrations of these pesticides in the liver of *Tilapia zilli* range between 0.22 ± 5.64 and 0.05 ± 0.65µg/g; 0.26 ± 4.11 and 0.05 ± 0.67µg/g gills; 0.24 ± 3.86 and 0.02 ± 0.28µg/g stomach and 0.15 ± 2.88 and 0.01 ± 0.22µg/g flesh. The highest concentrations of all the pesticides were recorded in the liver, while the flesh recorded the lowest value. The concentrations of some organochlorine pesticides (o,p-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, Alpha BHC, Gamma BHC, metoxichlor, lindane, Endosulfan, dieldrin and aldrin) residues in liver, gills, stomach and flesh of *Clarias gariepinus* from Alau dam are presented in Table 2. The levels of these pesticides in the liver range between 0.23 ± 7.54 and 0.05 ± 1.43µg/g liver; 0.33 ± 5.11 and 0.12 ± 1.21µg/g gills; 0.56 ± 4.35 and 0.01 ± 0.76µg/g stomach and 0.27 ± 3.84 and 0.24 ± 0.43µg/g flesh. The maximum concentrations of all the pesticides were significantly observed in the liver while flesh shows the minimum value. The concentrations of organochlorine pesticides (o,p'-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, Alpha BHC, Gamma BHC, metoxichlor, lindane, Endosulfan, dieldrin and aldrin) residues in different organ of *Heterotis niloticus* are as presented in Table 3. The concentrations of pesticides in the liver of *Heterotis niloticus* ranged between 0.23 ± 4.55 and 0.18 ± 0.35µg/g; 0.22 ± 3.06 and 0.01 ± 0.22µg/g gills 0.28 ± 2.65 and 0.22 ± 0.17µg/g stomach and 0.66 ± 2.23 and 0.01 ± 0.12µg/g flesh.

Table 4 represent the mean concentrations of some organochlorine pesticides residue (o, p'-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, Alpha BHC, Gamma BHC, metoxichlor, lindane, Endosulfan, dieldrin and aldrin) in different organ of *Oreochromis niloticus* from Alau dam. The concentrations range between 0.02 ± 8.98 and 0.55 ± 3.45µg/g liver; 0.22 ± 7.45 and 0.13 ± 2.66µg/g gills; 1.11 ± 5.43 and 0.44 ± 1.87µg/g stomach and 0.71 ± 4.81 and 0.11 ± 1.45µg/g flesh. Figure 2 shows the comparison in concentrations of some organochlorine pesticides in the liver of *Tilapia zilli, Clarias gariepinus, Heterotis niloticus* and *Oreochromis niloticus*. The concentration of o, p'-DDE ranged from 2.17 to 6.32 µg/g; 2.45 to 5.66 µg/g p,p'-DDD; 1.31 to 3.72 µg/g o,p'-

		Concentrations (µg/g)		
	LIVER	GILLS	STOMACH	FLESH
o, p'-DDE	2.73^{a} ± 0.34	1.74^{b} ± 0.14	1.01^{c} ± 0 .12	0.65^{d} ± 0.04
p,p'-DDD	3.12^{a} ± 0.06	2.04^{b} ± 0.02	1.93^{c} ± 0.11	1.22^{d} ± 0.01
o,p'-DDD	1.65^{a} ± 0.03	1.43^{b} ± 0.11	0.76^{a} ± 0.04	0.55^{d} ± 0.01
p,p'-DDT	0.98^{a} ± 0.12	0.67^{a} ± 0.05	0.53^{c} ± 0.03	0.33^{d} ± 0.01
Alpha BHC	4.21^{a} ± 0.23	2.65^{b} ± 0.11	1.85^{c} ± 0.06	1.23^{a} ± 0.25
Gamma BHC	4.67^{a} ± 0.22	3.57^{b} ± 0.17	2.74^{c} ± 0.06	1.98^{d} ± 0.13
Metoxichlor	0.65^{a} ± 0.05	0.34^{b} ± 0.01	0.28^{c} ± 0.02	0.23^{d} ± 0.01
Lindane	2.85^{a} ± 0.15	1.83^{b} ± 0.05	1.42^{c} ± 0.12	0.86^{d} ± 0.03
Endosulfan	5.64^{a} ± 0.22	3.21^{b} ± 0.31	2.94^{c} ± 0.15	1.75^{d} ± 0.11
Aldrin	1.23^{a} ± 0.04	0.87^{b} ± 0.07	0.54^{c} ± 0.08	0.22^{d} ± 0.01
Dieldrin	4.65^{a} ± 0.45	4.11^{a} ± 0.26	3.86^{c} ± 0.24	2.88^{d} ± 0.15

Within rows mean and standard deviation with difference letters are statistically significant, P<0.0.

Table 1: Mean Concentrations of Some Organochlorine Pesticide Residues in different organs of *Tilapia zilli* from Alau Dam.

		Concentrations (µg/g)		
	LIVER	GILLS	STOMACH	FLESH
o, p'-DDE	5.86^{a} ± 0.24	4.65^{b} ± 0.25	4.21^{c} ± 0.35	2.76^{d} ± 0.25
p,p'-DDD	4.65^{a} ± 0.53	2.84^{b} ± 0.25	2.21^{c} ± 0.16	1.45^{a} ± 0.25
o,p'-DDD	2.33^{a} ± 0.17	2.06^{a} ± 0.44	1.34^{b} ± 0.27	0.88^{c} ± 0.01
p,p'-DDT	3.31^{a} ± 0.54	2.06^{b} ± 0.22	1.22^{c} ± 0.32	0.65^{d} ± 0.04
Alpha BHC	6.21^{a} ± 0.77	4.32^{b} ± 0.54	2.44^{c} ± 0.32	1.76^{d} ± 0.33
Gamma BHC	5.87^{a} ± 0.34	4.33^{b} ± 0.22	3.06^{c} ± 0.45	2.66^{d} ± 0.64
Metoxichlor	1.43^{a} ± 0.05	1.21^{a} ± 0.12	0.76^{b} ± 0.01	0.43^{c} ± 0.24
Lindane	3.65^{a} ± 0.76	2.77^{b} ± 0.65	2.24^{c} ± 0.05	1.87^{d} ± 0.15
Endosulfan	7.54^{a} ± 0.23	5.11^{b} ± 0.33	4.22^{c} ± 0.83	3.84^{d} ± 0.27
Aldrin	2.68^{a} ± 0.12	2.11^{b} ± 0.16	1.75^{c} ± 0.42	0.92^{d} ± 0.02
Dieldrin	5.14^{a} ± 0.27	4.75^{b} ± 0.76	4.35^{c} ± 0.56	3.21^{d} ± 0.32

Within rows mean and standard deviation with difference letters are statistically significant, P<0.05

Table 2: Mean Concentrations of Some Organochlorine Pesticide Residues in different organs of *Clarias gariepinus* from Alau Dam.

		Concentrations (µg/g)		
	LIVER	GILLS	STOMACH	FLESH
o, p'-DDE	2.17^{a} ± 0.05	1.05^{b} ± 0.07	0.56^{c} ± 0.04	0.22^{a} ± 0.01
p,p'-DDD	2.45^{a} ± 0.33	1.44^{b} ± 0.05	1.05^{c} ± 0.01	0.54^{d} ± 0.03
o,p'-DDD	1.31^{a} ± 0.01	1.04^{a} ± 0.07	0.33^{b} ± 0.02	0.26^{c} ± 0.04
p,p'-DDT	0.77^{a} ± 0.05	0.54^{a} ± 0.01	0.25^{b} ± 0.02	0.16^{c} ± 0.03
Alpha BHC	3.44^{a} ± 0.11	2.15^{b} ± 0.24	1.34^{c} ± 0.08	0.43^{d} ± 0.12
Gamma BHC	4.21^{a} ± 0.44	3.06^{b} ± 0.16	2.21^{c} ± 0.16	1.65^{d} ± 0.22
Metoxichlor	0.35^{a} ± 0.18	0.22^{b} ± 0.01	0.17^{c} ± 0.02	0.12^{d} ± 0.01
Lindane	2.32^{a} ± 0.23	1.65^{b} ± 0.33	1.22^{c} ± 0.07	0.65^{d} ± 0.01
Endosulfan	4.55^{a} ± 0.23	2.43^{b} ± 0.17	2.11^{c} ± 0.43	1.27^{d} ± 0.47
Aldrin	0.85^{c} ± 0.22	0.54^{b} ± 0.06	0.41^{c} ± 0.02	0.13 ± ^{d}0.01
Dieldrin	3.43^{a} ± 0.77	2.89^{b} ± 0.51	2.65^{c} ± 0.28	2.23^{d} ± 0.66

Within rows mean and standard deviation with difference letters are statistically significant P<0.05

Table 3: Mean Concentrations of Some Organochlorine Pesticide Residues in different organs of *Heterotis niloticus* from Alau Dam.

		Concentrations (µg/g)		
	LIVER	GILLS	STOMACH	FLESH
o, p'-DDE	6.32^{a} ± 0.19	5.43^{b} ± 0.27	5.11^{c} ± 0.43	4.32^{d} ± 0.87
p,p'-DDD	5.66^{a} ± 1.09	4.32^{b} ± 0.87	3.54^{c} ± 0.58	2.43^{a} ± 0.11
o,p'-DDD	3.72^{a} ± 0.18	3.22^{a} ± 0.08	2.86^{b} ± 0.37	2.32^{c} ± 0.16
p,p'-DDT	4.55^{a} ± 0.06	4.21^{a} ± 0.23	3.67^{b} ± 1.21	2.76^{c} ± 0.15
Alpha BHC	7.56^{a} ± 1.73	6.54^{b} ± 1.27	5.34^{c} ± 0.66	4.33^{d} ± 0.14
Gamma BHC	6.22^{a} ± 0.37	4.77^{b} ± 1.03	4.35^{c} ± 0.63	3.65^{d} ± 0.24
Metoxichlor	3.54^{a} ± 0.27	2.66^{b} ± 0.13	1.87^{c} ± 0.44	1.45^{d} ± 0.11
Lindane	4.07^{a} ± 1.31	3.25^{b} ± 0.42	3.78^{c} ± 0.01	2.65^{d} ± 0.37
Endosulfan	8.98^{a} ± 0.02	7.45^{b} ± 0.22	5.43^{c} ± 1.11	4.81^{d} ± 0.71
Aldrin	3.45^{a} ± 0.55	3.07^{a} ± 0.15	2.42^{b} ± 0.61	1.72^{c} ± 0.02
Dieldrin	5.65^{a} ± 1.25	5.22^{a} ± 0.52	4.66^{b} ± 0.82	4.07^{c} ± 0.18

Within rows mean and standard deviation with difference letters are statistically significant P<0.05.

Table 4: Mean Concentrations of Some Organochlorine Pesticide Residues in different organs of *Oreochromis niloticus* from Alau Dam.

DDD; 0.77 to 4.55 µg/g p,p'-DDT; 3.44 to 7.56 µg/g α-BHC; 4.21 to 6.22 µg/gβ-BHC; 0.35 to 3.54 µg/g metoxichlor; 2.32 to 4.07µg/g lindane; 4.55 to 8.98µg/g endosulfan; 3.43 to 5.65 µg/g dieldrin and 0.85 to 3.45 µg/g aldrin. The highest concentration of 8.98 µg/g endosulfan was recorded in the liver *Oreochromis niloticus*, while metoxichlor recorded the lowest value of 0.35 µg/g *Heterotis niloticus*. Figure 3 present the comparison in the concentrations of some organochlorine pesticides in the gills of *Tilapia zilli, Clarias gariepinus, Heterotis niloticus and Oreochromis niloticus*. The concentrations of o, p'-DDE ranged from 1.05 to 5.43 µg/g; 1.44 to 4.32 µg/g p,p'-DDD; 1.04 to 3.22 µg/g o,p'-DDD; 0.54 to 4.21 µg/g p,p'-DDT; 2.15 to 6.54 µg/g α-BHC; 3.06 to 4.77 µg/g β-BHC; 0.22 to 2.66 µg/g metoxichlor; 1.65to 3.25 µg/g lindane; 2.43 to 7.45 µg/g Endosulfan; 2.89 to 5.22 µg/g dieldrin and 0.54 to 3.07 µg/g aldrin. The highest concentration of 7.45 µg/g for Endosulfan was significantly recorded in *Oreochromis niloticus* while *Heterotis niloticus* recorded the lowest value of 0.22 µg/g for metoxichlor. Figure 4 shows the comparison in the concentrations of some organochlorin pesticide residues in the stomach of *Tilapia zilli, Clarias gariepinus, Heterotis niloticus* and *Oreochromis niloticus*. The concentration of o, p'-DDE ranged from 0.56 to 5.11 µg/g; 1.05 to 3.54 µg/g p,p'-DDD; 0.33 to 2.86 µg/g o,p'-DDD; 0.25 to 3.67 µg/g p,p'-DDT; 1.34 to 5.34 µg/g α-BHC; 2.21 to 4.35 µg/g β-BHC; 0.17 to 1.87 µg/g metoxichlor; 1.22 to 3.78 µg/g lindane; 2.11 to 5.43 µg/g endosulfan; 2.65 to 4.66 µg/g dieldrin and 0.41 to 2.42 µg/g aldrin. The maximum concentration of 5.43 µg/g for endosulfan was significantly recorded in *Oreochromis niloticus*, while *Heterotis niloticus* recorded the lowest value of 0.17 for metoxichlor. Figure 5 shows the comparison in the concentrations of some organochlorine pesticide residues in the flesh of *Tilapia zilli, Clarias gariepinus, Heterotis niloticus* and *Oreochromis niloticus*. The concentration of o, p'-DDE ranged from 0.22 to 4.32 µg/g; 0.54 to 2.43 µg/g p,p'-DDD; 0.26 to 2.32 µg/g o,p'-DDD; 0.16 to 2.76 µg/g p,p'-DDT; 0.43 to 4.33 µg/g α-BHC; 1.65 to 3.65 µg/g β-BHC; 0.12 to 1.45 µg/g metoxichlor; 0.65 to 2.65 µg/g lindane; 1.27 to 4.81 µg/g endosulfan; 2.23 to 4.07 µg/g dieldrin and 0.13 to 1.72 µg/g aldrin. Similarly, *Oreochromis niloticus* recorded the highest value of 4.81 µg/g for endosulfan, while *Heterotis niloticus* recorded the least value of 0.12 µg/g for metoxichlor.

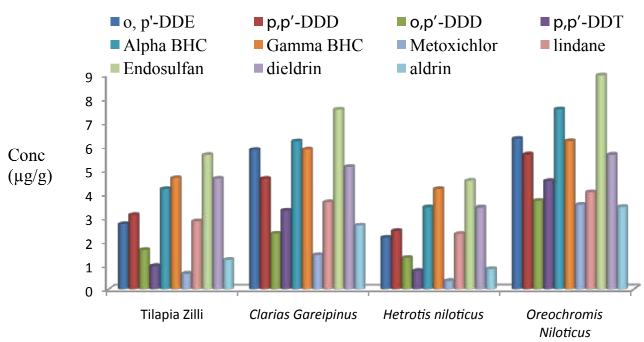

Figure 2: Comparison in the concentrations of some organochlorine pesticides residues in the liver of four species of fish from Alau Dam.

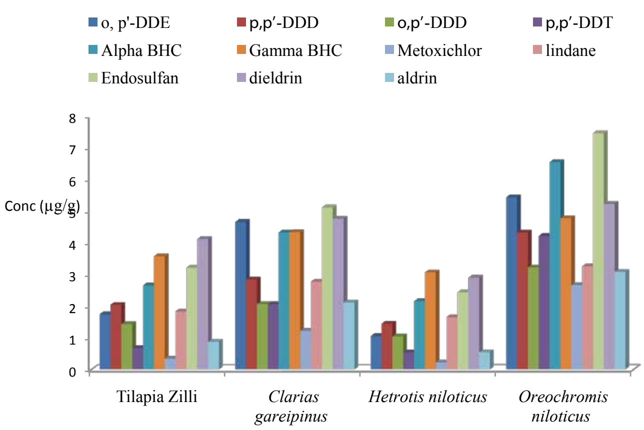

Figure 3: Comparison in the concentrations of some organochlorine pesticides residues in the Gills of four species of fish from Alau Dam.

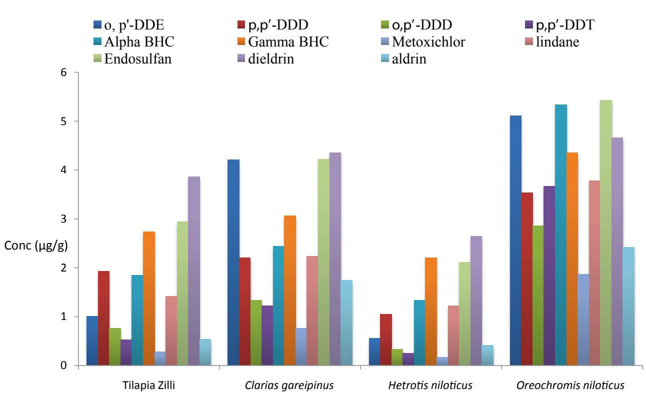

Figure 4: Comparison in the concentrations of some organochlorine pesticides residues in the stomach of four species of fish from Alau Dam.

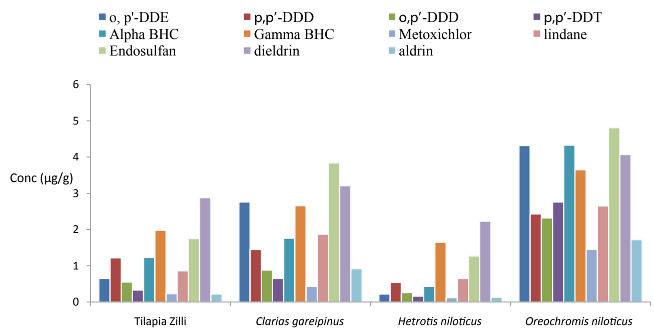

Figure 5: Comparison in the concentrations of some organochlorine pesticides residues in the Flesh of four species of fish from Alau Dam.

Discussion

Endosulfan

Organochlorine pesticides tend to accumulate in living organisms especially in aquatic organisms and they substantially settle on the sediments [13]. The result of this work indicates that endosulfan is the most abundant pesticides residue in fish sample. Endosulfan accumulation was the highest in all the organs, but it is highest value was observed in the liver of *Oreochromis niloticus,* while the lowest value was observed in flesh of *Heterotis niloticus*. Despite the adverse side effect of pesticides, organochlorine pesticides (OCPs) form an integral component of modern agriculture. The benefit are increase supply of food, but problems arise when significant amount of the chemicals are left on the field as residue which tend to affect non target organisms and river bodies are one of the main recipient of pesticide residues generated on the field. These results are in agreement with the study carried out by [14] which indicates high level of endosulfan residue in fish. However, level of this pesticide residues were also reported in lagos lagoon [15] were extremely low compared to the level recorded in this work. The concentrations endosulfan in all the fish samples were much higher than the WHO and FAO [16] set maximum residue limit (MRL) 0.1 µg/kg and the Acceptable Daily Intake value (ADI) of 0.006 µg/kg. Agricultural runoff is the primary source of this pesticide in aquatic ecosystems. Endosulfan has been shown to be highly toxic to fish and marine invertebrates and is readily absorbed in sediments. It therefore represents a potential hazard in the aquatic environment [17].

p,p'-DDT, o,p'-DDD p,p'-DDD and o,p'-DDE

The highest levels of p,p'DDT and its metabolites in the present study were observed in the liver of *Oreochromis niloticus* while the flesh of *Heterotis niloticus* recorded the lowest value, This outcome is expected because of the high lipophilic and hydrophobic nature of the compound, and the possibility of being retained on the organic phase of sediment and organisms [15,18]. The detection of p,p'-DDE is an indication of photochemical degradation of p,p'-DDT [19]. Although the use of DDT has being banned in the Nigeria in 2008, but still in used. DDT and its DDE and DDD metabolites persist in the environment and are known to bioaccumulate in aquatic organism.

DDT, DDD, and DDE have all been classified by NAFDAC as probable human carcinogens. DDT and its metabolites have been included as target pesticides residues in four species of fish; similar studies reported that there is a widespread of DDT and its metabolites in tissue of fish samples [20-22]. The concentrations of DDT and its metabolites in all the fish samples were much higher than the WHO and FAO [16] set maximum residue limit (MRL) of 1.0 µg/kg, indicating contamination of the aquatic environment by pesticides.

Dieldrin and Aldrin

The highest level of Dieldrin and Aldrin were recorded in the liver of *Oreochromis niloticus,* while the least value was recorded in the flesh of *Heterotis niloticus*. A similar observation was reported by [23]. Other work also reported the highest level of aldrin and dieldrin in the aquatic environment [22], dieldrin is a chlorinated cyclodiene that was widely used in the Nigeria. The National Agency for Food and Drug Administration and Control (NAFDAC) has banned the sale and supply of 30 different agrochemical products in the country which include dieldrin and aldrin. 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. In 1984 and 1985, the U.S. Fish and Wildlife Service collected 321 composite samples of whole fish from 112 stations nationwide as part of the National Contaminant Biomonitoring Program. Maximum and geometric mean tissue concentrations of dieldrin and aldrin in 1984 were 1.39 and 0.04 ppm (wet weight), respectively [22]. The present data also indicated the accumulation levels of dieldrin and aldrin in the fish species study. The concentrations of aldrin and dieldrin in all fish samples were much higher than the WHO and FAO [16] set maximum residue limit (MRL) of 0.2 µg/kg and the Acceptable Daily Intake values (ADIs) of 0.0001µg/kg.

The concentration of dieldrin was slightly significantly higher than that of aldrin in all the species of fish studied. This could be an indication that there is more dieldrin in the environment compared to aldrin. This trend is supported by the fact that aldrin photolysis to dieldrin in the fish organs. These results are in agreement with those of the United States Department of Health and Human services [24] who reported that aldrin is readily and rapidly converted into dieldrin in plant and animal tissues. This is so because dieldrin is extremely non-polar and therefore has a strong tendency to adsorb tightly to lipids such as animal fat and plant waxes. It is for this reason that dieldrin bioconcentrates and biomagnifies through the terrestrial and aquatic food webs [25]. Pointed out dieldrin is one of the most persistent chemicals known. He also reported that dieldrins bioaccumulation in animal tissue is due to its resistance to degradation and biologic metabolism. Similar to DDT and its metabolites, dieldrin is not easily metabolized in water and has limited capacity of being digested and excreted from the body. It is, however, easily absorbed and transported throughout the blood of vertebrates and hemolymph of invertebrates.

Hexachlorobenzene, Lindane, α-BHC and β-BHC

The highest levels of these pesticides were recorded in the liver of *Oreochromis niloticus,* while the least value was recorded in the flesh of *Heterotis niloticus*. Hexachlorobenzene is a fungicide that was widely used as a seed protecting in Nigeria. The use of hexachlorobenzene and the presence of hexachlorobenzene residues in food are banned in many countries including Nigeria [26], but are still in used by farmers. The results of this study is in line with the work of [27] which indicates the presence of alfa BHC, gamma BHC and lindane in fish samples. Lindane is a mixture of homologues of hexachlorocyclohexane ($C_6H_6Cl_6$), whose major component (99 percent) is the gamma isomer. It is commonly referred to as either HCH (hexachlorocyclohexane) or BHC (benzene hexachloride). Lindane is used primarily in seed treatments, soil treatments for tobacco transplants, foliage applications on fruit and nut trees and vegetables, and wood and timber protection. Lindane is used as a therapeutic scabicide, pediculicide, and ectoparasiticide for humans and animals [28]. The concentrations of this pesticide in all the fish samples were much higher than the WHO and FAO [16] set maximum residue limit (MRLs) of 0.01 µg/kg for α-BHC and γ-BHC. The high significant concentrations of BHC isomers in the fish's samples from Alau Dam may be attributed to the heavy use of this pesticide in the agriculture sites located around the Dam.

Metoxichlor

The maximum concentration of metoxichlor was detected in liver of *Oreochromis niloticus*, while the least value was recorded in the flesh of *Heterotis niloticus*. Methoxychlor is used to protect crops, ornamentals, livestock, and pets against fleas, mosquitoes, cockroaches, and other insects. It was intended to be a replacement for DDT, but has since been banned based on its acute toxicity, bioaccumulation, and endocrine disruption activity. The amount of methoxychlor in the environment changes seasonally due to its use in farming and foresting. It does not dissolve readily in water, so it is mixed with a petroleum-based fluid and sprayed, or used as a dust. Sprayed methoxychlor settles on the ground or in aquatic ecosystems, where it can be found in sediments. Its degradation may take many months. Methoxychlor is ingested and absorbed by living organisms, and it accumulates in the food chain. Some metabolites may have unwanted side effects.

Conclusion

Endosulfan was the most abundant pesticides residue in the studied tissues of all the fish species. The highest levels of these organochlorine pesticides were observed in the liver of *Oreochromis niloticus* and *Clarias gariepinus*, compared to other tissues. This study revealed that pesticide residue levels in the fish samples study were above the maximum residue limits (MRLs) and acceptable dietary intake (ADI) and could be an important process of transferring pesticides to humans. It also indicated the extensive presence and usage of these pesticides in the study environment, which include recent use of this pesticide for pest control. Thus, the use of these pesticides to control pest by farmers within the study area with little or no knowledge must be checked through adequate control of the trade and use of pesticides and the enforcement of appropriate sanctions.

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