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Original Research Article

Cabamates and Pyrethroid Pesticide Residues in Fish from Owena River, Ondo State, Nigeria and their Health Risk Evaluation

Adegun Ayodeji O*, Akinnifesi, Thompson A, Ololade Isaac A, Olonisakin A, Omodara, Niyi B

Department of Chemical Sciences, AdekunleAjasin University, Akungba Akoko, Nigeria

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***Corresponding author:** Adegun Ayodeji O

Abstract

This study assessed the effect of cabamate and pyrethroid pesticide residues from agricultural activities on fish samples from the Owena river, Ondo State, Nigeria. The aim of the study was to assess the bioaccumulation and the health risk implication of consuming polluted fish from the river. The fish samples were extracted with an ultrasonic bath extractor and the extracts were analysed with a gas chromatograph coupled to a mass spectrometry detector. The mean level of carbamate pesticide contaminants in dry season for *Oreochromis niloticus*, *Gvmnarchus niloticus*, *S. galileaus* and *Claria gariepinus* are 0.25±0.02µg/g, 0.24±0.01µg/g, 0.30±0.03µg/g and 0.26±0.02µg/g respectively. Their level in wet season for *Oreochromis niloticus, Gvmnarchus niloticus, S. galileous*, *Clarias anguillaris* and *Parachanna obscura* were 0.11±0.03µg/g, 0.21±0.02µg/g, 0.10±0.04µg/g, 0.14±0.03, 0.13±0.03µg/g and 0.12±0.05 µg/g respectively. The level of pyrethroid contaminants in dry season for *Oreochromis niloticus*, *Gvmnarchus niloticus*, *S. galileaus* and *Claria gariepinus* are 0.82±0.79µg/g, 0.53±0.04µg/g, 0.39±0.04µg/g and 1.91±1.99µg/g respectively. Their level in wet season for *Oreochromis niloticus, Gvmnarchus niloticus, S. galileous*, *Claria gariepinus. Clarias anguillaris* and *Parachanna obscura* were 0.22±0.05µg/g, 0.18±0.06µg/g, 0.13±0.05µg/g, 0.19±0.10, 0.12±0.02µg/g and 0.22±0.04 µg/g respectively. The concentrations of some of pollutants in the fish samples were higher than the FAO/WHO maximum residue limit of 0.5µg/g. The health risk evaluation indicates that there is no health risk. Nevertheless, strict monitoring of the handling and usage of these chemicals should continue to be enforced strictly by Nigerian government.

Keywords: pesticide, carbamate, pyrethroid, fish, health risk, Owena river.

INTRODUCTION

River Owena runs along the major coca producing area of Ondo State where insecticides are frequently sprayed to control cocoa mirids. These cocoa mirids are the major problems facing cocoa farmers in Ondo State as they cause diseases to cocoa plant [1]. These pesticide residues in cocoa producing soils may be discharged through runoff into ephemeral streams as well as surface impediments and finally into the river. River Owena is the major source of drinking water supply in Ondo Central Senatorial district. Nevertheless, there is paucity of information on the effects of these pesticide residues introduced into the river via runoff on the river water quality and its aquatic communities such as fish, micro invertebrates, algae as well as their predators. Pesticides are chemicals used to control or kill the pest species, which include plants that are not required [2].

Pesticides are groups of hazardous contaminants [3], posing potential risk to human life and environment [4]. Thus, deaths and chronic diseases are sometimes reported wordwide to have resulted from pesticide poisoning [5]. The contamination of water by these pesticides have been an important issue in many parts of the world and has they could also accumulate in aquatic plants and bio-concentrates and in gill tissues [11, 13]. Deltamethrin is the most toxic pyrethroid for fishes. Some of its effects include damage to the gills changes in behaviour of the fish hitherto been posting problems in environmental, management of water and health sectors as a wide some activities have the potential to contaminate both surface and ground waters [5, 6]. Inspite of the benefits derived from pesticides application, the environmental consequences of the widespread use, handling and disposal of pesticides are of great concern [7]. Human health effects of pesticides are caused by inhalation and ingestion. It could also be caused through skin contact, handling of pesticide products, breathing of dust or spray. Others include

pesticides consumed in water, food and aquatic biota. Pesticides usage in Nigeria has continued to increase, in Commercial farming due to need to intensify agricultural production [8]. Carbamates present low bioaccumulation potentials with short-term toxicity [9]. They are fairly rapidly metabolized and excreted. They are considered hazardous to the environment and human health due to their inclusion in the priority list of environmental pollutants released by the United States Environmental Protection Agency [10-12]. They are commonly used in, structural pest control, residential gardens and home [13]. These pyrethroids are more toxic to mammals and birds at low than the hig.

Temperature sensitivity to toxic agents via gills but also insufficient hydrolytic enzymes for pyrethroids in fish [8, 13]. Pyrethrins and pyrethroids are very toxic to fish other lethal effect of deltamethrin include accelerated respiration, loss of movement coordination, and convulsions [13-16]. The hypothesis of this study is based on determining the pollution level of Owena river with carbamates and pyrethroid pesticides via monitoring of biota.

Therefore, this study is aimed to determine the contamination level of fish samples from Owena River, Ondo State, Nigeria with pesticide residues in view of assessing their bioaccumulation in fish and their health risks implication.

MATERIALS AND METHODS

Description of the sampling area: The study area was the Owena river which is located on geographical coordinates 7^0 12′ 0″ and 5^0 1′ 0″E in Ondo East local government area of Ondo State, South-Western, Nigeria. This river is in Owena river basin and the people in the study area are mostly farmers and fishermen. The area is a major producer of cocoa and the fish samples were collected from the river at the basin.

Sample collection, preservation and preparation:

Twelve fish samples of four species were caught with gill nets at Owena river in dry season and eighteen fish samples of six species were caught in wet season. They were all transported to the laboratory the same day. They were identified at the Department of Fisheries and Aquaculture, Adekunle Ajasin University. The fish species caught in dry season include: Nile tilapia (*Oreochromis niloticus*), Africansharp tooth cat fish (*Clarias gariepinus*),African fish (*Gvmnarchus niloticus*) and Mango tilpia (*Sarotherodon galileous*). The fish species caught in raining season include: Nile tilapia (*Oreochromis niloticus*), African sharp tooth cat fish (*Clarias gariepinus*), African knife fish (*gvmnarchus niloticus*), mango tilapia (*Sarotherodon* galileous), mud fish (*Clarias anguillaris) and* obscure snakehead fish *(Parachanna.*. The fish samples were frozen until analysis [17]. The muscle tissues were homogenized with a meat grinder. The mixing was repeated until the composition appeared to be homogenized and kept frozen until extraction [16-17].

The extracts were concentrated to 20mL [19], volume with a gentle N_2 current. About 10ml of 0.1mL Na_2CO_3 solution was added to the extracts and shaken for 10 minutes to remove free fatty acids [20]. The aqueous phase which contains free fatty acids was discarded. The organic phase was further purified using 10g of alumina placed in a chromatographic column. Two grammes of anhydrous Na_2SO_4 was added to the top of the column. The column was pre- eluted with 40mL of hexane at elution rate of 2mL/min. Twenty mL sample extracts were quantitatively transferred into the column using additional 2mLof hexane to complete the transfer. The column was finally eluted with 140mL ethyl ether/hexane (1/4) (v/v). The eluate was concentrated to 2mL with a gentle stream of nitrogen current. The cleaned concentrated extracts were transferred into amber vials for analysis with GC/MS analysis.

GC-MS analysis

The cleaned extracts were analysed thrice on a gas chromatograph from Agilent USA hyphenated to a mass spectrophotometer (5975C) with triple axis detector. Separations were performed on carpilarry column having specification: lengh; 30m, internaldiameter (0.2µm), thickness; 250µm, treated with phenyl methyl silox. Other GC-MS conditions are ino source temperature(EI) 250°C,interface temperature; 230°C,pressure;16.2 psiaout time,1.8mm, 1 µL injector in split mode with split ratio 1:50 with injection temperature of 300°C .The column temperature started with 35°C for 5 minutes and changed to to 150°C at the rate of 4°C/min. The temperature was raised to 250°C at the rate of 20°C/min. and held for 5 minutes wit solvent delay of 5 minutes. The total elution was 47.5 minutes.MS solution software provided by the supplier was used to control the system and to acquire the data. Identification of the compounds was carried out by comparing the mass spectra obtained with those of the standard mass spectra from NIST library.

Calculation of concentrations of analytes:

Concentration (µg/g) = (Ax)(Vt)(D)/(CF)(Vi)(Ws) [21]
Where: Ax = Area of the peak for the analyte in the sample.

Vt = Total volume of the concentrated extract.
D = Dilution factor =1
CF= Mean calibration factor from the initial calibration
Vi = Volume of the extract injected (µL).
Ws=weight of fish samples

Estimation of daily intake of Fish

The estimated daily intakes (EDIs) of the various pesticides in each fish species was determined by using equation;

$$EDI = \frac{C \times D}{B} \quad \text{equation 1}$$

Where, C, D and B represent the concentrations of pesticide residues in fish (µg/g) on wet weight basis, average daily intake of fish estimated at 65.5g/person/day for adults [28], and the average body weight was considered to be 60kg for adults [29]. Health risk assessment of consumers from the intake of pesticides contaminated fish was characterized by using health risk index (HI). The estimated HIs were obtained by dividing the EDI by their corresponding values of accepted daily intake (ADI) [22]. The Health risk (HR) index was calculated by the equation shown as equation:

$$HR = \frac{EDI}{ADI} \quad \text{equation 2}$$

Where HR >1 showed health risk due to the consumption of the studied fish matrice while HR <1 showed no healthrisk due to the consumption of the fish [22].

RESULTS AND DISCUSSION

Carbamates Pesticide Residues in Fish Samples

Table 1 shows the mean concentration of carbamate pesticide residues in dry and wet seaons. The level of these contaminants in dry season for *Oreochromis niloticus*, *Gvmnarchus niloticus*, *S. galileaus* and *Claria gariepinus* are 0.25±0.02µg/g, 0.24±0.01µg/g, 0.30±0.03µg/g and 0.26±0.02µg/g respectively. Their level in wet season for *Oreochromis niloticus*, *Gvmnarchus niloticus*,*S. galileous*, *Clarias anguillaris* and *Parachanna obscura* were 0.11±0.03µg/g, 0.21±0.02µg/g, 0.10±0.04µg/g, 0.14±0.03, 0.13±0.03µg/g and 0.12±0.05 µg/g respectively. The trend in the level of carbamate residues as shown in Figure 1 in dry season is *Claria gariepinus* > *Oreochromis niloticus*> *S. galileous*>*Gymnarchus niloticus*.Their level in wet season is *Gvmnarchus niloticus* > *Clarias anguillaris Clarias*> *anguillaris*> *Parachanna obscura* > *Gvmnarchus niloticus* (Figure 2). The presence of these contaminants in the fish samples revealed that carbamate insecticides were used in the study area. The specific gravities of these chemicals are higher than the specific gravities of water, they tend to sink into the sediment and bioaccumulate in the fatty tissues of aquatic animals. Almost all the fishes of genus of *Clarias* and *Gvmnarchus niloticus* had high level of these pollutants in dry and raining seasons. This could be as a result of their their feeding habits as carnivores as they eat mainly contaminated fishes which cause biomagnification. Therefore, it is not surprising that higher level of these contaminants were detected in them than the others due to their feeding mode. Moreover, *Oreochromis niloticus*, which is an omnivore also had high level of these pollutants as they feed on water plants, insects and smaller fishes. Generally, the bioaccumulation of pesticide residue in fish tissues is always due to their feeding habits [15- 17. The mean concentrations of carbamate residues in the fish samples were below 0.5 µg/g and 0.01mg/kg WHO/FAO and former Nigerian Federal Environmental Protection Agency MRL respectively [22].

Carbamate can inhibit the the activities of cholinesterase. High concentration of carbaryl in water leads to fish and fish-food mortality [23]. This study reported higher carbamates maximum level of 0.30µg/g (Table1 than the 0.0425-0.066 µg/g for *Labeo rohita* but lower than 0.613-0.946 µg/g in *Channa marulius* muscles as reported by Jabeen *et al.* [23] in a study of carbamates, pyrethroid, and neonicotinoid in fish, water and sediments from the Indus river for potential health effects.Research reports revealed chronic and acute toxic *effects* of carbamates o*n fish* and *fish* food. The concentrations of carbaryl could also pose harmful effects on *fish* during spawning period [24]. Carbaryl is a Cholinesterase Inhibitor, and causes acute symptoms in animals and humans. They cause mutagenic effects in humans.

Exposure to carbaryl and isoprocarbarb could cause cancer, endocrine distruption, reproductive failure and developmental problems [24]. Therfore, the high concentration of carbaryl in the fish and its health implications need concern for the people eating fish in the study area. The pollution level in fish species in raining season was lower than the dry season (Figure3).

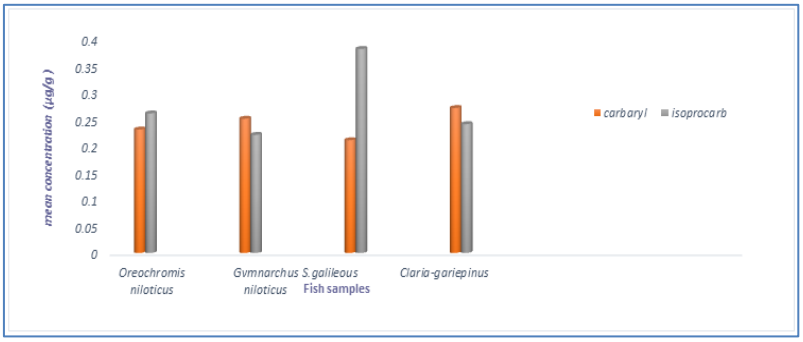

Fig-1: Distribution of carbamates pesticide residue residues in the fish samples during dry season

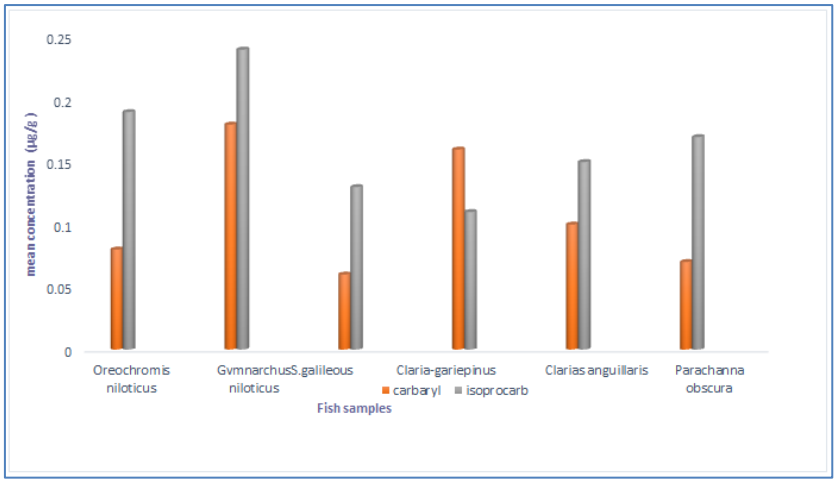

Fig-2: Distribution of carbamates pesticide residue residues in the fish samples during wet season

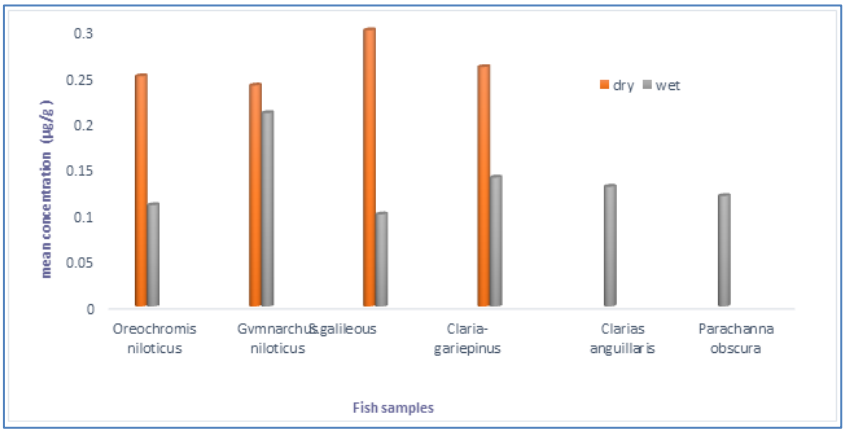

Fig-3: Comparative Level of occurrence of compounds of carbamate pesticide residues in fish samples during dry and wet season

Table-1: Health Risk Evaluation of Carbamate Pesticide Residues in Fish Samples from River Owena, Nigeria

Species of fish	Pesticide	mean±sd	Range	AD1	EDI	HI	HR
		Dry Season					
Oreochromis niloticus	Carbaryl	0.23± 0.05	0.19-0.32	0.008	$2.60x10^{-4}$	0.32	No
	Isoprocarb	0.26± 0.06	0.22-0.30	0.01	$2.58x10^{-4}$	0.03	No
Gvmnarchus niloticus	Carbaryl	0.25± 0.02	0.21-0.35	0.008	2.5810^{-4}	0.03	No
	Isoprocarb	0.22± 0.02	0.17-0.28	0.01	$2.67x10^{-}$	0.03	No
S.galileous	Carbaryl	0.21± 0.04	0.16-0.29	0.008	$2.58x10^{-4}$	0.03	No
	Isoprocarb	0.38± 0.04	0.30-0.42	0.01	$2.52x10^{-4}$	0.03	No
Claria gariepinus	Carbaryl	0.27± 0.00	0.22-0.39	0.008	$2.94x10^{-4}$	0.04	No
	Isoprocarb	0.24± 0.02	0.18-0.31	0.01	$2.62x10^{-4}$	0.03	No
		Wet Season					
Oreochromis niloticus	Carbaryl	0.08±0.02	0.19-0.32	0.008	$8.73x10^{-5}$	0.01	No
	Isoprocarb	0.19 ±0.012	0.22-0.30	0.01	$2.1.53x10^{-4}$	0.02	No
Gvmnarchus niloticus	Carbaryl	0.18 ± 0.09	0.21-0.35	0.008	2.0710^{-4}	0.03	No
	Isoprocarb	0.24± 0.17	0.17-0.28	0.01	$2.67x10^{-}$	0.03	No
S.galileous	Carbaryl	0.06± 0.01	0.16-0.29	0.008	$6.55x10^{-4}$	0.01	No
	Isoprocarb	0.13± 0.09	0.30-0.42	0.01	$1.42x10^{-4}$	0.01	No
Claria gariepinus	Carbaryl	0.16± 0.07	0.10-0.22	0.008	$1.744x10^{-4}$	0.04	No
	Isoprocarb	0.11±0.08	0.09-0.21	0.01	$1.20x10^{-4}$	0.03	No
Clarias anguillaris	Carbaryl	0.10±0.06	0.08-0.19	0.008	$1.09x10^{-4}$	0.01	No
	Isoprocarb	0.15± .09	0.12-0.25	0.01	$1.64x10^{-4}$	0.02	No
Parachanna obscura	Carbaryl	0.07± 0.04	0.05-0.16	0.008	$1.70x10^{-5}$	0.00	No
	Isoprocarb	0.17± 0.06	0.12-0.26	0.01	$1.86x10^{-4}$	0.02	No

ADI = Acceptable Daily Intake; EDI= Estimated Daily Intake; HI = Health Index; HR = Health Risk; HR > 1 showed health risk due to the consumption of the studied fish species while HR < 1 showed no health risk due to the consumption of the fish studied

Pyrethroid Pesticide Residues in Fish Samples

Tables 2 show the mean concentration of pyrethroid pesticide residues in dry and wet seaons. The level of these contaminants in dry season for *Oreochromis niloticus*, *Gvmnarchus niloticus*, *S. galileaus* and *Claria gariepinus* are 0.82±0.79µg/g, 0.53±0.04µg/g, 0.39±0.04µg/g and 1.91±1.99µg/g respectively.

Their level in wet season for *Oreochromis niloticus, Gvmnarchus niloticus, S. galileous, Claria gariepinus. Clarias anguillaris* and *Parachanna obscura* were 0.22±0.05µg/g,0.18±0.06µg/g,0.13±0.05µg/g,0.19±0.10 , 0.12±0.02µg/g and 0.22±0.04 µg/g respectively. The fish species get the pollutants from water and bio accumulate them by feeding on smaller fishes and insects wet season, *Oreochromis niloticus* and *Parachanna obscura* had the same high level of contamination. This scenario could be attributed to their feeding habit as an omnivorous and carnivorous fishes respectively. However, cis-permethrin was not detected in the studied fish species analyzed in wet season (Figure4).

This could be pesticide formulation with its active ingredient was not used by the farmers during that period.It could also be that its residues had degraded from the aquatic system. Nevertheless, cypermethrin was detected in all the fish samples studied in both seasons. The presence of cypermethrin in all the studied fish species is an indication that pesticides containing cypermethrin active ingredients were frequently used in the study area. The trend in the distribution of pyrethroids is: *Claria gariepinus* >*Oreochromis niloticus* > *Gymnarchus niloticus* > *S. galileous* for dry season (Figure 4). The trend in raining season contamination is *Oreochromis niloticus, Parachanna obscura* > *Claria gariepinus*> *S. galileous*> *Gvmnarchus niloticus*> *Clarias anguillaris* (Figure 5).

Table-2: Health Risk Evaluation of Pyrethroid Pesticide Residues in Fish Samples from River Owena, Nigeria

Species of fish	Pesticide	mean±sd	Range	AD1	EDI	HI	HR
Oreochromis niloticus	Dry season	0.38± 0.21	0.29-0.46	0.05	$1.97x10^{-3}$	0.04	No
	Cis-permethrin	1.73± 1.06	1.69.-1.87	0.05	$4.33 x10^{-4}$	0.01	No
	Cypermethrin	0.36 ± 0.07	0.28-0.48	0.01	$3.88 x10^{-4}$	0.04	No
	Deltamethrin						
Gvmnarchus niloticus	Cis-permethrin	0.50± 0.09	0.49-0.72	0.05	$6.37x10^{-4}$	0.01	No
	Cypermethrin	0.56± 0.06	0.45-0.67	0.05	$5.72x10^{-4}$	0.01	No
S.galileous	Cypermethrin	0.36± 0.04	0.25-0.56	0.05	$3.95x10^{-4}$	0.01	No
	Deltamethrin	0.37± 0.09	0.36-0.59	0.01	$3.91x10^{-4}$	0.04	No
Claria gariepinus	Cis-permethrin	0.50± 0.1 1	0.44-0.62	0.05	$3.78x10^{-3}$	0.08	No
	Cypermethrin	3.31± 2.14	3.04-3.95	0.05	$5.83x10^{-4}$	0.01	No
	Wet season						
Oreochromis niloticus	Cypermethrin	0.27± 0.05	0.21-0.39	0.05	$2.95 x10^{-4}$	0.01	No
	Deltamethrin	0.17 ±0.09	0.15-0.28	0.01	$1.86 x10^{-4}$	0.02	No
Gvmnarchus niloticus	Cypermethrin	0.24 ±0.06	0.18-0.32	0.05	$2.62x10^{-4}$	0.01	No
	Deltamethrin	0.12± 0.03	0.09-0.22	0.01	$1.31x10^{-4}$	0.01	No
S.galileous	Cypermethrin	0.20±0.14	0.16-0.31	0.05	$2.18x10^{-4}$	0.00	No
	Deltamethrin	0.10±0.04	0.06-0.19	0.01	$1.09x10^{-4}$	0.01	No
Claria gariepinus	Cypermethrin	0.29 ± 0.17	0.22-0.35	0.05	$3.17x10^{-4}$	0.01	No
	Deltamethrin	0.09± 0.06	0.05-0.16	0.01	$1.53x10^{-5}$	0.00	No
Clarias anguillaris	Cypermethrin	0.14± 0.03	0.10-0.24	0.05	$1.54x10^{-4}$	0.00	No
	Deltamethrin	0.11± 0.09	0.07-0.19	0.01	$1.20x10^{-4}$	0.01	No
Parachanna obscura	Cypermethrin	0.25 ± 0.08	0.20-0.33	0.05	$2.73x10^{-4}$	0.01	No
	Deltamethrin	0.17± 0.10	0.11-0.24	0.01	$1.97x10^{-4}$	0.02	No

ADI = Acceptable Daily Intake; EDI= Estimated Daily Intake; HI = Health Index ; HR = Health Risk; HR > 1 showed health risk due to the consumption of the studied fish species while HR < 1 showed no health risk due to the consumption of the fish studies

The observation from this study area shows that the farmers might have been using more pyrethroid based insecticdes in protecting their crops against pests. This is evident as pyrethroid active ingredients are sold in markets in Nigeria. Akinrotimi *et al.* [25] recommended the most toxic level of cypermethrin as 0.25mg/kg in his study on *Claria gariepinus*. Comparing the value with that obtained from this study, it could be inferred that the level of concentration of cypermethrin in this study was lower than that of Akinrotimi *et al.*,[25]. The mean concentration of pyrethroid residues in some of the fish samples is higher than the 0.5 limit set by FAO and Akinrotimi toxicity level in dry season but lower than it in the wet season. However, dry season polllution level is higher than that of wet season. This could be as a result of the dilution of the acquatic environment in which these organic pollutants are transported to. Thus, their effect could be felt in matriice outside this current study. Area The general partern in the distribution of these pyrethroids pollutants in all the investigated biotic and abiotic matrices (Figure 6).

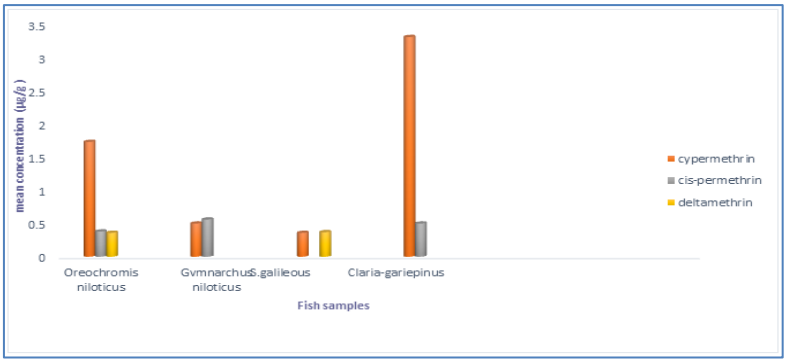

Fig-4: Distribution of pyrethroid pesticide residues in fish samples during dry season

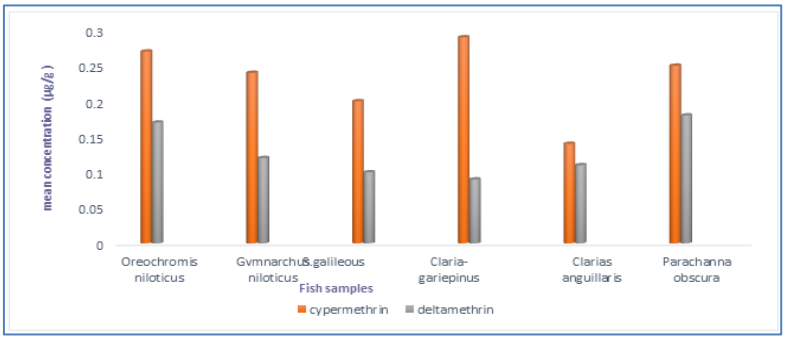

Fig-5: Distribution of pyrethroid pesticide residues in fish samples during wet season

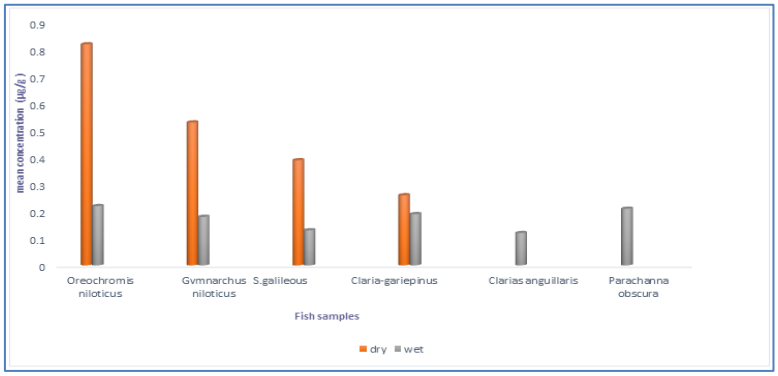

Fig-6: Comparative level of occurrence of compounds of pyrethroid pesticide residues in fish samples during dry and wet season

CONCLUSION

This study concluded that the fish samples from the study area were contaminated with carbamate and pyrethroid pesticide residues. However, their contamination level did not constitute any appreciable health risks in all the studied fish species. Nevertheless, there should be public awareness campaign on the presence of these contaminants in fishes in the river. Therefore, the application of pesticides by the farmers in the study area should be at considerable safe distance from the river in order to protect aquatic lives and health of humans consuming the contaminated fishes. The Federal government of Nigeria should continue to enforce the laws on the handling and usage of these chemicals for cocoa pest control.

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