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Concentration and Potential Health Risks Associated with Organophosphorus Pesticides Residues in Fish from Three Rivers in Ekiti State, South-Western Nigeria

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Abstract: A total of 30 fish samples were collected from Elemi, Ogbese and Ero rivers in southwestern Nigeria, to determine the concentration of thirteen organophosphorus pesticides (OPPs) residues and estimate the potential health risk as a result of human consumption. Diazinon, mevinfos, dimethoate and dichlorvos were only detected with concentration range of BDL - 19.2µg/kg and BDL - 2.48µg/kg during the dry and wet season while diclofenthion, phosphamidon, pirimiphos-methyl, parathion, isofenfos, bromophos, fenthion, chlorpyrifos and ethion showed no detectable level. The contamination pattern of OPPs in the fish samples were in the order dichlorvos diazinon mevinfos dimethoate with none exceeding the maximum residue limit (MRL) for OPPs in food as established by European Union. Statistical analysis using ANOVA in SPSS showed no significant difference in mevinfos and dimethoate whilst dichlorvos, diazinon and TOPP showed some levels of significant variation. The few OPPs detected in the fish showed no evidence of potential threat to human health.

Key words: Organophosphorus · Pesticides · Concentration · Gas chromatography · Residues · Fish

INTRODUCTION

Pesticides uses are indispensable in the area of agricultural production and public health vector control [1]. Runoff from various agricultural lands as a result of pesticide usage particularly cocoa and maize has contributed to OPs levels in Nigeria rivers. Inappropriate use of pesticides and washing of empty bottles in the river contribute to pesticide release [2].

The excessive usage is harmful to ecosystem and they contaminate soil, surface and underground water resources [3, 4]. Pesticides contaminate the environment and accumulate in the food chain thereby posing hazard to human health [5-7].

Fish samples can be considered as one of the most significant indicators in fresh water systems for the estimation of pesticides pollution level [8]. The region of accumulation of pesticides within fish varies with route of uptake. Their potential use as biomonitors is significant in the assessment of bioaccumulation and biomagnifications of contaminants within the ecosystem [9]. Bioaccumulation and bioconcentration of pesticides in fish species are capable of reaching toxic levels even when exposure is low. At low concentrations, the combined effect of persistent synthetic pesticides causes suppression of immune response and hypersensitivity to chemical agents. Causes of breast cancer, reduced sperm count, male sterility and death are well documented as a result of pesticide ingestion [10].

Assessment of risks to human health have been undertaken worldwide to examine the potential health risk due to exposure to toxic contaminants in various environmental media and foodstuff [11]. U.S. National Research Council of the National Academy of Sciences (NRC) and the Environmental Working Group reported that pesticide exposures to children could be high enough to cause immediate adverse health outcomes [11, 12]. This study, therefore, seeks to provide baseline information on the levels of organophosphorus pesticides (OPPs) residues in three major rivers in Ekiti state, south-western Nigeria and estimate the potential health risk as a result of human consumption.

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MATERIALS AND METHODS

Study Area: Fish samples were collected from three different rivers in Ekiti state south-western, Nigeria. The rivers are Elemi, Ogbese and Ero. Elemi river with estimate terrain elevation of 355 meters above sea level. Ero river had been built as a dam for the purpose of serving as a source of potable water for the people within the northern part of the state. Ogbese, a major river in southwestern region of Nigeria with many tributaries. Ekiti state lies between latitude 7° 40' N and longitude 5° 15' E in the western part of Nigeria. The rivers play important roles in the socio-economic development of the people living around them, such as fishing, farming (irrigation) and washing.

Sample Collection and Preparation: Fish samples were caught from the rivers with the assistance of local fishermen. The fishes were identified at the Department of Fisheries and Aquaculture, Ekiti State University, Ado-Ekiti. The fish samples were wrapped in aluminium foil and stored in a deep freezer prior to sample preparation for analysis. The whole fish samples were removed from the freezer, cleaned with deionized water and ground by agate mortar and later blended with Excella Mixer blender. Thirty fish samples were collected for both seasons.

Reagents Used: The reagents used were of spectra purity. They were: GC grade n-hexane, analytical grade acetone, analytical grade diethyl ether; silica gel 60 F_{254} and anhydrous sodium sulphate (Na_2SO_4).

Extraction Procedure and Clean-Up: Extraction of pesticides from the fish samples was carried out by EPA 3550C method [13]. Fish samples were prepared by the method described by Afful *et al.* [14]. Ten gramme each of properly homogenised muscle tissue of fish samples were separately placed in a beaker containing 25 g of anhydrous sodium sulphate (Na_2SO_4) and mixed thoroughly. Acetone: n-hexane (1:1 v/v) of 40 ml was added and the mixtures were sonicated for 15 minutes. The extracts were filtered, concentrated to 2 ml using a rotary evaporator. The extraction process was repeated with additional 50 ml (acetone and n-hexane mixture), sonicated and allowed to settle and decanted into the same round bottom flask. The combined extract was concentrated to 2 ml using a rotary evaporator. This was later cleaned up using activated silica gel.

The clean up involved the use of a column of about 15 cm (length) x 1cm (internal diameter) packed with 2 g of activated silica gel and 1 g anhydrous Na_2SO_4 on top of the silica gel (adsorbent). The column was conditioned with 15 ml n-hexane prior to clean up.

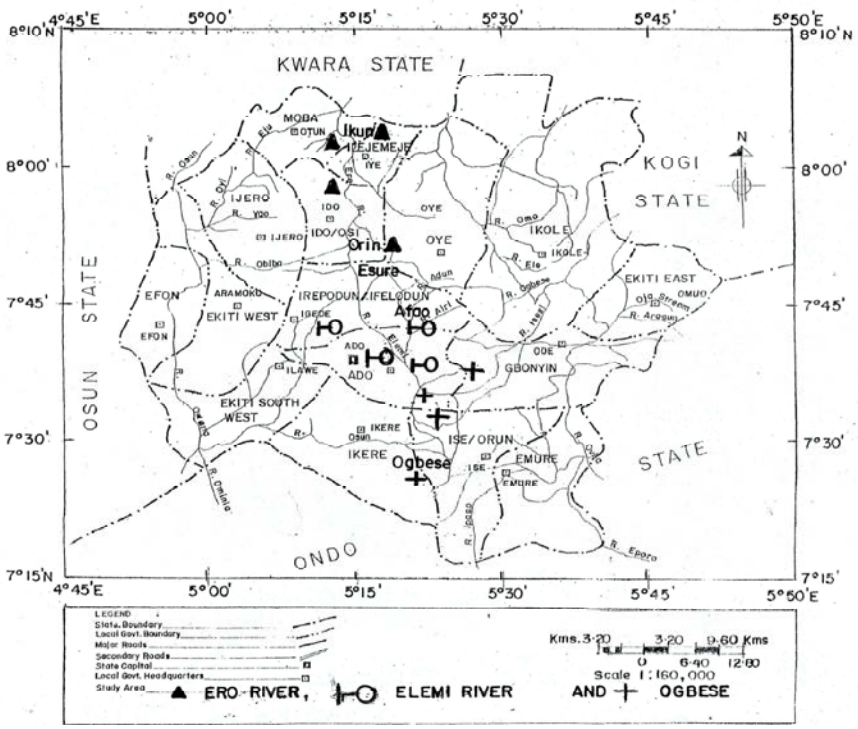

Fig. 1: Ekiti State water bodies showing the selected three different rivers as sampling areas

The extract was introduced into the column and eluted with 20 ml of n-hexane and diethyl ether (1:1 v/v). The eluate was concentrated to dryness on the rotary evaporator and recovered into 2 ml n-hexane. The extract was transferred into glass GC vials for subsequent injection into the GC. The OPPs in the extracts were determined by a Gas Chromatograph (GC) coupled with flame photometric detector (FPD).

Identification, Quantification and Quality Control: The validation of the analytical method was performed by the accuracy, precision, linearity, limit of detection (LOD) and quantification (LOQ). All the analysis was carried out using the same blank samples. Similar volume of solvents (n-hexane/acetone) and anhydrous sodium sulphate used in the extractions were subjected to similar extraction and clean-up procedures to detect any possible traces of the studied pesticides. To determine the validity of the methodology, a recovery study was performed using standard addition method. Three samples were spiked with the mixture of pesticides standard solutions (1, 2 and 5 µg/L). The spiked samples were allowed to stand for some hours and then extracted, cleaned up and analysed as described in the method above. The results showed that the mean recovery values ranged from 79 to 87%. This indicated that the analytical procedures were reliable, reproducible and efficient. Precision of the method was evaluated through the relative standard deviation associated with pesticides measurements during recovery.

Standard solutions of OPPs were run in GC-(FPD) under set chromatographic conditions and mean peak areas were plotted against concentrations to obtain calibration curves of individual pesticides. Stock solutions of organophosphorus (dichlorvos, mevinfos, diazinon, chlorpyrifos, dimethoate, diclofenthion, phosphamidon, pirimiphos-methyl, parathion, fenthion, isofenfos, bromophos and ethion) were prepare and stored in amber coloured bottles at 4° C in a refrigerator where working standard solutions were prepared fresh before use. Under the set chromatographic conditions, standard calibration curve was prepared for each OPP. The signatory retention time for each OPPs was used as confirmatory indicator. Linearity was determined by plotting calibration curve with standard solution in n-hexane containing four different concentrations (0.1, 0.25, 0.5, 1.0 ng/µL). The limit of detection (LOD) and quantification (LOQ) were calculated according to standard guidelines [15, 16].

Gas Chromatographic Operating Condition: The gas chromatography conditions for the analysis were as follows: GC model: Agilent 7693 Autosampler; the carrier gas flow rate was 2.7 ml/min; Injector temperature: split injection: 20:1; carrier gas: nitrogen; inlet temperature: 250 °C; column type: HP5 MS; column dimension: 30 m x 0.25 µm x 0.32 mm; oven program: initial temperature at 60°C for 1 minute, first ramping 10 °C/min for 14 min (200 °C); maintained for 2 min; second ramping at 10 °C/min for 8 min (280 °C); maintained for 3 min; detector: flame photometric detector (FPD); detector temperature: 250 °C; hydrogen pressure: 22 psi; compressed air: 35 psi. The total run time was 28 minutes.

Hazard Index Estimation: Health risk estimation was formed on the basis of organophosphorus pesticides residues analysis data obtained from the present study and daily fish consumption rate in Nigeria per person. The Available Daily Intake (ADI) is a measure for the toxicity of a substance by long term and repeated ingestion. The EDI was calculated as per international guideline [17, 18] using the equation EDI= C x F/W. Estimated daily intake (EDI) was found by multiplying the average residual pesticide concentration (µg/kg) in the fish species by the fish consumption rate in Nigeria (kg/day) and divided through by the average body weight (kg). The estimated hazard indices for children (1- 11 years) and adults were obtained by estimating the ratios between the EDI (mg/kg/day) by their daily intakes. In this study C = mean of individual pesticide concentration (µg/kg), F is the fish consumption rate per person (kg/day). The fish consumption rate for an adult was calculated from the annual per capital consumption (12.5 kg/year) to be 0.034 kg/day [19]. The average body weights of adult and child used were 60kg and 30kg respectively.

Statistical Analysis of the Data: Data generated in the study were subjected to statistical analysis to test for spatial and seasonal variations with analysis of variance (ANOVA) using SPSS 15.0 package. One level of confidence limit ($p = 0.05$) was considered in the interpretation of the statistical results.

RESULTS AND DISCUSSIONS

The concentrations of organophosphorus pesticide residues in the fish samples are shown in Tables 1- 3. The detectable mean total OPPs residues ranged from 0.077 ± 0.27µg/kg (diazinon) to 6.58 ± 0.84 (dichlorvos).

Table 1: Mean concentration (µg/kg) of organophosphosphorus pesticides residues in the fish samples

River	Dichlorvos	Mevinfos	Diazinon	Dimethoate	Diclofenthion	Phosphamidon	Pirimiphos-methyl	Chlorpyrifos	Parathion
Ogbese	6.58^{b}±0.84	0.431^{a}±0.24	0.077^{a}±0.27	0.126^{a}±0.77	BDL	BDL	BDL	BDL	BDL
Ero	1.75^{a}±0.84	BDL	0.451^{a}±0.27	BDL	BDL	BDL	BDL	BDL	BDL
Elemi	1.64^{a}±0.84	0.113^{a} ±0.24	1.57^{b}±0.27	BDL	BDL	BDL	BDL	BDL	BDL

Table 1 cont.: Mean concentration (µg/kg) of organophosphosphorus pesticides residues in the fish samples

River	Fenthion	Isofenfos	Bromophos	Ethion	TOPP
Ogbese	BDL	BDL	BDL	BDL	7.21^{b}±0.59
Ero	BDL	BDL	BDL	BDL	2.20^{a}±0.59
Elemi	BDL	BDL	BDL	BDL	3.24^{a}±0.59

Data are presented as mean ± S.E (30). Values within column with the same superscript letter are not significantly different ($p < 0.05$) using Duncan multiple range test.

Table 2: Mean concentration (µg/kg) of organophosphorus pesticides residues in fish samples for both seasons

Season	Dichlorvos	Mevinfos	Diazinon	Dimethoate	Diclofenthion	Phosphami don	Pirimiphos-methyl	Chlorpyrifos	Parathion
Wet	5.74^{b}±0.69	0.287^{a}±0.20	1.08^{b}±0.22	0.084^{a}±0.06	BDL	BDL	BDL	BDL	BDL
Dry	0.902^{a}±0.69	0.075^{a}±0.20	0.324^{a}±0.22	BDL	BDL	BDL	BDL	BDL	BDL

Table 2 cont.: Mean concentration (µg/kg) of organophosphorus pesticides residues in fish samples for both seasons

Season	Fenthion	Isofenfos	Bromophos	Ethion	TOPP
Wet	BDL	BDL	BDL	BDL	7.19^{b}±0.48
Dry	BDL	BDL	BDL	BDL	1.24^{a}±0.48

Data are presented as mean ± S.E (15). Values within column with the same superscript letter are not significantly different ($p < 0.05$) using Duncan multiple range test.

Table 3: Mean concentrations (µg/kg) of organophosphorus pesticides residues in the fish samples on pair-wise basis

	Dichlorvos		Mevinfos		Diazinon		Dimethoate		Diclofenthion	
River	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Ogbese	0.865^{a}±1.19	12.3^{b}±1.19	BDL	0.862^{a}±0.35	BDL	0.153^{a}±0.38	BDL	0.252^{a}±0.16	BDL	BDL
Ero	1.73^{a}±1.19	1.76^{a}±1.19	BDL	BDL	0.912^{a}±0.38	BDL	BDL	BDL	BDL	BDL
Elemi	0.11^{a}±1.19	3.176^{a}±1.19	0.226^{a}±0.35	BDL	0.059^{a}±0.38	3.09^{a}±0.38	BDL	BDL	BDL	BDL

Table 3 cont.: Mean concentrations (µg/kg) of organophosphorus pesticides residues in the fish samples on pair-wise basis

	Phosphamidon		Pirimiphos- methyl		Chlorpyrifos		Parathion		Fenthion		Isofenfos	
Rive	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Ogbese	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ero	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Elemi	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Table 3 cont.: Mean concentrations (µg/kg) of organophosphorus pesticides residues in the fish samples on pair-wise basis

	Bromophos		Ethion		TOPP	
River	Wet	Dry	Wet	Dry	Wet	Dry
Ogbese	BDL	BDL	BDL	BDL	0.865^{a}±0.83	13.6^{c}±0.83
Ero	BDL	BDL	BDL	BDL	2.640^{a}±0.83	1.76^{a}±0.83
Elemi	BDL	BDL	BDL	BDL	0.221^{a}±0.83	6.26^{b}±0.83

Data are presented as mean ± S.E (5). Values with the same superscript letter are not significantly different ($p < 0.05$) in seasons and rivers using Duncan multiple range test.

For samples in Ogbese (dry): CG= *Clarias gariepinus;* HN= *Heterotis niloticus; CN= Chrysichthys nigrodigitatus;* TZ= *Tilapia zilli;* ON= *Oreochromis niloticus;* Ogbese (wet): CG= *Clarias gariepinus;* Ero (dry) CN= *Chrysichthys nigrodigitatus and* ON= *Oreochromis niloticus;* Ero (wet): *Oreochromis niloticus;* Elemi (dry): *Oreochromis niloticus,* Elemi (wet): *Oreochromis niloticus*

Table 4: Estimated dose values and hazard indices of OPPs exposure in contaminated fish samples from Ogbese river

		EDI((µg/kg/day)		Hazard Index	
Pesticides	WHO/FAO ADI (µg/kg/day)	1-11yrs	Adult	1-11yrs	Adult
Dichlorvos	4.00	7.46e-3	3.73e-3	1.87e-3	9.32e-4
Mevinfos	1.50	4.88e-4	2.44e-4	3.25e-4	1.63e-4
Diazinon	2.00	8.73e-8	4.36e-8	4.36e-5	2.18e-5
Dimethoate	10.0	1.43e-4	7.14e-5	1.43e-5	7.14e-6
Diclofenthion	-	-	-	-	-
Phosphamidon	1.00	-	-	-	-
Pirimiphos-methyl	30.0	-	-	-	-
Chlorpyrifos	10.0	-	-	-	-
Parathion	5.00	-	-	-	-
Fenthion	1.00	-	-	-	-
Isofenfos	-	-	-	-	-
Bromophos	40.0	-	-	-	-
Ethion	2.00	-	-	-	-

Table 5: Estimated dose values and hazard indices of OPPs exposure in contaminated fish samples from Ero river

		EDI((µg/kg/day)		Hazard Index	
Pesticides	WHO/FAO ADI (µg/kg/day)	1-11yrs	Adult	1-11yrs	Adult
Dichlorvos	4.00	1.98e-3	9.91e-4	4.99e-5 2.48e-4	
Mevinfos	1.50	-	-	-	-
Diazinon	2.00	5.11e-4	2.55e-4	2.56e-4	1.28e-4
Dimethoate	10.0	-	-	-	-
Diclofenthion	-	-	-	-	-
Phosphamidon	1.00	-	-	-	-
Pirimiphos-methyl	30.0	-	-	-	-
Chlorpyrifos	10.0	-	-	-	-
Parathion	5.00	-	-	-	-
Fenthion	1.00	-	-	-	-
Isofenfos	-	-	-	-	-
Bromophos	40.0	-	-	-	-
Ethion	2.00	-	-	-	-

Table 6: Estimated dose values and hazard indices of OPPs exposure in contaminated fish samples from Elemi river

		EDI((µg/kg/day)		Hazard Index	
Pesticides	WHO/FAO ADI (µg/kg/day)	1-11yrs	Adult	1-11yrs	Adult
Dichlorvos	4.00	1.86e-3	9.29e-4	4.69e-5	1.86e-5
Mevinfos	1.50	1.30e-4	6.40e-5	8.67e-5	4.27e-5
Diazinon	2.00	1.78e-8	8.89e-8	8.90e-4	4.45e-4
Dimethoate	10.0	-	-	-	-
Diclofenthion	-	-	-	-	-
Phosphamidon	1.00	-	-	-	-
Pirimiphos-methyl	30.0	-	-	-	-
Chlorpyrifos	10.0	-	-	-	-
Parathion	5.00	-	-	-	-
Fenthion	1.00	-	-	-	-
Isofenfos	-	-	-	-	-
Bromophos	40.0	-	-	-	-
Ethion	2.00	-	-	-	-

Diclofenthion, phosphamidon, pirimiphos-methyl, parathion, isofenfos, bromophos, fenthion, chlorpyrifos and ethion were below detection limits for both seasons while diazinon, mevinfos, dimethoate and dichlorvos were detected with dichlorvos and diazinon being the most frequently found OPPs residues in the fishes. The concentration of OPPs in the fish samples during the dry season ranged from BDL - 19.2µg/kg while the wet season ranged from BDL – 2.48µg/kg. The total organophosphorus pesticides (TOPP) in individual fish samples for both seasons ranged from BDL - 19.2 µg/kg, 1.12 - 3.28 µg/kg and 1.06 – 8.22 µg/kg in Ogbese, Ero and Elemi. The mean TOPPs residues for the samples were 7.21 ± 0.59, 2.20 ± 0.59, 3.24 ± 0.59µg/kg in Ogbese, Ero and Elemi.

The study showed the presence of dichlorvos from the three rivers for both seasons while diazinon was only recorded in Elemi during the dry season. Regarding diazinon, 30% of the total samples contained diazinon with concentration range of BDL - 4.78 µg/kg and average concentration of 0.077 - 1.57µg/kg. The contamination patterns of diazinon were in the order: Elemi Ero Ogbese. None of the samples exceeded the maximum residue limit of 100 ug/kg for diazinon in food as established by [20]. The diazinon values obtained in this study were comparatively lower to those reported in Egypt (Chicken, 4.28 - 15.3, average concentration of 8.89 µ/kg) [21], Alau Dam, Borno Nigeria (Fish liver, 0.56 - 2.43 µg/kg) [22]. Dichlorvos, diazinon, chlorpyrifos and fenitrothion are readily degraded by microorganisms and therefore do accumulate [23]. The accumulation of these pesticides in the fish could be as a result of detoxification mechanisms and may originate from pesticides deposited in the sediments and food in the aquatic environment.

Dichlorvos was the most frequently found OPs in the samples. About 96.7% of the total fish samples contained dichlorvos with the concentration range of BDL - 19.2 µg/kg and mean concentration of 0.865 – 12.3 µg/kg. Dichlorvos contamination pattern were in the order: Ogbese ? Ero ? Elemi. Dichorvos in the fish samples generally showed high concentration in the dry as compared to wet season. None of the 30 samples exceeded the maximum residue limit (50µg/kg) for dichlorvos in food samples.

For mevinfos and diazinon, only one sample contained residues of these pesticides (both in Ogbese). The result from this study showed that none of the detected organophosphorus pesticide residues exceeded the EU maximum residue limit of OPs in food. The OP levels in this study were lower than the level reported in fish for dichlorvos (0.11 to 1.23µg/g), chlorpryifos (0.34 to 1.89µg/g) and fenitrothion (0.23 to 1.54µg/g) from Alau dam, in Borno State [22]. Akan et al. [22] reported highest concentration of OPPs in stomach of *Oreochromis niloticus* while *Heterotis niloticus* had the lowest concentration. Accumulation of pesticides in different species is the function of their respective membrane permeability and enzyme system, which is highly specie specific. The contamination pattern of OPPs in the fish samples were in the order: dichlorvos diazinon mevinfos dimethoate. The below detectable limits of most OPPs in the fish samples could be attributed to the fast degradable nature of OPPs in the environment particularly in aquatic environment, detoxification or metabolism ability of the fish and so on.

Statistical analysis using ANOVA in SPSS showed no significant difference in mevinfos and dimethoate while dichlorvos, diazinon and TOPP showed some levels of significant variation. Seasonable variation showed significant difference $p < 0.05$ in dichorvos, diazinon and TOPP while mevinfos and dimethoate showed no significant difference in the seasons. Interactions between the season and the rivers showed no significant difference in mevinfos and dimethoate while the TOPP, diazinon and dichlorvos showed significant difference. The significant variation in these OPPs could be as a result of fate of the individual's pesticides in biota, metabolism and detoxification capacity of the fish, etc.

The estimated daily intakes of all the detectable OPPs in the fish were significantly lower than the WHO/FAO ADI [24]; IPCS [25] as shown in Tables 4 - 6. The four OPPs detected in the fish showed no evidence of potential threat to human health. The estimated daily intake in Ogbese (dichlorvos, mevinfos, diazinon and dimethoate), Ero (dichlorvos and diazinon) and Elemi (Dichlorvos, mevinfos and diazinon) showed a wide range difference from their reference doses, in other words, all the calculated EDI<<< ADI. The hazard index (HI) ranged from 7.14e-7 (dimethoate, Elemi) to 1.87e-3 (dichlorvos, Ogbese). The study showed that the fish from the studied rivers are not just safe but also pose no potential health hazard or risk to human.

CONCLUSION

The study showed the presence of four OPPs (diazinon, mevinfos, dimethoate and dichlorvos) residues from the sampled fishes with Ogbese showing highest mean total concentration. OPs pesticides intake by children and adults consuming the fishes from the study rivers is low and pose no potential health risk to people in the area.

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