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GC-ECD Organophosphate Pesticide Residues Analysis In Water, Fish AndSediment in River LOKO, Nasarawa State, Nigeria

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Abstract:*Levels of organophosphate pesticide residues (OPPs) in sediment, water and fish in Benue River at LokoNasarawa State, Nigeria were evaluated for possible pollution of the aquatic ecosystem. Water and sediment samples were collected were collected at from the river at 3 locations. Fish caught in the river were bought from fishermen at the bank of the river. Liquid-liquid extractions of samples were carried out, and then quantified using gas chromatography coupled electron caption detector (GC-ECD). Concentrations of OPPs ranged from 0.09±0.04 to 1.84±0.02, 0.04±0.03 to 1.79±0.01 and 0.01 to 1.81 µg/kg in sediment, water and fish respectively. Concentrations of dichlorovos was the highest in the samples; with the highest and lowest levels also recorded in sediment (1.84±0.02) and water (1.79±0.01 µg/kg) respectively. Level of OPPs Analysis of Variance (ANOVA) shows that the concentrations of OPPs in sediment and fish were not significantly different ($p \leq 0.05$) except for dichlorovos, triazophos and fenitrothion. Correlations for OPPs in sediment and water were almost perfectly positive (0.919 – 0.999) except for methidathion which was negatively weak (- 0.331). Between sediment and fish samples, correlations varied from negatively strong to moderately positive were weak and negative (-0.81 to 0.500). Concentrations of OPPs were within the FAO/WHO acceptable limits. However, strict law enforcement is still needed to manage the environmental hazards as a result of this toxic chemicals, for the protection of the aquatic ecosystem.*

Keywords:*Accumulation, Organophosphate, Pesticides, Aquatic environment.*

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I. Introduction

Environmental pollution is the introduction of harmful contaminants to the environment through various means such as gases, liquids and wastes, thereby making the surrounding unhealthy for living organisms. Because of the widespread of these contaminants (organic or inorganic), the ecosystem is at great risk[1]. The majority of these pollutants most especially the organic (herbicides and insecticides) are potentially toxic for organisms some being connected to disease development, including cancer and other related diseases in humans[2, 3, 4].

Organophosphates are insecticides containing phosphorus. They are often called organic phosphates, phosphorus insecticides, nerve gas relatives, phosphates, phosphate insecticides, and phosphorus esters or phosphoric acid esters[5]. Organophosphates (OPP) are less persistent in the environment than the organochlorine pesticides, because they are relatively soluble in water, and are mobilized by precipitation therefore, they tend to have virtually replaced the persistent organochlorine compounds[6, 7]. This research, therefore evaluates the levels of OPPs in water, sediment and fish samples in Loko River.

II. Materials and Methods

Description of Study Area

Loko in Nasarawa State of Nigeria is located on latitude 7^0 59' N /7^0 49 E and on longitude 7.983^0 N /7.817^0 E. The main activities of these communities especially in rainy season is farming and fishing.

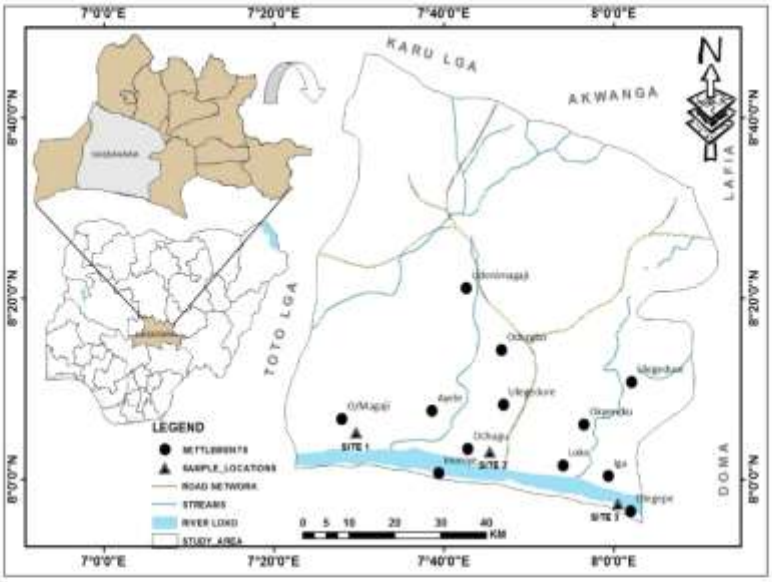

Figure 1: Map of Loko showing River Benue at Loko catchment

Samples Collection

Water samples were collected at 3 locations into clean 1L plastic bottles with screw cap preserved in ice-cold boxes at 0-4 properly washed 1L plastic containers from each of the sampling points in rainy season (July-August). The samples were immediately preserved in cold boxes at 0-4^o C.

Surface sediment samples were collected from the 3 sites at a depth of 0-20 cm along the bank of the river using Teflon coated spoon and wrapped in aluminum foil. Fish samples from the river were bought from fishermen and sorted out to sizes for uniformity. Fish of similar sizes were sorted out for uniformity. The fish samples were transported to laboratory in ice boxes.

Sample Extraction and Clean-up Process

Liquid-liquid extraction of OCPs in fish water and sediment sample were carried out according to [8]. The clean-up process was achieved by passing the extract to a chromatography column containing an anhydrous sodium sulphate and eluted with the acetonitrile and then concentrated to $5cm^3$ of the eluent[9]. The sample was then injected into gas chromatography coupled with electron capture detector (GC-ECD), model HP 6890, powered with ChemStation Rev. A09.01, for quantification of OCPs.

Quality Control

Quality control measures were assured through analysis of solvent blanks, method blanks which include reagents and all procedures on the blank as performed for all samples in the batch as evidence that the procedure will performed as validated in the absence of matrix effects. Each sample was analyzed in triplicate and mean concentration were calculated. Calibration curves were determined for the samples.

Statistical Analysis

Data collected were subjected to simple statistics (mean and standard deviation), ANOVA and Pearson Correlation matrix using Microsoft Excel and statistical package for Social Sciences (SPSS) computer software.

III. Results

Concentrations of OPPs in sediments (Table 1), ranges from (0.09 to 1.86 µg/kg), at site 2 and the lowest at site 3 (0.10 to 1.82 µg/kg).According to sampling points, the levels of OPPs varied in the order of site II > site I > Site III. Concentrations of organophosphorus pesticide residues in water (Table 2) sample were highest at site 2, with moderate concentration at site 1, while the lowest concentrations were recorded at site 3. Concentration of phosphamidon increased progressively from site I to site III. Generally, Concentration of OPPs in water varied in the order of site 2 > site 1 > site 3. The most abundant pesticide residues recorded in fish (Table 3) was dichlorvos (1.81 µg/kg), while the lowest level was in phosphamidon (0.01 µg/kg).

Pesticide	Molecular Structure	Sampling Points			Mean±SD
		1	2	3	
Phosphine	PH_3	1.42	1.61	1.30	1.44±0.13
Dichlorovos	$C_4H_7Cl_2O_4P$	1.84	1.86	1.82	1.84±0.02
Triazovophos	$C_{12}H_{16}N_3P_5$	0.26	0.34	0.21	0.27±0.05
Methidathion	$C_6H_{11}N_2O_4PS_3$	0.16	0.23	0.10	0.16±0.05
Fenitrothion	$C_9H_{12}NO_5PS$	0.66	0.74	0.61	0.67±0.05
Phosphamidon	$C_{10}H_{19}ClNO_5P$	0.04	0.09	0.15	0.09±0.04
Profenofos	$C_{11}H_{15}BrClO_3P_5$	0.25	0.31	0.20	0.25±0.04
Malathion	$C_{10}H_{19}O_6PS_2$	0.27	0.33	0.22	0.27±0.04
Chlorpyrifos	$C_9H_{11}C_{13}NO_3$	0.36	0.41	0.31	0.36±0.04
Primiphosmethyl	$C_{11}H_{20}N_3O_3PS$	0.61	0.68	0.53	0.61±0.06

Table 1: Concentrations of Organophosphate Pesticides in Sediment (µg/Kg)

Table 2: Concentrations of Organophosphate Pesticides in Water (µg/Kg)

Pesticide	Molecular Structure	Sampling Points			Mean±SD
		1	2	3	
Phosphine	PH_3	1.06	1.18	1.03	1.09±0.06
Dichlorovos	$C_4H_7C_{12}O_4P$	1.79	1.81	1.78	1.79±0.01
Triazovophos	$C_{12}H_{16}N_3P_5$	0.10	0.15	0.05	0.10±0.04
Methidathion	$C_6H_{11}N_2O_4PS_3$	0.00	0.05	0.08	0.04±0.03
Fenitrothion	$C_9H_{12}NO_5PS$	0.53	0.58	0.48	0.53±0.04
Phosphamidon	$C_{10}H_{19}ClNO_5P$	0.05	0.10	0.20	0.11±0.06
Profenofos	$C_{11}H_{15}BrClO_3P_5$	0.10	0.15	0.05	0.10±0.04
Malathion	$C_{10}H_{19}O_6PS_2$	0.15	0.17	0.06	0.12±0.05
Chlorpyrifos	$C_9H_{11}Cl_3NO_3$	0.20	0.26	0.15	0.20±0.04
Primiphosmethyl	$C_{11}H_{20}N_3O_3PS$	0.38	0.46	0.31	0.38±0.06

Table 3: Concentrations of Organophosphate Pesticides in Fish (µg/Kg)

Pesticide	Molecular Structure	Concentration
Phosphine	PH_3	1.18
Dichlorovos	$C_4H_7Cl_2O_4P$	1.81
Triazophos	$C_{12}H_{16}N_3P_5$	0.15
Methidathion	$C_6H_{11}N_2O_4PS_3$	0.16
Fenitrothion	$C_9H_{12}NO_5PS$	0.61
Phosphamidon	$C_{10}H_{19}ClNO_5P$	0.01
Profenofos	$C_{11}H_{15}BrClO_3P_5$	0.23
Malathion	$C_{10}H_{19}O_6PS_2$	0.27
Chlorpyrifos	$C_9H_{11}Cl_3NO_3$	0.36
Primiphosmethyl	$C_{11}H_{20}N_3O_3PS$	0.57

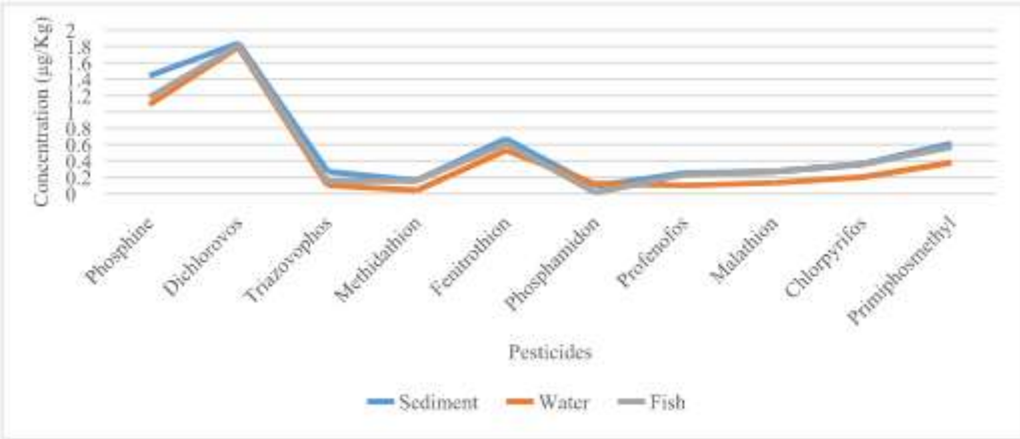

Figure 1: Variations in mean concentrations (µg/kg) of Organophosphate pesticide residues in sediment, water and fish samples.

Table 4: ANOVA for Organophosphate Pesticide Residues (OPPs) in Sediment, Water and Fish Samples

	Samples		
Pesticides	Sediment	Water	Fish
Dichlorovos	1.840^{b}	1.793^{a}	1.810^{ab}
Triazophos	0.270^{b}	0.100^{a}	0.150^{ab}
Methidathion	0.163^{b}	0.043^{a}	0.160^{b}
Fenitrothion	0.670^{b}	0.530^{a}	0.610^{ab}
Phosphamidon	0.933^{b}	0.117^{b}	0.010^{b}
Profenofos	0.253^{b}	0.100^{a}	0.230^{b}
Malathion	0.273^{b}	0.127^{a}	0.270^{b}
Chlorpyrifos	0.360^{b}	0.203^{a}	0.360^{b}
Primiphosmethyl	0.607^{b}	0.383^{a}	0.570^{b}

Table 5: Pearson correlation matrix (Correlation coefficient (r)) for OPP residues in water, sediment and fish samples from Benue River at Loko.

Pesticides	Sediment / Water	Sediment / Fish	Water / Fish
Phosphine	0.979	-0.384	-0.189
Dichlorovos	0.982	-0.500	-0.327
Triazophos	0.991	-0.381	-0.500
Methidathion	-0.331	-0.461	0.990
Fenitrothion	0.991	-0.381	-0.500
Phosphamidon	0.991	0.999	0.982
Profenofos	0.999	-0.454	-0.500
Malathion	0.919	-0.454	-0.768
Chlorpyrifos	0.919	-0.454	-0.768
Primiphosmethyl	0.999	-0.500	-0.454

Level of significance ($p \leq 0.05$)

IV. Discussion

The concentration of phosphamidon increased downstream. The most abundant organophosphate pesticide residue recorded was dichlorovos with mean concentration of 1.84±0.02 µg/kg, while phosphamidon recorded the lowest level (0.09±0.04 µg/kg). The concentration of chloropyrifos (0.31 to 0.41 µg/kg), dichlorovos (1.82 to 186 µg/kg), and fenitrothion (0.61 to 0.74 µg/kg) obtained in this research were similar to the results reported for Alao Dam, Borno State[10], where the concentrations of chloropyrifos ranged from 0.34 to 1.89 µg/kg, dichlorvos 0.11 to 1.23 µg/kg and 0.23 to 1.54 µg/kg for fenithrothion. Also, the concentration of chlorpyrifos (5.0371±1.4220 ppm) recorded in this research was lower compared to that reported for Deomoni River of West Bengal India[11]. Levels of pirimiphos-methyl (0.61±0.06 µg/kg) and chlorpyriphos (0.36±0.04 µg/kg) in this research were lower compared to the levels 0.080 ± 0.046 µg/g and 0.160 ± 0.037 µg/g respectively reported for Tono Reservoir, Ghana[12].

The low concentration of OPPs in water could probably be due to easy decomposition, hence, less persistence in the environment[13]. Among the detected OPPs residues, dichlorovos recorded the highest mean concentration (1.79±0.02 µg/kg,) while methidathion recorded the lowest mean concentration of 0.04±0.03 µg/kg (Table 2). The levels of pirimiphos-methyl (0.383 µg/kg) and chlorpyriphos(0.203 µg/kg) were higher compared to the results obtained from Tono Reservoir, Ghana[12].

The mean concentration of chlorpyriphos in water reported in this study (0.203 ± 0.04µg/kg) was lower compared to the result reported for Deomoni River of West Bengal India[11].

The concentrations of all the OPPs determined in this study were within the acceptable limit for drinking water[14].

Organophosphorus pesticides are lipophilic, hence, the tendency to concentrate in lipid rich tissues of aquatic organisms[15].

Concentration of chorpyrifos (0.36 µg/kg) reported in this study was lower compared to the results (0.77 to 2.22 µg/g) reported for Alao Dam Borno State, Nigeria[10]. Concentrations of OPPs obtained in this research were lower compared to fish samples from Fosu and Etsi Lagoon in Ghana[15]. High concentration of dichlorvos in fish sample may be as a result of the recent used of this pesticide. Accumulation of these pesticides in fish is a function of their membrane permeability and enzyme system, and may originate from pesticides deposited in the sediments and food in the aquatic environment[10].

Comparison of concentrations of OPPs (Figure 2) varied in the order of sediment > fish > water. OPP with the highest concentration was dichlorovos, which ranged from 1.82 to 1.86 µg/kg in sediment, 1.78 to 1.81 µg/kg in water and 1.81 µg/kg in fish. The lowest concentration was recorded for phosphamidon, which varried from 0.04 to 0.09 µg/kg in sediment, 0.05 to 0.1 µg/kg in water and 0.01 µg/kg in fish. The result of this study is not in congruence with the results reported for Yala/Nzoia River, Kenya[16], where OPPs were not detected in water and sediment samples except for diazinon and malathion.

Analysis of variance (NOVA) (Table 4) shows that the concentrations of OPPs in sediment and fish were not significantly different ($p \leq 0.05$) except for dichlorovos, triazophos and fenitrothion. Correlations for OPPs (Table 5) in sediment and water were almost perfectly positive (0.919 – 0.999) except for methidathion (-0.331). For sediment and fish, correlations were weak and negative (-0.81 – 0.500) except for phosphamidon which had a very strong and positive correlations (0.999). Correlations for methidathion (0.990) and phosphamidon (0.982) in water and fish were also positively strong. Correlation for phosphamidon in all the samples were strong and positive (0.991 – 0.999). Organic matter (OM) content in sediments and water might have influenced the retention of the organochlorine and organophosphate pesticide molecules. This is also in congruity with the results reported for three major cocoa - producing Local Governments within the Ondo State Central Senatorial District, Nigeria[17].

V. Conclusion

The present study shows that River Loko, one of the major rivers in Nasarawa LGA of Nasarawa State, was contaminated with organochlorine pesticides. It is also very much clear that the order of concentrations of these pesticides in this river varied in the order of sediment > fish >water. Concentrations of OPPs were within the FAO/WHO acceptable limits. Regular monitoring of OPPs accumulation in the aquatic ecosystem becomes necessary to avert any unprecedented health hazard that may occur overtime from consumption of fish from the river.

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