International Journal of Advances in Scientific Research and Engineering (ijasre)

E-ISSN : 2454-8006

DOI: 10.31695/IJASRE.2022.8.4.6

Volume 8, Issue 4
April - 2022

Study of Organochlorine Pesticide Residues Analysis in Water, Fish and Sediment using GC-ECD in River Loko, Nasarawa State, Nigeria

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ABSTRACT

Levels of organochlorine pesticide (OCPs) residues in sediment, water and fish in River Loko, Nasarawa State, Nigeria, were evaluated for possible pollution of the aquatic system. Water and sediment samples were collected from the river at 3 locations. Fish caught in the river were bought from fishermen at the bank of the river. The samples were collected in rainy season and preserved according to standard methods. Liquid-liquid extractions of samples were carried out, and then quantified using Gas Chromatography Coupled with Electron Capture Detector (GC-ECD). The OCPs levels ranged from 0.06 to 1.53 µg/Kg in sediment, 0.03 to 1.34 µg/Kg in water and 0.02 to 1.34 µg/Kg in fish. 2, 4-Dichlorophenoxacetic acid (2,4-D) was the most accumulated OCP in sediment (1.64±0.10 µg/Kg), water (1.34±0.08 µg/Kg), and fish (1.34 µg/Kg). Concentrations of OCPs generally varied in the order of sediment > water > water ~ fish. ANOVA shows that concentrations of OCPs in water and fish were significantly ($p \leq 0.05$) lower compared to sediment, except for mecoprop, imidacloprid, 2,4-D, and aldrin, which were not significantly different in the samples. Pearson correlation matrix for OCPs in water and sediment show moderate to very strong and positive correlations except for mecoprop (-0.705), alachlor (-0.217), imidacloprid (-0.082), permethrin (-0.339) and aldrin (-0.795). Concentrations of OCPs were within the FAO/WHO acceptable limits except for aldrin, mecoprop, metolachlor, simazine, DDT and dieldrin. Regular monitoring of the quality of River Loko becomes necessary due to accumulation of OCPs.

Keywords: Accumulation, Organochlorines, Pesticides, Aquatic Environment.

1. INTRODUCTION

Pesticides are very important group of environmental pollutants used intensively in agriculture for protection against diseases and pests. The estimated annual application of pesticides is more than 4 million tons, but only 1% of this target pest [1]. Though they improve the quantity of agricultural products, but can potentially affect their quality. This however, posed a potential risk to humans and other life forms as food chain grows among the ecosystem [2]. Pesticides may be grouped as the organochlorines, organophosphate and carbamates.

Organochlorine pesticides (OCPs) are compounds that contain carbon, chlorine, and hydrogen, with high solubility in water, and are lipohilic in nature [3]. Organochlorines are persistent in the environment because they resist biodegradation. The organochlorines can bioaccumulate in aquatic organisms, marine mammals, fish and humans through food chain, depending on their hydrophobic properties [4]. Among the organochlorine pesticides, the DDT and HCH have been listed as the top-most persistent organic pollutants, because of their remarkable toxic properties and acute poisoning with anti-estrogenic (androgenic) activity [5]. OCPs can accumulate in water, sediment, and fish, with some ecological effects [6]. This research, therefore evaluates the levels of OCPs in water, sediment and fish samples from the study area.

2. MATERIALS AND METHODS

2.1 Description of Study Area

River Loko in Nasarawa State of Nigeria is located on latitude 7^0 59’ N -$7^0$49 E and on longitude 7.983^0N -7.817^0E. Farming and fishing are the major anthropogenic activities that take place along the river, especially in rainy season.

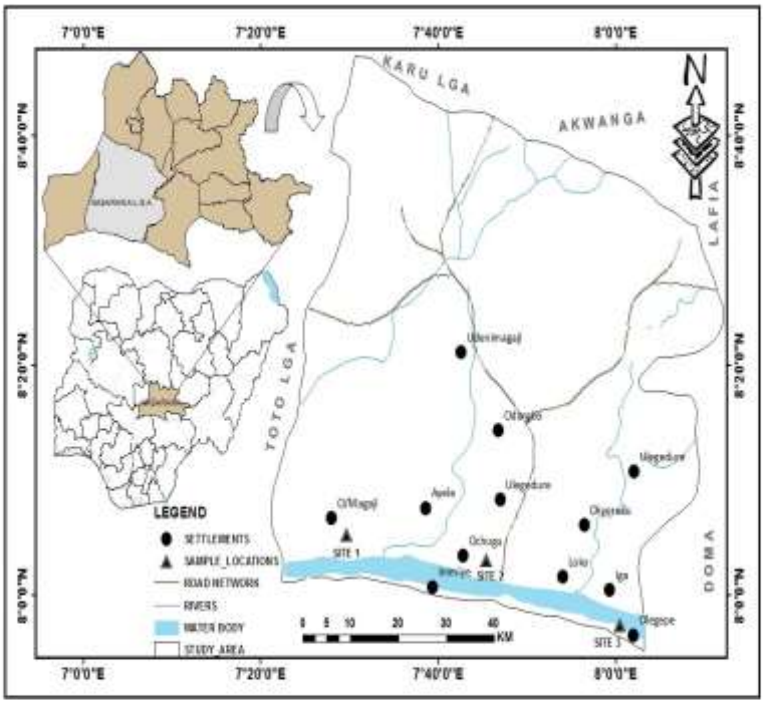

Figure 1: Add Figure caption

2.2 Samples Collection

Water samples were collected at 3 locations into clean 1L plastic bottles with screw cap and preserved in ice-cold boxes at 0 - 4 ºC. Surface sediment samples were also collected into clean polythene bags from the 3 sites at a depth of 0-20 cm in the river using Teflon coated spoon, and wrapped in aluminum foil. Fish samples from the river were bought from fishermen and sorted out according sizes for uniformity. The fish samples were transported to laboratory in ice boxes.

Sample Extraction and Clean-up Process

Liquid-liquid extractions of OCPs in fish, water and sediment samples were carried out according to the AOAC (2007) [7]. The clean-up process was achieved by passing the extract through a chromatography column containing anhydrous sodium sulphate and eluted with the acetonitrile, and then concentrated to 5 cm^3 (US EPA Method 1699 2007) [8]. The sample was then injected into Gas Chromatograph coupled with electron capture detector (GC-ECD), model HP 6890, powered with ChemStation Rev. A09.01, for the quantification of OCPs.

Quality Control

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

3. RESULTS AND DISCUSSION

Concentrations of OCPs in sediment (Table 1) ranged from 0.04 µg/kg to 1.23 µg/kg at site 1, 0.20 µg/kg to 1.38 µg/kg at site 2, and 0.003 µg/kg to 1.38 µg/kg at site 3. The highest concentrations of OCPs were recorded at site 2. This might be attributed to an increase in discharge from the many farmlands around the site into the river. The results also show that 2,4-D had the highest concentrations across the three sites. This may also suggest higher agricultural activities at site 2, involving high applications of different kind of pesticides on the farms in the area including 2,4-D. The present study has shown that concentrations of aldrin (0.26µg/kg), dieldrin 0.59µg/kg and methoxyclor (1.04 µg/kg) were lower compared to that reported for Yala/Nzoia River, within Lake Victoria Basin, Kenya[9]. Also, the mean concentrations of aldrin (0.26±0.08 µg/kg) reported in this study was higher

DOI: 10.31695/IJASRE.2022.8.4.6

compared to the result (0.090 ± 0.050 µg/g) reported for Tono Reservoir [10]. Concentrations of aldrin and dieldrin were above the FAO/WHO acceptable limits [11].

The concentrations of OCPs in water (Table 2) ranged from 0.03 µg/kg to 1.34 µg/kg at site 0.008 µg/kg to 1.44 µg/kg at site 2, 0.008 µg/kg to 1.25 µg/kg at site 3. Concentration of OCPs at the different sites varied in the order of site II > site I > site III, except for alachlor and mecoprop. The discharge of agro-chemicals from flood plains and agricultural fields through agricultural runoff might have contributed to the elevated pesticide concentration at site II. The present result is in accordance with that reported for river Ganga Bhagalpur, India [12]. Concentration of DDT obtained in this work was higher compared to 0.016 ppb reported for Lake Parishan, Iran [13]. However, the concentration of aldrin (0.021 mg/kg) and dieldrin (0.105 mg/kg) were higher than the result reported for three major cocoa - producing Local Governments within the Ondo State Central Senatorial District, Nigeria [14]. Concentrations of aldrin (0.1 µg/kg) and dieldrin 0.31 µg/kg) recorded were higher than the acceptable limit for drinking water FA/WHO (2011) [11].

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

Pesticides	**Molecular Structure**	**Sampling Points** 1	2	3	**Mean±SD**
Bromoethane	C_2H_5Br	1. 23	1.38	1.13	1.26±0.13
Simazine	$C_7H_{12}ClN_5$	1.56	1.74	1.44	1.58±0.12
2,4,6-trichlorophenol	$C_6H_2Cl_3OH$	1.23	1.38	1.13	1.25±0.10
Chlorotoluron	$C_{10}H1_3ClN_2O$	1.10	1.21	1.03	1.11±0.07
Mecoprop	$C_{10}H_{11}ClO_3$	0.48	0.52	0.46	0.49±0.02
2,4-D	$C_8H_6Cl_2O_3$	1.62	1.77	1.53	1.64±0.10
Imidacloprid	$C_9H_{10}ClN_5O_2$	0.12	0.20	0.06	0.13±0.06
Dichloroprop	$C_9H_8ClO_3$	0.33	0.41	0.28	0.34±0.05
Pentachlorophenol	C_6HCl_5O	0.49	0.60	0.42	0.50±0.07
Fenoprop	$C_9H_7ClO_3$	0.92	1.04	0.84	0.93±0.08
Alachlor	$C_{14}H_{20}ClNO_2$	0.27	0.39	0.19	0.28±0.08
Acetochlor	$C_{14}H_{20}ClNO_2$	0.25	0.33	0.20	0.26±0.05
DDT	$C_{14}H_9Cl_5$	0.27	0.34	0.21	0.27±0.05
Endosulfan	$C_9H_6Cl_6O_3S$	0.31	0.38	0.23	0.31±0.06
Methoxychlor	$C_{16}H1_{15}Cl_3O_2$	0.79	0.85	0.73	0.79±0.05
Aldrin	$C_{12}H_8Cl_6$	0.27	0.35	0.15	0.26±0.08
Dieldrin	$C_{12}H_8Cl_6O$	0.59	0.68	0.49	0.59±0.08
Metolachlor	$C_{15}H_{22}ClNO_2$	1.03	1.11	0.98	1.04±0.05
Permethrin	$C_{21}H_{20}Cl_2O_3$	0.04	0.20	0.003	0.08±0.09

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

Pesticide	**Molecular Structure**	**Sampling Points** 1	2	3	**Mean±SD**
Bromoethane	C_2H_5Br	0.93	1.10	0.69	0.91±0.17
Simazine	$C_7H_{12}ClN_5$	1.20	1.32	1.02	1.18±0.12
2,4,6-trichlorophenol	$C_6H_2Cl_3OH$	0.94	1.03	0.83	0.93±0.08
Chlorotoluron	$C_{10}H1_3ClN_2O$	0.96	0.99	0.85	0.93±0.06
Mecoprop	$C_{10}H_{11}ClO_3$	0.40	0.43	0.76	0.53±0.16
2,4-D	$C_8H_6Cl_2O_3$	1.34	1.44	1.25	1.34±0.08

DOI: 10.31695/IJASRE.2022.8.4.6

Imidacloprid	$C_9H_{10}ClN_5O_2$	0.06	0.01	0.01	0.03±0.02
Dichloroprop	$C_9H_8ClO_3$	0.17	0.22	0.12	0.17±0.04
Pentachlorophenol	C_6HCl_5O	0.27	0.34	0.20	0.27±0.06
Fenoprop	$C_9H_7ClO_3$	0.69	0.77	0.65	0.70±0.05
Alachlor	$C_{14}H_{20}ClNO_2$	0.03	0.11	0.15	0.10±0.05
Acetochlor	$C_{14}H_{20}ClNO_2$	0.10	0.15	0.04	0.10±0.04
DDT	$C_{14}H_9Cl_5$	0.11	0.16	0.06	0.11±0.04
Endosulfan	$C_9H_6Cl_6O_3S$	0.08	0.16	0.01	0.08±0.06
Methoxychlor	$C_{16}H1_{15}Cl_3O_2$	0.54	0.60	0.48	0.54±0.05
Aldrin	$C_{12}H_8Cl_6$	0.03	0.07	0.19	0.10±0.07
Dieldrin	$C_{12}H_8Cl_6O$	0.31	0.4	0.22	0.31±0.07
Metolachlor	$C_{15}H_{22}ClNO_2$	0.87	0.92	0.82	0.87±0.04
Permethrin	$C_{21}H_{20}Cl_2O_3$	0.07	0.02	0.02	0.04±0.02

The concentration of OCPs in fish (Table 3) ranged from 0.02 µg/kg to 1.34 µg/kg, with the highest and lowest levels recorded for 2,4-D (1.34 µg/kg) and permethrin (0.02 µg/kg) respectively. Concentration of aldrin (0.19 µg/kg) and dieldrin (0.54 µg/kg) were above the FAO/WHO acceptable limits [11]. Feeding on sediment and continuous interaction with water by the fish might be responsible for the increase in levels of OCPs. Research has shown that aldrin is readily converted into dieldrin in plant and animal tissues in the environment by photolysis [15]. The concentration of DDT reported in this research was lower than the result reported for fish sample in Lake Bosomtwi of Ghana and Lake Parishan, Iran, respectively [4,13].

Comparison in the levels of OCPs (Figure 1) shows that accumulation in the samples varied in the order of sediment > fish > water. 2, 4-D had the highest concentration in all the samples, varying from 1.52 to 1.77 µg/kg in sediments, 1.25 to 1.44 µg/kg in water and 1.34 µg/kg in fish; while permethrin recorded the lowest concentration. The trend revealed that OCPs present in water will preferably be adsorbed to sediment or bioaccumulate in fish due to low water solubility and high affinity for fat [16] [17]. Pesticides enter fishes not only by ingestion but also through integument absorption and respiration [18]. This research is in agreement with the results reported for lake Parishan, Iran [13].

ANOVA (Table 4) shows that concentrations of OCPs in water were significantly ($p \leq 0.05$) lower compared to sediment, except for the levels of mecoprop, imidacloprid and permethrin that were not significantly different in the three samples. Concentrations of bromoethane, simazine, chlorotoluron, endosulfan, methoxychlor, dieldrin and metolachlor in fish and water were not significantly different ($p \leq 0.05$). Pearson correlation coefficients (Table 5) between water and sediment show moderate to very strong and positive correlations except for mecoprop (-0.705), alachlor (-0.217), imidacloprid (-0.082), permethrin (-0.339) and Aldrin (-0.795). Correlations between sediment and fish were generally weak and negative. However, between fish and water the correlations for mecoprop (0.901) and Aldrin (0.961) were positively strong. Strong and positive correlations may imply similar sources and mechanism, suggesting anthropogenic origin for the OCPs in the aquatic ecosystem

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

Pesticide	Molecular Structure	Concentration
Bromoethane	C_2H_5Br	1.18
Simazine	$C_7H_{12}ClN_5$	1.32
2,4,6-trichlorophenol	$C_6H_2Cl_3OH$	0.93
Chlorotoluron	$C_{10}H1_3ClN_2O$	1.03
Mecoprop	$C_{10}H_{11}ClO_3$	0.44
2,4-D	$C_8H_6Cl_2O_3$	1.34
Imidacloprid	$C_9H_{10}ClN_5O_2$	0.14
Dichloroprop	$C_9H_8ClO_3$	0.20
Pentachlorophenol	C_6HCl_5O	0.31
Fenoprop	$C_9H_7ClO_3$	0.69
Alachlor	$C_{14}H_{20}ClNO_2$	0.11
Acetochlor	$C_{14}H_{20}ClNO_2$	0.12

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DDT	$C_{14}H_9Cl_5$	0.14
Endosulfan	$C_9H_6Cl_6O_3S$	0.27
Methoxychlor	$C_{16}H1_{15}Cl_3O_2$	0.73
Aldrin	$C_{12}H_8Cl_6$	0.19
Dieldrin	$C_{12}H_8Cl_6O$	0.54
Metolachlor	$C_{15}H_{22}ClNO_2$	1.00
Permethrin	$C_{21}H_{20}Cl_2O_3$	0.02

Table 4: ANOVA for Organochlorine (OCPs) in Sediment, Water and Fish samples

Pesticides	Samples		
	Sediment	**Water**	**Fish**
Bromoethane	1.247^{b}	1.017^{a}	1.180^{ab}
Simazine	1.580^{b}	1.180^{a}	1.323^{ab}
2,4,6-trichlorophenol	1.247^{b}	0.933^{a}	0.930^{a}
Chlorotoluron	1.113^{b}	0.933^{a}	1.030^{ab}
Mecoprop	0.487^{a}	0.530^{a}	0.440^{a}
2,4-D	1.640^{a}	1.343^{a}	0.938^{a}
Imidacloprid	0.267^{a}	0.027^{a}	0.137^{a}
Dichloroprop	0.327^{b}	0.170^{a}	0.200^{ab}
Pentachlorophenol	0.503^{b}	0.270^{a}	0.310^{a}
Fenoprop	0.937^{b}	0.703^{a}	0.690^{a}
Alachlor	0.283^{b}	0.097^{a}	0.110^{a}
Acetochlor	0.260^{b}	0.097^{a}	0.120^{a}
DDT	0.273^{b}	0.110^{a}	0.140^{a}
Endosulfan	0.307^{b}	0.083^{a}	0.270^{b}
Methoxychlor	0.790^{b}	0.540^{a}	0.730^{b}
Aldrin	0.257^{a}	0.097^{a}	0.190^{a}
Dieldrin	0.587^{b}	0.310^{a}	0.540^{b}
Metolachlor	1.040^{b}	0.870^{a}	1.000^{b}
Permethrin	0.081^{a}	0.037^{a}	0.020^{a}

Values with different superscript on the same row are significantly different ($p \leq 0.05$).

Table 5: Pearson correlation matrix for OCP residues in water, sediment and fish samples from River Loko

Pesticide	Correlation Coefficients (r)		
	Sediment / Water	Sediment / Fish	Water / Fish
Bromoethane	0.568	-0.397	0.529
Simazine	0.974	-0.803	-0.918
2,4,6-trichlorophenol	0.985	-0.397	-0.549
Chlorotoluron	0.902	-0.386	-0.746
Mecoprop	-0.705	-0.327	0.901
2,4-D	0.994	-0.934	-0.888
Imidacloprid	-0.082	0.082	-1.000
Dichloroprop	0.999	-0.529	-0.500
Pentachlorophenol	0.992	-0.386	-0.500

DOI: 10.31695/IJASRE.2022.8.4.6

Fenoprop	0.991	-0.449	-0.327
Alachlor	-0.217	-0.397	0.982
Acetochlor	0.983	-0.381	-0.545
DDT	0.999	-0.461	-0.500
Endosulfan	0.997	-0.533	-0.466
Methoxychlor	1.000	-0.500	-0.500
Aldrin	-0.795	-0.596	0.961
Dieldrin	1.000	-0.500	-0.500
Metolachlor	0.991	-0.381	-0.500
Permithrin	-0.339	-0.177	-0.866

Level of significance ($p \leq 0.05$)

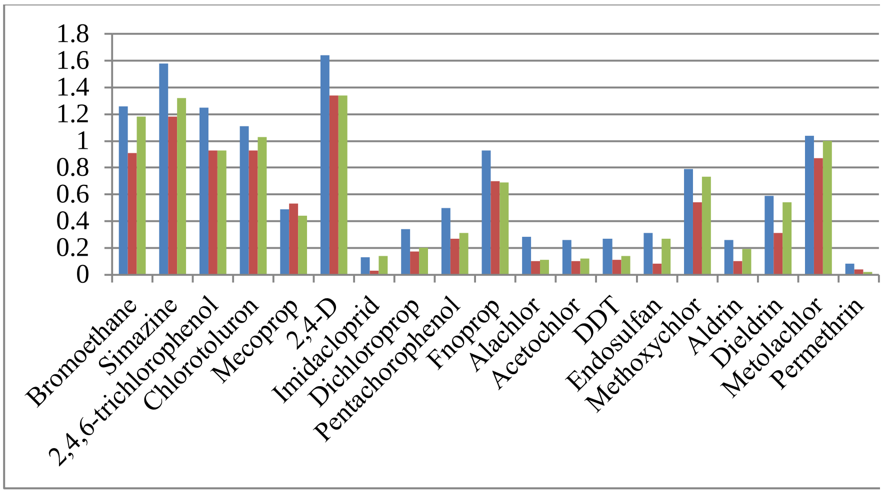

Figure 2: Variations in mean concentrations (µg/kg) of Organochlorine pesticide residues in sediment, water and fish samples.

4. CONCLUSIONS

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 OCPs were within the FAO/WHO acceptable limits except for aldrin and dieldrin. Regular monitoring of OCPs 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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DOI: 10.31695/IJASRE.2022.8.4.6