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Original Research Article

Organochlorine Pesticide Residues Level in Fish, Water and Sediments in South-South Nigeria

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Abstract: This study reveals the distribution and levels of the organochlorine pesticide residues in fish, water and sediments in South-South, Nigeria. They were extracted with dichloromethane and screened for organochlorine pesticides with Gas Chromatography-Mass Spectrophotometry (GC-MS). All data collected were exposed to analysis of variance at ($p<0.05$) and the means were separated by means of Duncan Multiple Range Test (DMRT). It was discovered in this study that organochlorine pesticide residues were not discovered in all the fish and water sampled, while there was significant difference ($P<0.05$) in the levels of some organochlorine pesticides detected in the sediments. Sediment samples from Oron in Akwa-Ibom State recorded 1.50±0.25 µg/kg and 30.80±0.20 µg/kg for lindane and aldrin residues respectively; Mkpana Beach (Akwa-Ibom State) had lindane (3.70±0.20 µg/kg), aldrin (4.20±0.20 µg/kg), endosulfan (0.60±0.30 µg/kg) and ortho-para-dichloro-diphenyl-trichloro ethane (o,p'- DDT) (0.20±0.10 µg/kg). Illushin and Agenebode in Edo State had 0.10±0.02 µg/kg and 1.00±0.30 µg/kg of aldrin residues correspondingly. They were all above the allowable limit of 0.05 µg/kg recommended by Environmental Protection Agency (EPA). The pesticide-free fish and water could be as a result of the fact that the Fisher folks no longer use pesticides in fishing due to the awareness of the imminent dangers involved. However, the high levels of Pesticide residues in sediments may be as a result of overtime bioaccumulation of extensive and repeated use of the pesticides in fishing.

Keywords: Organochlorine Pesticide; Fish, Sediment; Water; GC/MS; South-South Nigeria.

INTRODUCTION

Pesticide residues are substances in foods meant for man or animals consequential from the use of pesticide comprising of derivatives, such as impurities and contaminants known to be hazardous [1]. Organochlorines are tenacious contaminants that have triggered global attention as one of the most toxic environmental pollutants [2]. They are lipophillic, have affinity for water and are found everywhere because of their persistence in nature, stemming from water currents and other anthropogenic passageways [3]. Organochlorine pesticides have extensively used in the world and have been found in foodstuffs, water, fish and sediments [4, 5].

The production as well as usage of most pesticides have been proscribed in most nations but are still in use by majority of the uncivilized nations by health and agricultural sectors [6].

Most fishermen, farmers have abused their use for the purpose of agriculture [4]. Chlorinated pesticides residues can enter aquatic ecosystem via discharges of effluents and domestic sewage and industrial wastewater and so on [7]. Pesticide residues could be dispersed amongst water sediments and fish components of the ecosystem. Most studies on humans and experimental animals prove the toxic potential of contact to organochlorine pesticides [8, 9].

This study was therefore aimed at determining the amounts and distributions of organochlorines residues in fish, water and sediments in South-South, Nigeria.

MATERIALS AND METHODS

Collection of fish Samples

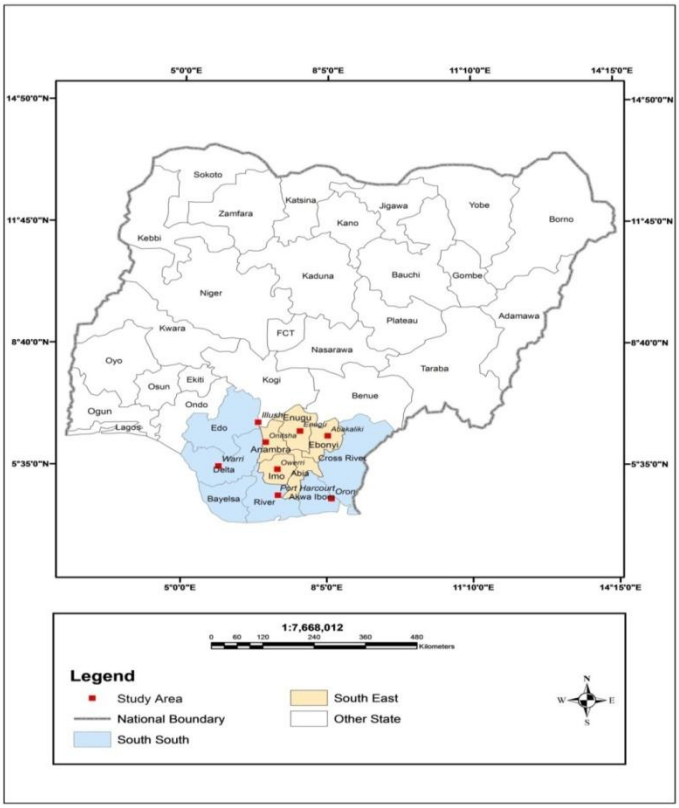
Fish samples were captured with the assistance of artisanal fishermen using local fish traps, cast nets and baited hooks. Fish were washed in flowing water to eliminate adhering debris before they were conveyed to the laboratory within 24 hours in an ice chest.

Collection of Water samples

Surface water samples were taken from three sampling stations (1-downstream, 2-midstream and 3-upstream) from each water body at 30 cm depth into amber glass bottles (2 ml) already washed using detergents, rinsed with distilled water, soaked overnight in 10 % nitric acid and finally rinsed using distilled water. Water samples were taking from three sampling stations each from Koko, Ekehuan, Illushin, Agenebode, Old Nigeria Port Authority (NPA), Brass, Choba, Oron water bodies. All the samples of water were acidified using 5 ml of 10 % nitric acid to minimize adsorption of heavy metals to the walls of the plastic bottles [10].

Collection of Sediment Samples

Samples of sediment were taken from three sampling stations of the selected water bodies in the study areas using an Eckman's grab to get and put the samples into plastic bags. The plastic bags were initially cleaned using detergents and treated with 10 % nitric acid. They were dehydrated at 105^0C in a kiln to a constant weight and ground to powder. The powder samples were sieved through a 0.5 mm sieve to remove ungrounded materials. 1 g of the fine filtrate was digested and subsequently analyzed [10].



Extraction Procedure of Water Samples

Water sample of 250 ml was measured into an already washed separating funnel. 20 ml of dichloromethane was poured in the separating funnel, after which, it was covered and vigorously shaken for 30 mins while the cover of the separating funnel was open and closed intermittently to expel gas from it. The extract was then recovered from dichloromethane and the process was repeated thrice to ensure complete extraction [11]. The extract was taken for cleaning to remove impurities.

Extraction Procedure of Sediment Samples

The grounded sample of 10g was extracted in a Soxhlet apparatus with 150ml dichloromethane for 3 hrs. at a temperature of 40^0C [12]. The dichloromethane containing the extract was left overnight to dry. The extract was weighed and taken for cleaning.

Extraction Procedure of Fish Samples

The crushed sample of 20g was extracted in a Soxhlet apparatus with 150ml dichloromethane for 3 hrs. at a temperature of 40^0C [12]. The dichloromethane containing the extract was left overnight to dry. The extract was weighed and taken for cleaning.

Clean-up Procedures of the Extracts

The extract from fish, water and sediment samples were cleaned-up (Solid Phase Extraction) using a short column (15cm) diameter silica gel (200-400µm) particles mesh size with dichloromethane (CH_2Cl_2) as the mobile phase.

Silica gel of 10 g prepared in slurry form and 10 g anhydrous sodium sulphate was inserted in the column to grip water from the extract. The extract was put in the column and sinks through the sodium sulphate and silica gel packed layers. Elution was done with 20 ml dichloromethane. The elute was pipetted into plastic vessels and evapourated to dryness under a stream of analytical grade nitrogen in readiness for GC-MS [12].

GC-MS

GC-MS was employed to identify and quantify the residues of organochlorine in the extracts replicated from the cured-fish samples. A Shimadzu GC-MS P-2010 was employed to classify specified compounds, built with split/splitless injector and Restek Stx-Cl pesticide column (Length 30 m, 0.25 mm I.D, and 0.25 µm thickness). Electron ionization mass spectra were generated at 70 eV, monitoring for ions m/z 50 to 450 in full-scan as well as designated ion record mode. Injection volume and temperature were 1µL and 250 ^{0}C respectively. Interface and iron source temperature are 250 ^{0}C and 200 ^{0}C respectively, injection temperature and detection hotness were set as 250 ^{0}C. while that of the column was set as 60 ^{0}C and increased immediately at the rate of 10 ^{0}C /min. to 180 ^{0}C where it was seized for 2 min, this was improved by 15 ^{0}C /min., to 280 ^{0}C, seized finally for 4 min.

STATISTICAL ANALYSIS

A GENSTAT® computer software (Version 13.1 for Windows) was used for statistical analysis. Analysis of variance (ANOVA) was used to test for significant differences (P<0.05) between mean values of metals while Duncan Multiple Range Test (DMRT) was used to separate significant means.

Tabl-1: Analysis of fresh fish samples from some water bodies in South-South

S/N	Water bodies	Sampling Stations	Sample Name	Ave. wt of whole Fish (g)	Wt of Ext. Analyzed with GC/MS (g)	Pesticides/Conc. Found
1	Ekehuan	1	*C. gariepinus*	365	0.44	N.D
		2	*P. obscura*	459	0.65	N.D
		3	*S. clarias*	320	0.52	N.D
2	Illushin	1	*C. gariepinus*	600	0.80	N.D
		2	*E. fimbriata*	250	0.76	N.D
		3	*P. obscura*	355	0.52	N.D
3	Agenebode	1	*P. obscura*	420	0.56	N.D
		2	*S. clarias*	463	0.64	N.D
		3	*C. senegalensis*	250	0.51	N.D
4	Old NPA (Warri)	1	*S. clarias*	405	0.98	N.D
		2	*H. niloticus*	900	0.46	N.D
		3	*P.senegalensis*	400	0.66	N.D
5	Koko	1	*C. senegalensis*	310	0.57	N.D
		2	*P.senegalensis*	290	0.76	N.D
		3	*E. fimbriata*	320	0.86	N.D
6	Oron	1	*E. fimbriata*	450	0.68	N.D
		2	*C. senegalensis*	290	0.50	N.D
		3	*P.senegalensis*	195	0.70	N.D
7	Choba	1	*H. niloticus*	545	0.85	N.D
		2	*C. gariepinus*	654	0.80	N.D
		3	*S. clarias*	343	0.45	N.D
8	Mkpana (Ibeno LGA)	1	*P.senegalensis*	255	0.76	N.D
		2	*C. senegalensis*	321	0.65	N.D
		3	*E. fimbriata*	254	0.56	N.D
9	Brass (Yenegoa)	1	*C. gariepinus*	250	0.78	N.D
		2	*S. clarias*	435	0.50	N.D
		3	*H. niloticus*	565	0.60	N.D

* N.D – Not Detected

RESULTS

The results of the organochlorine residues analysed in the fish, water and sediment samples in South-South Nigeria are shown in Tables I - III.

Analyses of fresh fish samples from some water bodies in South-South

It can be seen in Table I that no organochlorine pesticide was detected in fresh fish samples from South-South Nigeria.

Analysis of Organochlorine Residues in the Water from South-South

The analysis of organochlorine residues in the water samples from South-South Nigeria are presented in the Tables II. The study revealed that there were no residues of organochlorine in water.

Table-2: Concentrations of Organochlorine Pesticide Residues in some Water Bodies in South-South

S/N	Water bodies	Sampling stations	P^H	Wt of Extract (g)	Lindane Conc. (µg/l)	Aldrin Conc. (µg/l)	Endosulfan Conc. (µg/l)	DDT Conc. (µg/l)
1	Ekehuan	1	6.3	0.03	N.D	N.D	N.D	N.D
		2	6.5	0.02	N.D	N.D	N.D	N.D
		3	6.0	0.03	N.D	N.D	N.D	N.D
2	Illushin	1	5.9	0.02	N.D	N.D	N.D	N.D
		2	6.2	0.04	N.D	N.D	N.D	N.D
		3	5.8	0.02	N.D	N.D	N.D	N.D
3	Agenebode	1	6.5	0.02	N.D	N.D	N.D	N.D
		2	6.8	0.06	N.D	N.D	N.D	N.D
		3	6.1	0.05	N.D	N.D	N.D	N.D
4	Old NPA (Warri)	1	7.8	0.02	N.D	N.D	N.D	N.D
		2	6.5	0.02	N.D	N.D	N.D	N.D
		3	6.6	0.03	N.D	N.D	N.D	N.D
5	Koko	1	7.1	0.01	N.D	N.D	N.D	N.D
		2	6.9	0.04	N.D	N.D	N.D	N.D
		3	6.5	0.02	N.D	N.D	N.D	N.D
6	Oron	1	5.5	0.03	N.D	N.D	N.D	N.D
		2	5.2	0.05	N.D	N.D	N.D	N.D
		3	5.5	0.02	N.D	N.D	N.D	N.D
7	Choba	1	5.4	0.07	N.D	N.D	N.D	N.D
		2	5.0	0.04	N.D	N.D	N.D	N.D
		3	5.3	0.05	N.D	N.D	N.D	N.D
8	Mkpana (Ibeno LGA)	1	6.2	0.01	N.D	N.D	N.D	N.D
		2	6.0	0.03	N.D	N.D	N.D	N.D
		3	5.9	0.05	N.D	N.D	N.D	N.D
9	Brass (Yenegoa)	1	5.8	0.02	N.D	N.D	N.D	N.D
		2	6.0	0.04	N.D	N.D	N.D	N.D
		3	6.6	0.03	N.D	N.D	N.D	N.D

*N.D - Not detected

Analysis of Residues of Organochlorines in Sediments

The results of the analyses of organochlorine pesticide residues in sediments from South-South Nigeria are presented in Tables III.

It can be observed in Table III that there was significant difference ($P<0.05$) in the levels of the organochlorine pesticides detected in the sediments. The sediment samples from Mkpana Beach in Ibeno Local Government Area of Akwa-Ibom State had the highest frequency of pesticides having lindane (3.70 µg/kg), aldrin (4.20 µg/kg), endosulfan (0.60 µg/kg) and D.D.T (0.0002 µg/kg) residues. It can also be seen that lindane (1.50µg/kg) as well as aldrin (30.80 µg/kg) was discovered in sediments from Oron beach in Oron local Government area also in Akwa-Ibom State. The least amount and frequency of pesticide (1.00 µg/kg) of aldrin was only recorded in Agenebode of Etsako-East Local Government Area in Edo State.

Table-3: Mean Concentration of Organochlorine Pesticide Residues in Sediments of some Water Bodies in South-South

S/N	Location	Sampling Stations	Wt of Extract	Lindane (µg/kg)	Aldrin (µg/kg)	Endosulfan (µg/kg)	DDT (µg/kg)
1	Ekehuan	1	0.03	N.D	N.D	N.D	N.D
		2	0.02	N.D	N.D	N.D	N.D
		3	0.03	N.D	N.D	N.D	N.D
2	Illushin	1	0.03	N.D	0.10 ± 0.02^{d}	N.D	N.D
		2	0.04	N.D	N.D	N.D	N.D
		3	0.02	N.D	N.D	N.D	N.D
3	Agenebode	1	0.06	N.D	1.00 ± 0.30^{c}	N.D	N.D
		2	0.05	N.D	N.D	N.D	N.D
		3	0.03	N.D	N.D	N.D	N.D
4	Old NPA	1	0.07	N.D	N.D	N.D	N.D
		2	0.03	N.D	N.D	N.D	N.D
		3	0.05	N.D	N.D	N.D	N.D
5	Koko	1	0.07	N.D	N.D	N.D	N.D
		2	0.05	N.D	N.D	N.D	N.D
		3	0.06	N.D	N.D	N.D	N.D
6	Oron	1	0.06	1.50 ± 0.25^{a}	30.80 ± 0.20^{a}	N.D	N.D
		2	0.04	N.D	N.D	N.D	N.D
		3	0.05	N.D	N.D	N.D	N.D
7	Choba	1	0.03	N.D	N.D	N.D	N.D
		2	0.06	N.D	N.D	N.D	N.D
		3	0.04	N.D	N.D	N.D	N.D
8	Mkpana Beach	1	0.03	3.70 ± 0.20^{b}	4.20 ± 0.20^{b}	$0.60\pm0.30d^{a}$	0.20 ± 0.10^{a}
		2	0.04	N.D	N.D	N.D	N.D
		3	0.07	N.D	N.D	N.D	N.D
9	Brass	1	0.03	N.D	N.D	N.D	N.D
		2	0.03	N.D	N.D	N.D	N.D
		3	0.05	N.D	N.D	N.D	N.D

*N.D-Not detected

*Means with different superscript were significantly different at P<0.05

DISCUSSION

Fresh fish

The results of the analyses of fresh fish samples from water bodies in South-South reveals that no pesticide traces were found in the fresh fish samples from South-South. The results of this study correspond with the report of [13] who analysed *Chrysichthys nigrodigitatus*, *Tilapia guinenses*, *Mugil cephalus*, crayfish (*Penaeus sp.)*, African red snapper (*Latjanus agennes*) from Lagos lagoon in Nigeria and discovered dichlorodiphenyltrichloroethane, dichlorodiphenyl-dichloroethane (DDD), dichloro-diphenyl-dichloro ethylene (DDE) ranged between 0.023 and 0.069 µg/g. The absence of organochlorine pesticides in fresh fish in this study showed that people in the South-south may have abolished the use of obnoxious fishing methods (pesticides) in fishing maybe as a result of the awareness of threats to the aquatic ecosystem and man.

Water

This study revealed that water samples from South-south Nigeria had no organochlorine pesticide residues. There were higher amounts of pesticide residues in sediments than fish and water probably because of the hydrophobic tendency of pesticides that makes their existence in water to be in low amounts which makes their evaluation difficult.

The adsorption of organochlorines to sediment is a vital process for their elimination from the water body; ultimately, the sediments will be the final receptacle for organochlorines [14, 15].

The results also showed that the people of South-south of Nigeria have probably abolished the use of some obnoxious fishing methods (pesticides) as a result of the awareness of threats to the aquatic ecosystem and man.

Sediments

In this study, the amounts of organochlorines in sediments of this study is in line with that of [14] who revealed that sediments are known to serve as a receiving end for the contaminants and could accumulate pesticides overtime.

Since organochlorines have been shown to be willingly absorbed in sediments, they can, serve as a real hazard in the aquatic habitat [16]. The available of pesticides in sediments and not in fish and water could be as a result of the accumulation of the pesticides from the obnoxious fishing methods and wash off of herbicides used in farmlands close to the water bodies that must have settled down over time. The high levels of pesticide residues in sedimentsin Oron, Mkpana, Illushin and Agenebode water bodies above the allowable limit of 0.05 µg/kg recommended by the [17, 18] may be as a result of overtime bioaccumulation of extensive and repeated use of the pesticides in fishing. The presence of these organochlorine pesticides also agrees with the report [11, 19].

CONCLUSION

The outcome of this study have provided insights into the organochlorine pesticides contamination levels in fish, water and sediment samples from some water bodies in South-South, Nigeria. Organochlorine pesticide residues were not found in all the fish and water samples but found in some sediment samples analysed. This depicts the hydrophobic nature of pesticides which means that sediments act as a receiving end for contaminants and hence, have the propensity to accumulate pesticides. The study also reveals that people in this region are gradually abolishing the use of pesticides directly in killing fishes in their water bodies because they may be mindful of the hazards of the use of pesticides in fishing to man and the aquatic ecosystem. The high levels of pesticide residues in sedimentsin Oron, Mkpana, Illushin and Agenebode water bodies above the allowable limit of 0.05 µg/kg recommended by the EPA and USEPA may be as a result of overtime bioaccumulation of extensive and repeated use of the pesticides in fishing.

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Conflict of Interest

There is no conflict of interest in relation to this work.

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