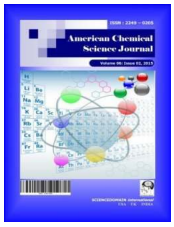

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Determination of Organochlorine Pesticide Residues in Water and Sediment Samples from Selected Areas of River Ilaje, Nigeria

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

Water and sediment samples were collected from 4 different locations along the coastal areas of river Ilaje in Ondo state, Nigeria. The water samples were subjected to liquid-liquid while the sediment samples were subjected to solid-liquid extraction, the extracts were later analyzed for organochlorine pesticide residues using gas chromatography coupled with mass spectrometer. The result shows that organochlorine pesticide residues were not detected in the water samples from all the sampling sites but were detected in some of the sediment samples, Lindane 0.303-0.344 µg/g in Abereke sampling site, while in Ogogoro sampling site Lindane 0.217-0.391 µg/g, Dieldrin 0.103 µg/g and Endosulfan II 0.176 µg/g. The absence of organochlorine pesticide residue in water samples shows that the water is free from organochlorine pesticide contamination but the presence of organochlorine pesticide residues in sediment shows that there is bioaccumulation of organochlorine pesticide residues in the sediment of river Ilaje in the Ondo coastal area of Nigeria.

Keywords: Bioaccumulation; liquid-liquid extraction; organochlorine; solid-liquid extraction; sediment.

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1. INTRODUCTION

Organochlorine pesticides are chlorinated hydrocarbons, which are among the oldest and most toxic synthetic pesticides. First introduced in the 1940's, these chemicals were used extensively from the 1940's through the 1960's in agriculture and mosquito control until most of them were banned in the 1970's and 1980's due to their health risks. Organochlorines are neurotoxic, mutagenic and some organochlorine compounds are suspected carcinogens. A byproduct contaminant of the manufacturing process for 2,4,5- trichlorophenoxyacetic acid (2,4,5-T) is 2,3,7,8- tetrachlorodibenzo-para-dioxin (TCDD), commonly referred to as dioxin has been known to be related to serious health problems [1-3], organochlorines such as DDT and Lindane, also break down slowly once released into the environment [4,5]. Pesticides when used properly are of tremendous benefits to human beings but their indiscriminate use however may cause considerable hazards to health and environment. The controversy of use and abuse of pesticides has surfaced, water pollutions by pesticides result from massive application of these chemicals in agriculture and other branches of economy. Pesticides can reach surface water along with dripping waters and by infiltration may reach the groundwater layers, organochlorine pesticides are most often found in the water sources due to their increased persistence in the external environment [6]. Their persistence in the environment causes organochlorines to be incorporated into the ecosystems where they remain for a long period of time therefore the lipophilicity and persistence of these organic chemical compounds contribute to their bioaccumulation and biomagnification in the food chain [7]. Ideally a pesticide must be lethal to the targeted pests, but not to non-target species, including man. Unfortunately, this is not so. The rampant use of these chemicals, under the adage, "if little is good, a lot more will be better" has played havoc with human and other life forms even in the aquatic environment [8]. The use of pesticides for fishing by artisanal fishermen and discharge of the municipal water into the lagoon as one of the major underground drainage systems in that part of the State empties into the lagoon few meters away has lead to some degree of water contamination and bioaccumulation of organochlorine pesticides in sediment, fin fish and shell fishes in Ologe Lagoon, Lagos State [9]. It was also observed that there was an increase in the level of organochlorine pesticide residues in water and fish samples from some selected rivers in Edo State, Nigeria due to the use of pesticides for fishing and farming by farmers in the areas [10]. Recent study on the concentration of organochlorine in cocoa farmland in Ondo state central district, Nigeria shows the concentrations and frequency of occurrence of endosulfan I, endosulfan II, heptachlor epoxide and aldrin in the soil samples were very high and are of serious concern. Apart from the potential danger they may pose to the soil organisms, their possible translocation into edible parts of crops and emission into surrounding water bodies [11]. It has been observed that various blood components are affected by exposure to pesticide contamination, as reported in the alteration of red blood cells (RBC) membrane in rats by HCH exposure. It has also been observed that there was a development of chronic leukemia in Egyptian farm workers [12-14]. The purpose of this paper is to access the drinking water quality, in terms of contamination of organochlorine pesticides in Abereke, Ayetoro, Ogogoro and Awoye counties of river Ilaje.

2. MATERIALS AND METHODS

2.1 The study Area

The study areas are Abereke, Ayetoro, Awoye and Ogogoro communities within the river Ilaje. The river Ilaje in Ondo State coastal area of Nigeria is located on Latitude 5°50'N-6°09'N and on Longitude 4°45'E-5°05'E, river Ilaje is a deltaic region which takes its origin from river Oluwa in Ondo State. The Ilaje communities depend on river Ilaje for their economic and domestic activities.

2.2 Sampling and Pre-treatment of Samples

Water samples were collected in a 2L glass bottles, while sediment samples were collected using a soil hugger. Water and sediment samples were collected 3 months interval (December 2014 –March 2015 –June 2015) from each of the sampling site. The sediment samples were air dried for two weeks and pulverized using laboratory mortar and pestle. It was later sieved using a 2 mm mesh size sieve, and then it was subjected to solid-liquid extraction. All chemicals used were of analytical grade.

2.2.1 Extraction procedure

Liquid-liquid extraction of organochlorine pesticide residues in water samples was carried out using Method 3510 as described by USEPA [15] was used to extract organochlorine pesticide residues from the water samples. 50 mL of dichloromethane (DCM) was introduced into a separating funnel containing 100 mL of the water sample and shaken vigorously for 5 minutes. The sample was allowed to settle for 30 minutes to facilitate effective separation of the organic and aqueous phases. After separation, the organic layer was filtered into a 250 mL volumetric flask through anhydrous sodium sulphate (Na_2SO_4) that has been prewashed with DCM. The extraction was repeated twice using 50mL of dichloromethane (DCM). The extracts were later combined to make a whole. The extracts were concentrated to 5 mL using a rotary evaporator at a temperature of 45℃, during concentration the solvent is exchanged with n-hexane. The level of organochlorine pesticide residues in the water samples was determined using gas chromatography coupled with a mass spectrometer (GC-MS).

Solid-liquid extraction of organochlorine pesticide residues in the sediment samples was carried out using the EPA 3550C method as described by USEPA [16]. A mixture of 20 g of sediment samples and 20 g of anhydrous sodium sulphate (Na_2SO_4) was thoroughly mixed with a mixture of 50mL acetone and n-hexane (1:1 v/v). The mixture was sonicated for 30 minutes in a high frequency ultrasonic bath at 60℃, the organic extract was decanted. The extraction process was repeated twice using 50 mL of a mixture of acetone and n-hexane (1:1 v/v). The extracts were later combined to make a whole. The extracts were concentrated using a rotary evaporator at a temperature of 45℃.

2.2.2 Clean up procedure

The clean up procedure is required for the pesticide residues analysis in sediment sample in order to avoid interferences. The extracts from the sediment samples were clean up using a column packed with 2 g of octadecyl (C_{18}) modified silica gel and 2 g of anhydrous sodium sulphate (Na_2SO_4). Prior to the clean up, the column was conditioned with 20 mL of n-hexane. The extract was introduced into the column and eluted using a mixture of n-hexane and diethyl ether (1:1 v/v). The elute was concentrated to 5 mL using a rotary evaporator at a temperature of 45℃, during concentration the solvent is exchanged with n-hexane.

2.2.3 Gas chromatographic conditions

The following instrumentals conditions were maintained. Gas pressure was 60 psi and injector temperature was 220℃, GC column temperature was 190℃, detector temperature was 270℃, the carrier gas was nitrogen (at 30 ml/min), column length 200 cm, id 2 mm, the glass spiral column packed with 1.5% 0V - 17 and 1.95% 0V-210 on chromosorb WHP 80/100 mesh. There were no peaks when solvents and blanks were chromatographed, before the samples were analyzed under the same condition. Known standards, were also chromatographed, the retention time were used to identify the compounds present in the samples.

3. RESULTS AND DISCUSSION

From the results of the organochlorine pesticide residues analyzed in water samples from river Ilaje, it was observed that organochlorine pesticide residues were not detected (N.D) in the water samples from Abereke, Ayetoro, Ogogoro and Awoye sampling sites, this shows that the river may be free from organochlorine pesticide contamination. But the result from Table 1 shows that the sediment samples from Abereke sampling site were contaminated to some degree with Lindane in the range of 0.303-0.344 µg/g while the sediment samples at Ayetoro were free from organochlorine pesticide residues. Table 2 shows that the sediment samples from Awoye were free from organochlorine pesticide residues while the sediment samples from Ogogoro sampling site has the highest degree of organochlorine pesticide contamination in the following order Lindane (0.217-0.391 µg/g) > Endosulfan II (0.176 µg/g) > Dieldrin (0.103 µg/g). It was observed that organochlorine pesticide residues were detected during the month of December and March (dry season) at Abereke and Ogogoro sampling sites but were not detected during the month of June (rainy season), this could be attributed to the process by which soil drying during dry season promote adsorption of pesticide to soil particles [17,18]. The absence of organochlorine pesticide residues in the water samples and some of the sediment samples may have resulted due to the

Table 1. Concentration (µg/g) of organochlorine pesticide residue in sediment sample at Abereke and Ayetoro sampling site

OCPs/sample code	Abereke					Ayetoro				
	Ab_1	Ab_2	Ab_3	Mean	S.D	Ay_1	Ay_2	Ay_3	Mean	S.D
Alpha BHC	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Beta BHC	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Lindane	0.344	0.303	N.D	0.324	0.029	N.D	N.D	N.D	Nil	Nil
Chlorothalonil	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Delta Lindane	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Heptachlor-epoxide	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Dieldrin	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Endosulfan II	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
p,p'-DDD	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
PCB-153	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Endosulfan-sulphate	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
p,p'DDT	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
d-BHC	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Aldrin	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
TOCP	0.344	0.303	N.D	0.324	0.029	N.D	N.D	N.D	Nil	Nil

OCP= organochlorine pesticide, TOCP= Total organochlorine pesticide, N.D = Not detected, Ab_1= Abereke (December), Ab_2= Abereke (March), Ab_3= Abereke (June). Ay_1= Ayetoro (December), Ay_2= Ayetoro (March), Ay_3= Ayetoro (June)

Table 2. Concentration (µg/g) of organochlorine pesticide residue in sediment sample at Ogogoro and Awoye sampling site

OCPs/Sample code	Ogogoro					Awoye				
	Og_1	Og_2	Og_3	Mean	S.D	Aw_1	Aw_2	Aw_3	Mean	S.D
Alpha BHC	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Beta BHC	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Lindane	0.217	0.391	N.D	0.304	0.123	N.D	N.D	N.D	Nil	Nil
Chlorothalonil	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Delta Lindane	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Heptachlor-epoxide	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Dieldrin	0.103	N.D	N.D	0.103	Nil	N.D	N.D	N.D	Nil	Nil
Endosulfan II	0.176	N.D	N.D	0.176	Nil	N.D	N.D	N.D	Nil	Nil
p,p'-DDD	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
PCB-153	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Endosulfan-sulphate	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
p,p'DDT	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
d-BHC	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
Aldrin	N.D	N.D	N.D	Nil	Nil	N.D	N.D	N.D	Nil	Nil
TOCP	*0.496*	*0.391*	*N.D*	*0.444*	*0.074*	*N.D*	*N.D*	*N.D*	*Nil*	*Nil*

OCP= organochlorine pesticide, TOCP= Total organochlorine pesticide, N.D = Not detected, Og_1= Ogogoro (December), Og_2 = Ogogoro (March), Og_3= Ogogoro (June). Aw_1= Awoye (December), Aw_2= Awoye (March), Aw_3= Awoye (June)

fact that organochlorine pesticides have been banned for decades in the Nigeria. Although the water samples are free from organochlorine pesticide contamination but it could later be contaminated by organochlorine pesticide residues due to water runoff or leaching as a result of the bioaccumulation of organochlorine pesticide residue in the sediment of some of the sampling sites.

4. CONCLUSION

Rural areas are always exposed to pesticide contamination as a result of many environmental factors such as leaching, water runoff and indiscriminate application of pesticides. Pesticide contamination has a negative impact on the ecosystem as well as on the health of the human population in the environment. This present study

shows that the water samples from river Ilaje is free from organochlorine pesticide contamination so it may be considered safe for domestic use in terms of organochlorine pesticide contamination but the presence of organochlorine pesticide residues in the sediment samples of some sampling sites indicate that the organochlorine pesticide has bioaccumulated in the sediment at the sampling site where they were detected, and could be leached into the river body. Therefore continuous monitoring of river Ilaje needs to be done on routine basis in order to adequately access the water quality and to prevent future environmental pollution as a result of organochlorine pesticide contamination of the water and sediment of the river. From the outcome of this research it can be concluded that sediment of rivers could act as possible sink and storage site for organochlorine pesticide residues.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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