Full Length Research Paper

Organochlorine pesticide residue levels in river water and sediment from cocoa-producing areas of Ondo State central senatorial district, Nigeria

Idowu G. A.*, Aiyesanmi A. F. and Owolabi B. J.

Department of Chemistry, Federal University of Technology, P. M. B. 704, Akure, Nigeria.

The health risks posed by organochlorine compounds to the total environment have continued to elicit concern among researchers worldwide. Hence, this study focused on investigating the varieties and concentrations of organochlorine pesticide residues in river water and sediments from cocoa-producing areas in Ondo Central Senatorial District of Nigeria. The organochlorine pesticides extracted with a mixture of organic solvents were quantified by Gas Chromatography – Mass Spectrometry (GC-MS). Aldrin, dieldrin, lindane, heptachlor epoxide, α-endosulfan, β- endosulfan, β- benzene hexachloride, and δ-benzene hexachloride were detected in the samples, with endosulfan isomers occurring most frequently. The findings provide no evidence of accumulation of organochlorine compounds in the river benthics but the total organochlorine compounds measured gave a significant positive correlation ($p < 0.05$) with the organic and clayey matter contents of the river sediments, suggesting that these components of river sediments play important role in retaining organochlorine compounds. This study constitutes an initial investigation of the levels of organochlorine compounds in the area and will thus serve as a reference for future investigations and environmental performance measurements.

Key words: Organochlorine compounds, cocoa farm, water, sediment, Nigeria.

INTRODUCTION

Organochlorine pesticides are an important group of chemical pollutants found in many parts of the global aquatic environment (Pandit et al., 2001). They are non-polar chemical compounds containing mainly carbon, hydrogen, and chlorine. Organochlorines are composed of five broad groups namely: the Dichloro-diphenyl-trichloro ethane (DDT) and analogues; the Hexacholrocyclohexanes or Benzene hexachlorides; the Cyclodienes; the Chlordecones, Kelevan, and Murex; and the toxaphenes (Pope et al., 1994). Discharge from sewage systems and run-off from agricultural fields are believed to be the main sources of these compounds in the environment.

Organochlorine residues in the environment have continued to attract the attention of researchers worldwide and are being closely monitored in most developed nations. The reason for this is the health risk they pose due to their acute toxicity and their potential for bioaccumulation. Organochlorine compounds are toxic to humans and animals, and are highly toxic to most aquatic life. They can have serious short-term and long-term impacts even at low concentrations. They may also have

*Corresponding author. E-mail: gaidowu@futa.edu.ng. Tel: +234-803 443 2595.

very significant non-lethal effects such as immune system and reproductive damages (Le Maire et al., 2004).

Organochlorines have a high tendency to be attracted to the fatty tissues of humans, animals and plants. Most of them can build up in fatty tissues and organs, and are accumulated significantly in animals such as fish (Bentzen et al., 2008; Swackhamer and Hites, 1988). They have also been detected and quantified in human fluids such as urine, serum and breast milk (Campoy et al., 2001; Burns et al., 2012). Apart from their bioaccumulation in fatty tissues, organochlorines can be absorbed orally, transdermally, by inhalation, and through the gastro-intestinal tract (Pope et al., 1994). Their environmental concern is further heightened by the fact that they are not easily broken down in the environment, as they resist degradation by chemical, physical, micobiological, and biological means (Le Maire et al., 2004; Darko and Acquaah, 2007).

These many adverse consequences associated with the use of organochlorine pesticides are the reason why many of them were banned or have their use restricted. However, they continue to be widely used for the control of agricultural pests in most developing countries (Pandit et al., 2001). This continued use of organochlorine pesticides remains a matter of international concern because of their long-distance carriage through oceanic currents and atmospheric transports (Bentzen et al., 2008; Caldas et al., 1999). The high potency/efficacy and lower cost of organochlorine pesticides compared to alternative pesticides are believed to be the reasons for their continued usage, for instance, in Nigeria and in most part of Africa (Osibanjo, 1994). The main use of organochlorine pesticides in West Africa is for the control of insects on cash crops such as cocoa.

Ondo state being the highest producer of Cocoa in Nigeria, with an estimated output of 45,004.5 metric ton. in 2007, representing 40% of the total annual cocoa production in Nigeria (Aikpokpodion, 2010; Ajayi et al., 2010), constitutes the most probable area with the highest agricultural use of organochlorine pesticides in Nigeria, particularly in the extensive cocoa plantations found in the Central Senatorial District of the state. Unfortunately, the few available reports and reviews on the level of organochlorine pesticides contamination of water and aquatic biota of some parts of Nigeria (Osibanjo and Adeyeye, 1995; Osibanjo and Bambgose, 1990; Atuma and Okor, 1985; Ize-Iyamu et al., 2007; Uyimandu, 2002; Adeyemi et al., 2008) provide no data about this region with a presumably heavy use of organochlorine pesticides for cocoa production.

This has been the impetus behind the many recent environmental studies being undertaken in this area to determine the level of contamination by chemical pesticides. Thus, this current study extends our works on the investigation of pesticide residues in various phases of the environment within the Ondo Central Senatorial District of Nigeria.

Previous studies have investigated the level of Organo-Phosphorous Pesticides (OPPs) and contamination of cocoa farm soils by organochlorine pesticide residues within the area (Aiyesanmi and Idowu, 2012a, b).

This present study is intended to provide complementary data by investigating the concentration of Organo-Chlorine Pesticides (OCPs) in selected rivers and river sediments within the area.

MATERIALS AND METHODS

The study area

The study area for the project covers three major cocoa - producing local governments within the Ondo State Central Senatorial District, Nigeria, where farmers apply pesticides on their cocoa farms. These are Akure-South, Ifedore and Idanre local government areas, lying within latitude 07° 04'– 07° 20' N and longitude 005° 06'-005° 14'E, and are in the same geographical zone (Figure 1). A major river which flows across the cocoa farms in each area was selected for study.

Sampling and sample nomenclature

From each river, water and sediment samples were taken at three locations along its course. Grab sampling technique (Staare et al., 2000) was employed for the collection of the water samples; upstream, midstream, and downstream at each of the three local government areas studied.

The water samples were kept in screw-cap bottles under refrigeration pending their extraction. Also, Grab sediment samples were taken at the same spots as for the water samples using a hand scoop. The sediment samples were drained and air-dried in the laboratory for about 2 weeks, picked for obvious extraneous materials, ground with porcelain mortar and pestle, and sieved through a 2 mm wire mesh. These were stored in brown sample bottles prior extraction. The sampling points were all geographically referenced with a Global Positioning System (GPS Garmin 12 Model)

The general sample coding used is: the first two letters of the name of the area; S or W, for sediment or water sample respectively; and 1, 2 or 3 for the point on the stream where the particular sample was taken. Code 1, 2, and 3 respectively refer to upstream, midstream, and downstream sample. Thus, AKS1 refers to the upstream sediment sample obtained from Akure –south area, while IDW3 refers to the downstream water sample obtained from Idanre area.

Materials and preparations

All the reagents used were of analytical grade from British Drug House (BDH) and include: n-hexane, acetone, diethyl ether, ethyl acetate, methylene chloride, sodium sulphate, silica gel, toluene, and methanol. As proper cleaning of glass wares is extremely important to pesticide residues analysis (since they may contaminate the samples or remove the analytes by adsorption on glass surface), all glass wares used for the organochlorine determination were cleaned as recommended by Method 1699 of US EPA (2007).

The activated Silica gel for clean up procedure and the anhydrous sodium sulphate used for drying the samples were also prepared in accordance with the US EPA Method 1699. The micro-
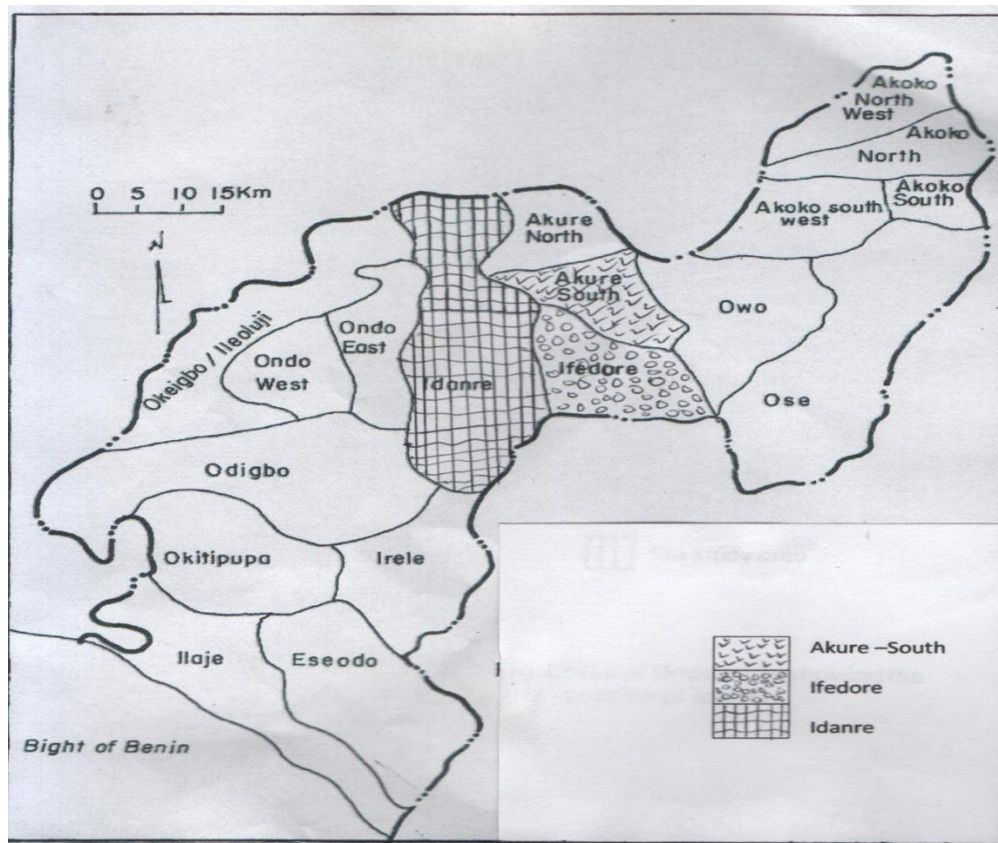
Figure 1. Map of Ondo State showing the study area within the Central Senatorial District.

column for the clean-up procedure was fabricated at the glass-blowing unit of the Department of Chemistry,Federal University of Technology, Akure, Nigeria.

Physico-chemical analysis of the sediment samples

The pH of the sediment samples was determined by the method described by Hendershot et al. (1993). The particle size distribution was determined by hydrometer method described by Shedrick and Wang (1995), involving mainly the dispersion of the sediments with Sodium hexametaphosphate (Calgon). The Wet Oxidation Method (Schulte, 1995) was used to determine the organic carbon contents of the sediment samples, and hence the organic matter content.

Extraction of organochlorine compounds from water and sediment samples

Extraction of the sediment samples was carried out by the method described by Ize-Iyamu et al. (2007), with slight modification. About 10 g of each sediment sample and 20 g of anhydrous Sodium sulphate was ground into dry powder using a set of mortar and pestle. The ground sample was extracted with 150 ml of a mixture of Acetone and n-Hexane (2:1). The extract was transferred into a round bottomed-flask connected to a receiver through a Liebig condenser and concentrated to about 20 ml on a water bath maintained between 50 and 55°C. The remaining solvent in the concentrated extract was evaporated using a rotary evaporator.

The water samples were extracted using the procedure described by Osibanjo and Adeyeye (1997), also with slight

modification. The solvents used were n-Hexane and diethyl ether. 60 ml of 15% diethyl ether in hexane was introduced into a 1 L separatory funnel containing 250 ml of water sample. The mixture was shaken vigorously for 2 m, with periodic venting and was allowed to stand for about 10 m for complete separation. The bottom aqueous layer was drained into the original sample bottle, while the organic layer was filtered into a 250 ml conical flask through anhydrous sodium sulphate layer that has been pre-washed with the 15% diethyl ether in hexane.

The extraction and filtration process was repeated for two more times, while the separatory funnel was rinsed with 50 ml hexane, filtered through the anhydrous sodium sulphate and added to the extracts. The organic extract was concentrated to 10 ml on a rotary evaporator set at 45°C. The 10 ml extract was further reduced to 1 ml under nitrogen gas at 50°C and transferred into vial before analysis with the gas chromatograph.

Clean up procedure for the sample extracts

Since various components with large molecular size such as lipids, proteins, pigments, and resins are often co-extracted with pesticide molecules (Tiryaki and Baysoyu, 2006), these substances referred to as 'dirts' are necessarily removed from the extracts before subsequent chromatographic analysis, as they may cause interference in the chromatographic system and detection, and may also damage the GC equipment.

The procedure normally used to achieve this is called clean-up. No clean-up was, however, required for the water samples as they were relatively clean with no obvious co-extracted dirts (Osibanjo and Adeyeye, 1995; US EPA, 2007).

Organic extracts from the sediment samples were cleaned up using a glass micro-column of 10 mm internal diameter and 10 cm long (Ize-Iyamu et al., 2007). 2 g of activated silica gel was packed into the micro-column and was conditioned with 10 ml n-Hexane. The extracts were dissolved in 5 ml n-Hexane before they were loaded separately onto the micro-column. Elution of each of the sample was done with 50 ml ethyl-acetate: hexane mixture (9:1). The eluents were then concentrated on a rotary evaporator at about 45°C and under a gentle stream of Nitrogen gas. The almost-dry concentrates were then dissolved in about 2 ml acetone and were transferred into vials for subsequent injection into the Gas Chromatograph.

Quantification of organochlorine residues in the samples

Both the concentrated extracts from the water samples and the cleaned-up residues from the sediments were analysed for organochlorine compounds by the method of internal standards. Organochlorine standards containing a mixture of 14 organochlorine compounds of high purity (alpha-BHC, beta-BHC, Lindane, delta-BHC,Heptachlor, Aldrin, Heptachlor – epoxide, Endosulfan I, p,p'- DDE, Dieldrin, Endrin, Endosulfan II, p,p'- DDT, and Endosulfan sulphate) were prepared at concentrations ranging from 0.100 to 2.000 ppm, with Anthracene, PCB-153, and PF-38 added as internal standards. The modern Shimadzu GC-MS QP-2010 was employed in analysing the standards and the calibration curve for each organochlorine compound was prepared automatically.

The sample extracts were then analysed under the same conditions as for the standards, and in the Selective Ion Mode (SIM) with m/z values ranging from 65 to 410. Splitless injection mode was used with the injection temperature as 250°C while the column oven temperature was ramped between 80 and 280°C. The GC-MS was operated at a pressure of 79.5 kPa and the flow rate was 1.18 ml/m. The efficiency of the method used was validated with recovery studies. Reference soil samples containing no pesticides residues were fortified with four organochlorine compounds at concentration levels of 1.0 mg/kg while analysis was carried out in triplicate with the same GC-MS system and following the same extraction and clean-up procedures as for the sediment samples.

RESULTS AND DISCUSSION

Table 1 presents the physico-chemical properties of stream sediments from each of the local government areas. The result shows that the sediments from Akure – south and Idanre streams are mainly sandy – loamy, while those for Ifedore stream have higher proportions of clayey matter. The sediment pH values also differed considerably. While the sediments from Idanre stream showed a consistently acidic nature along the course of the stream; those of Ifedore changed from slightly alkaline nature upstream to very slightly acidic sediment downstream; the sediments for Akure – south change from neutral upstream to a strongly acidic nature downstream. Only the sediments of the stream at Ifedore area showed high organic matter content, while much lower values were recorded for the other two areas. This may be partly due to the relatively high proportion of clayey matter in the sediment samples from Ifedore to which organic matter may be bound, as against the more porous/more permissible structure of the Akure –south and Idanre sediment samples. Another reason for this observation may be the less acidic nature of the sediments of the stream at Ifedore area when compared to the more acidic sediments of the other two areas, as has been reported by Vitosh et al. (1995) that soil/sediment pH has a profound effect on soil organic matter preservation and decomposition. The degradation of organic matter is greater under acidic conditions than in other pH ranges.

Table 2 shows the result of recovery studies conducted using fortified samples. The percentage recovery of the four organochlorine compounds ranges from 82 to 90% and this indicates that the method is sensitive and accurate enough for the determination of organochlorine pesticides in the samples. The standard deviations also show that the reproducibility of the results is satisfactory. The concentrations of the various organochlorine pesticides detected in the water samples are shown in Table 3, while those for the sediment samples are presented in Table 4. The specific organochlorine compounds detected in the samples and their concentrations differ markedly. However, concentrations of each compound within the same phase of the environment appear to be of similar orders of magnitude.

The Y-isomer of hexa-chlorocyclohexane (HCH) or benzene hexachloride (BHC), lindane, was detected in the mid – stream water sample from Akure- south (AKW2) at a concentration 0.37 mg/L, while none of the benzene hexachlorides was found in all the sediment samples from the area. This concentration of lindane measured in the sample AKW2 is far above the stated guideline limit value of 0.002 mg/L for lindane in drinking water by WHO (2011). This is important because water from this stream, being within rural settlements, may be used for drinking and other domestic purposes. Lindane was, however, not detected in all the water samples from Ifedore and Idanre areas. Also the concentration (2.31 $\times 10^{-3}$ mg/L) of dieldrin recorded in downstream water sample at Ifedore (IFW3) was greater than the guideline value of 3.00×10^{-5} mg/L for dieldrin in drinking water (WHO, 2011).

High concentrations of β – BHC and lindane were found in the sediment samples from Ifedore area. The concentration of β – BHC ranged from 4.86 mg/kg in IFS2 to 5.64 mg/kg in IFS3, while that of lindane ranged from 1.20 mg/kg in IFS2 to 3.285 mg/kg in IFS1. It is also noteworthy that the sediment samples from Ifedore area contained up to seven different kinds of organochlorine compounds, while the maximum number found in the sediments from the other areas was only three. This may be attributed to the influence of higher organic matter content in Ifedore area sediment compared to sediments from the other areas.

Organic matter in sediments contains plant and animal materials which may provide lipid-like substances to which the organochlorine pesticides are bound.

Table 1. Physico- chemical properties of the river sediments.

Sample code		Sand (%)	Clay (%)	Silt (%)	pH	[a]O.M (%)
Akure-Sth	AKS1	72.24	6.65	21.11	7.1	1.81
	AKS2	74.06	8.76	17.18	6.1	1.89
	AKS3	68.83	8.70	22.47	4.8	2.24
	IFS1	80.26	13.98	5.76	7.8	6.96
Ifedore	IFS2	78.41	14.39	7.20	7.6	6.01
	IFS3	69.56	14.41	16.03	6.8	5.96
	IDS1	73.24	7.30	19.46	6.6	0.72
Idanre	IDS2	72.85	6.97	20.18	6.5	0.98
	IDS3	72.93	6.32	20.75	6.6	1.38

([a]O.M – organic matter).

Table 2. Recovery of organochlorine pesticides from fortified samples.

Pesticide	Retention time (m)	Recovery (%)
α- endosulfan	12.10	92 ± 1.3
Heptachlor	10.00	90 ± 1.0
β – BHC	8.89	89 ± 2.0
Dieldrin	12.61	86 ± 1.0

Four organochlorine compounds belonging to the cyclodiene group were detected in the various sediment samples. These are heptachlor epoxide, aldrin, dieldrin, and endosulfan. Heptachlor epoxide was detected at a high concentration of up to 5.93 mg/kg in the sediment samples from Ifedore. The compound was not found in the sediment samples from the other two areas, and neither was it found in all the water samples. Heptachlor epoxide found in the environment is often linked with the application of the pesticide, heptachlor; since heptachlor epoxide is not available for direct use, but only enters the environment as a metabolic product of heptachlor formed in plant and insect tissues. Heptachlor epoxide has a more powerful insecticidal action than heptachlor itself (Cremlyn, 1991). Aldrin was not detected in all the water samples, but was found only in IDS1 sediment sample from Idanre. Similarly, dieldrin occurred in one sediment sample at Ifedore, IFS3; and in the corresponding water sample (IFW3) for that location.

The two conformational isomers of endosulfan: α- endosulfan (or endosulfan I) and β- endosulfan (or endosulfan II) occurred most frequently and were found in all the water and sediment samples from the three local government areas under study. Much higher concentrations of endosulfan I was found in the samples than the corresponding endosulfan II. α- endosulfan generally ranged between 0.38 mg/L and 6.49 mg/L in the water samples, while β- endosulfan only ranged between 1.4×10^{-3} mg/L and 33.5×10^{-3} mg/L. In the sediment samples, α- endosulfan ranged from of 0.198 mg/kg to a very high value of 98.09 mg/kg, whereas β- endosulfan ranged only from 5.90×10^{-3} mg/kg to 0.99 mg/kg. The higher concentrations of α- endosulfan detected in the samples relative to those of β- endosulfan may be attributed to the following reasons: Firstly, the manufactured technical endosulfan normally contains about 67% α- endosulfan by weight of the total endosulfan content, while β- endosulfan constitutes only 32% (WHO, 1990). It is, therefore, not unexpected that more of α- endosulfan would be found in the environment when the pesticide is applied. Secondly, α- endosulfan is thermally stable, while β- endosulfan is unstable and is converted to α- endosulfan in the environment (Hapeman et al., 1997; Rice et al., 1997).

However, the high concentrations of endosulfan compounds detected in the samples may be an indication of recent application of the pesticide, as endosulfan is easily degraded and does not accumulate in the environment like most other organochlorines (Cremlyn, 1991). This observation is further corroborated by the fact

Table 3. Concentration of organochlorine pesticides (mg/L) in water samples from the rivers.

Sample code	α-BHC	β-BHC	δ-BHC	(Lindane) Y - BHC	Heptachlor	Aldrin	Heptachlor epoxide	α-Endosulfan	Dieldrin	β-Endosulfan
AKW1	nd	nd	nd	nd	nd	nd	nd	1.924	nd	0.005
AKW2	nd	nd	nd	0.037	nd	nd	nd	1.808	nd	0.006
AKW3	nd	nd	nd	nd	nd	nd	nd	3.118	nd	0.012
IFW1	nd	nd	nd	nd	nd	nd	nd	0.379	nd	0.001
IFW2	nd	nd	nd	nd	nd	nd	nd	0.57	nd	0.002
IFW3	nd	nd	nd	nd	nd	nd	nd	6.491	0.002	0.030
IDW1	nd	nd	nd	nd	nd	nd	nd	3.415	nd	0.029
IDW2	nd	nd	nd	nd	nd	nd	nd	6.051	nd	0.026
IDW3	nd	nd	nd	nd	nd	nd	nd	5.055	nd	0.034

(nd- not detected at the limit of 1×10^{-5} mg/L).

Table 4. Concentration of organochlorine pesticides (mg/kg) in sediment samples from the rivers.

Sample code	α-BHC	β-BHC	δ-BHC	(Lindane) Y - BHC	Heptachlor	Aldrin	Heptachlor epoxide	α- Endosulfan	Dieldrin	β- Endosulfan
AKSD1	nd	nd	nd	nd	nd	nd	nd	0.188	nd	0.061
AKSD2	nd	nd	nd	nd	nd	nd	nd	0.765	nd	0.357
AKSD3	nd	nd	nd	nd	nd	nd	nd	1.760	nd	0.678
IFSD1	nd	5.028	nd	3.275	nd	nd	5.927	127.14	nd	0.006
IFSD2	nd	4.857	nd	1.200	nd	nd	nd	98.093	nd	0.041
IFSD3	nd	5.644	1.926	1.926	nd	nd	4.404	86.404	0.105	0.045
IDSD1	nd	nd	nd	nd	nd	0.021	nd	0.386	nd	0.057
IDSD2	nd	nd	nd	nd	nd	nd	nd	2.386	nd	0.272
IDSD3	nd	nd	nd	nd	nd	nd	nd	8.297	nd	0.991

(nd- not detected at the limit of 1×10^{-5} mg/kg).

that endosulfan sulphate, the primary degradation product of endosulfan, was not detected in all the water and sediment samples. The high frequency of occurrence and the relatively high concentrations of α- endosulfan and β- endosulfan in the water and sediment samples, as against

Table 5. Correlation matrix between sediment physico-chemical properties and total OCP concentration.

Parameter	Corelation Matrix	Sand	Clay	Silt	pH	O.M	Total OCP
Sand	Pearson Corr.	1	0.43988	-0.85745	0.75678	0.50761	0.59358
Clay	Pearson Corr.	0.43988	1	-0.83928	0.47688	0.96825	0.94052*
Silt	Pearson Corr.	-0.85745	-0.83928	1	-0.7314	-0.86209	-0.89825
pH	Pearson Corr.	0.75678	0.47688	-0.7314	1	0.56666	0.66223
O.M	Pearson Corr.	0.50761	0.96825	-0.86209	0.56666	1	0.97787*
Total OCP	Pearson Corr.	0.59358	0.94052*	-0.89825	0.66223	0.97787*	1

2-tailed test of significance is used. *:Correlation is significant at the 0.05 level.

those of other organochlorine compounds, may be linked to the high frequency of these isomers which have also been reported to occur in the sampled soils from cocoa farms in the studied area, and at concentrations of up to 350.10 and 3.55 mg/kg for the α- and β- isomers respectively (Aiyesanmi and Idowu, 2012b). This suggests the carriage of the compounds in run-off water from the cocoa farms to the surrounding water environment.

In general, there seems to be no specific relationship between the concentrations of the organochlorine pesticides residues in the water and those measured in the sediments, that is, our data provides no evidence of accumulation of OCPs in the river sediments, indicating that the positions on the rivers with high OCP concentration did not necessarily have high levels of the chemicals in the sediment sample from the same positions. Also, concentrations of the organochlorine compounds in the upstream, midstream, and downstream water and corresponding sediment samples do not appear to follow any specific trend as varying concentrations were measured at different instances of location within the rivers.

There are also no observable correlations between the concentration of the organochlorine compounds and the sediments' pH. However, the organic matter (O.M) content of the river sediments appears to influence the retention of the organochlorine pesticide molecules as reflected in the recorded significant positive correlation (0.9778) between the total OCP content of the sediments and the organic matter content at 95% confidence level($p<0.05$) as shown in Table 5. This is also in congruence with what was earlier reported (Aiyesanmi and Idowu, 2012b). The correlation analysis also shows a high positive correlation (0.94052) between the total OCP concentration and the clay content of the sediment samples, suggesting that the retention of organochlorine pesticide in river sediments is also influenced by the clayey matter of the sediments.

Conclusion

This study has presented information on the different

organochlorine pesticides residues and their levels in water and sediment around cocoa farms in the Ondo State Central Senatorial District of Nigeria. Endosulfan isomers were found most frequently in the water and sediment samples, and were also of the highest concentrations, believed to be connected with the high concentrations of the compounds previously reported in the soil samples from cocoa farms in the area.

Lindane, aldrin, dieldrin, β- BHC, δ-BHC and heptachlor epoxide were also detected in the various samples. The fact that there were no specific trends in the concentrations of organochlorine compounds found in the upstream, midstream, and downstream samples suggest that the pollution of the waters and sediments emanates from diverse non-point sources, and possibly from varied application of different kinds of pesticides and combinations of pesticides on the cocoa farms in the area.

The results also showed that the concentration of the organochlorine pesticides in the river sediments is associated with the organic and clayey matter contents of the sediments. The high concentrations of the pesticides found in the water and sediment samples pose a risk to human and aquatic life and provide an indication of wrong use of the associated pesticide preparations. This work will provide a reference with which future levels of organochlorine pesticides in rivers, and sediments can be monitored in these areas.

REFERENCES

Adeyemi D, Ukpo G, Anyakora C, Unyimadu JP (2008). Organochlorine Pesticide Residues in Fish Samples from Lagos Lagoon, Nigeria. Am. J. Environ. Sci. 4:649-653.
Aikpokpodion PE (2010). Nutrients dynamics in cocoa soils, leaf, and beans in Ondo State, Nigeria. J. Agric. Sci. 1:1-9.
Aiyesanmi AF, Idowu GA (2012a). Determination of organophosphorous pesticide residue in some selected cocoa farms in Idanre, Ondo

State, Nigeria. Electron. J. Environ. Agric. Food Chem. 11:118-127.

Aiyesanmi AF, Idowu GA (2012b). Organochlorine pesticide residues in soil of cocoa farms in Ondo State Central District, Nigeria. Environ. Nat. Resour. Res. 2:65-73.

Ajayi JR, Afolabi MO, Ogunbodede EF, Sunday AG (2010). Modelling rainfall as a constraining factor for cocoa yield in Ondo State. Am. J. Sci. Ind. Res 1:127-134.

Atuma S, Okor D (1985). Gas chromatographic determination of pentacholrophenol in human blood and urine. Bull. Environ. Contam. Toxicol. 62:199-206.

Bentzen TW, Follman EH, Amstrup SC, York GS, Woller MJ, Muir DCG, O'Hara TM (2008). Dietary biomagnification of organochlorine contaminants in Alaskan polar bears. Canadian J. Zool. 86:177-191.

Burns JS, Williams PL, Sergeyev O, Korrick SA, Lee MM, Revich B, Aithsul L, Del Prato JT (2012). Serum concentrations of organochlorine pesticides and growth among Russian boys. Environ. Health Perspec. 120:303-308.

Caldas ED, Coelho RLC, Souza KR, Siba SC (1999). Organochlorine Pesticides in water sediment and fish of Paranoia Lake of Brasilia. Brazilian Bull. Environ. Contam. Toxicol. 62:199-206.

Campoy C, Jimenez M, Olea-Serrano MF, Moreno Frias M, Canabate F, Olea N, Bayes R, Molina-Font JA (2001). Analysis of organochlorine in human milk: preliminary results. Early Hum. Dev. 65:183-190.

Cremlyn RJ (1991). Agrochemicals preparation and mode of action (New York: John Wiley & Sons), pp. 1-16, 79-101.

Darko G, Acquaah SO (2007). Levels of Organochlorine Pesticide Residues in Meat. Int. J. Environ. Sci. Technol. 4:1735-1742.

Hapeman CJ, Schmidt WF, Rice CP (1997). Structural and thermodynamic considerations in the isomeric conversion of endosulfan. In: 213th National Meeting of the American Chemical Society, San Francisco, California, USA, April 13-17.

Hendershot WH, Lalande H, Duquette M (1993). Soil reaction and exchangeable acidity, In: M.R. Carter (ed.) Soil sampling and Methods of analysis. Canadian Society of Soil Science (London: Lewis Publishers). pp. 141-145.

Ize-Iyamu OK, Abia IO, Egwakhide PA (2007). Concentrations of residues from organochlorine pesticides in water and fish from some rivers in Edo State, Nigeria. Int. J. Phys. Sci. 2:237-241.

Le Maire G, Terouanne B, Mauvais P, Michel S, Rahmania R (2004). Effect of organochlorine pesticides on human androgen receptor activation in vitro. Toxicol. Appl. Pharmacol 196:235– 246.

Osibanjo O, Adeyeye A (1997). Organochlorine pesticide residues in foodstuffs of animal origin in Nigeria. Bull. Environ. Contam. Toxicol. 58:206-21.

Osibanjo O, Bamgbose E (1990). Review of chlorinated substances in Marine fish and shellfish of Nigeria. Mar. Pollut. Bull. 21:581-586.

Osibanjo O (1994). Review of chlorinated hydrocarbon substances in African aquatic environment. Food and Agricultural Organisation, Fish Report. 502:37-45.

Osibanjo O, Adeyeye A (1995). Organochlorine residues increase. Toxicol. 54:460-465.

Pandit GG, Mohan RAM, Jha SK, Krishnamoorthy TM, Kale SP, Raghu K, Murthy NBK (2001). Monitoring of organochlorine pesticide residues in the Indian marine environment. Chemosphere 44:301-305.

Pope JV, Skurky-Thomas M, Rosen CL (1994). Toxicity, Organochlorine Pesticides (New York: Medscape). pp. 259-278.

Rice CP, Hapeman CJ, Chernyak SM (1997). Experimental evidence for the inter-conversion of endosulfan isomers. In: 213th National Meeting of the American Chemical Society, San Francisco, California, USA, April 13-17.

Schulte EE (1995). Recommended soil organic matter test. In: E.E. Schulte (ed.) Recommended soil testing procedures for the North-eastern United State. 2nd Edition.

Shedrick BH, Wang C (1995). Particle size distribution. In: Carter, M.R. (ed.) Soil sampling and methods of analysis. Canadian Society of Soil Science, Lewis Publishers, London. pp. 449-511.

Staare JU, Benhoft A, Derocher A, Gabrielsen GW, Gokbyr GW, Henriksen E (2000). Organochlorines in top predators at Svalbard – occurrence, levels and effects. Toxicol. Lett. 112:103-109.

Swackhamer D, Hites RA (1988) Occurrence and bioaccumulation of organochlorine compounds in fish from Siskiwit lake, Isle Royale, Lake Superior. Environ. Sci. Technol. 22:543–548.

Tiryaki O, Baysoyu D (2006). Estimation of sample processing uncertainty for chlorpyrifos residue in cucumber. Accredit. Qual. Assur. 10:550-552.

US EPA Method 1699 (2007). Pesticides in water, soil, sediment, biosolids, and tissue by high resolution gas chromatography with high resolution mass spectrometry. Available online at www.water.epa.gov (accessed 6th August 2012)

Uyimandu JP (2002). Comparative studies of Organochlorine and PCBs in Fish from the Lagos Lagoon. J. Agric. Biotechnol. Environ. 4:14-17.

Vitosh ML, John JW, Mengel B (1995). Tri-state recommendation for corn, soyabean and wheat. Extension Bulletin E. New York. P. 252.

World Health Organisation (WHO), (1990). Chemistry and specifications of pesticides. Thirteenth report of the WHO expert committee on vector biology and control, Geneva © WHO 1990.

World Health Organisation (WHO), (2011). Guidelines for drinking water quality. Fourth Edition © World Health Organisation. pp. 179-191, 307-443.