

This is the accepted version of this paper.

The final version of record is published in Nigerian Research Journal of Chemical Sciences.

<https://www.unn.edu.ng/nigerian-research-journal-of-chemical-sciences/>

Full citation:

Adegun, Ayodeji Oluwole, Akinnifesi, Thompson Akinyele, Adewunmi, Annabella Ademuyiwa, Alaba, Gbemisola Mary, Odeniran, Abosede Omolayo, Agboola, Olubukola Oyebimpe, Adeagbo, David Adeniyi, Adebayo, Olayinka Anthony, Aseperi, Kayode Adeniyi and Barker, James (2024) Organochlorine and organophosphate pesticides in cocoa-producing soil, sediment, surface and treated water from Owena River Basin, Nigeria. Nigerian Research Journal of Chemical Sciences, 12(2), pp. 418-447. ISSN (print) 2682-6054

Organochlorine and Organophosphate Pesticides in Cocoa-Producing Soil, Sediment, Surface and Treated Water from Owena River Basin, Nigeria

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Accepted: December 3, 2024. Published Online: December 17, 2024

ABSTRACT

This study monitored the occurrence and distribution of organochlorine (OC) and organophosphate pesticide (OP) residues from cocoa-producing soil farmland into river Owena in Ondo State, Nigeria. The aim of this study was to assess the impact of these chemicals on the quality of Owena River water. The soil and sediment samples were extracted using ultrasonic bath extractor while the water samples were extracted by liquid-liquid extraction method. All the extracted samples were analyzed with a gas chromatograph coupled to a mass spectrometer. The results indicated the total mean concentrations of organochlorine pesticide residues in the soil, sediment and surface water samples in dry season were 5.92 μ g/g and 3.92 μ g/g and < 0.01 μ g/L respectively while their wet season levels were 4.32 μ g/g, 2.89 μ g/g and below detection limit (BDL) for soil, sediment and surface water respectively. The dry season observations for organophosphate residues were 19.79 μ g/g, 4.49 μ g/g and < 0.01 μ g/L respectively for soil, sediment and surface water samples while the wet season values were 3.78 μ g/g, 2.51 μ g/g and BDL for soil, sediment and surface water respectively. The level of pesticide residues in some of soil samples was higher than the Food Agricultural Organization (FAO) maximum residues limit. Their level in the sediment samples was higher than EU MRL of 0.3 μ g/g. However, their levels in the water samples were lower than 10 μ g/L and 0.1 μ g/L limits by Nigerian Federal Ministry of Environment and WHO for pesticides in drinking water. This study concluded that the soil, sediment and water samples from the study area were contaminated with pesticides residues although the treated water is safe for drinking.

Nevertheless, the dry season contamination level was higher than wet season. The study recommended proper enforcement of the laws on the handling and usage of these chemicals for control of pests in the study area.

Keywords: Pesticides, organochlorine, organophosphate, soil, sediment, water, gas chromatograph

INTRODUCTION

Pesticides contamination of water is a global issue as it causes problems in the environment which could lead to serious health concern for man [1]. The high toxicity of organochlorine pesticides has particularly caused serious health problems which are of global concern. Apart from toxicity, OCP are persistent, bioaccumulative and have adverse effect on human health and ecosystem [2]. Human exposure to pesticide poisoning could be chronic or acute. This poisoning occurs when man inhales, or ingests the contaminant from polluted air or through skin contact during spraying as well as consuming contaminated food and drinking water [3].

In Nigeria, pesticide usage has continued to increase for improved agricultural yield [4]. Most of these pesticides especially organochlorine pesticides have been banned worldwide. However, some of these banned persistent organochlorine pesticides such as endosulfan are still being used by the farmers in Nigeria and some other developing countries [5].

Cocoa mirids are the major problems facing cocoa farmers in Ondo State, Nigeria as they cause diseases to cocoa plants [6]. These pesticide residues in cocoa-producing soils may be discharged through run off or other sources into ephemeral streams as well as surface impediments and finally into the river Owena which is the major source of drinking water supply in Ondo Central Senatorial District, Nigeria. River Owena runs along the major coca producing area of Ondo State where insecticides are frequently sprayed to control cocoa mirids.

The contamination of water by these pesticides have been an important issue in many parts of the world and has been posing problems in environmental, water management and health sectors as a wide range of activities have the potential to contaminate both surface and ground waters [6]. Despite the benefits derived from the application of these chemicals, the environmental consequences of the widespread use, handling and disposal of pesticides are of great concern [7].

Organochlorine pesticide (OCP) contamination may lead to memory loss, loss of coordination, reduced speed of response to stimuli, visual ability reduction, asthma allergies, hypersensitivity, cancer, hormone disruption, problems of reproduction and fetal development [8]. OCP residues in mother's blood during pregnancy may lead to poorer mental development

in children at tender age [9, 12]. It may also lead to neuro-developmental delays during early childhood [3, 7, 9]. Consequently, the application of OCP for agricultural activities was banned globally [10-11]. OPP residues exposure suggests a possible link to adverse effects in the neurobehavioral as it affects a large number of organs and physical processes [12-13]. Figures 1 and 2 give the structures of the OC and OP pesticides.

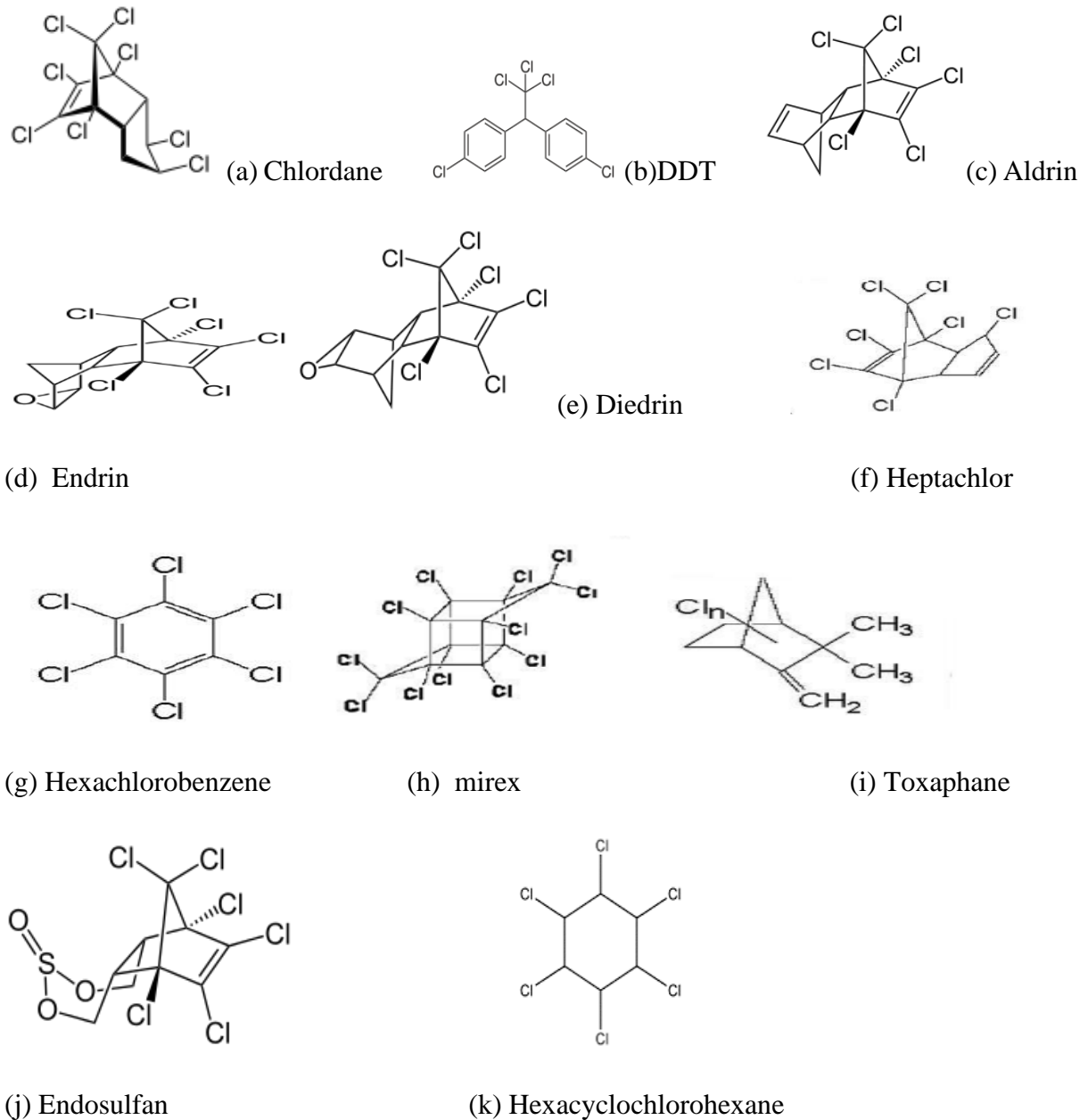
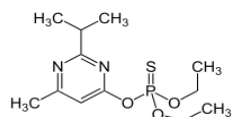
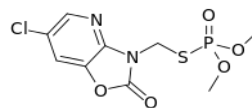


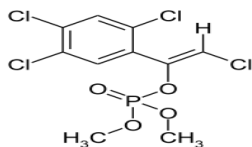
Figure 1(a-k): Chemical structures of some organochlorine pesticides



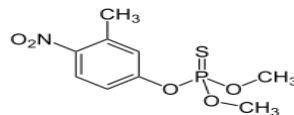
(a) Diazinon



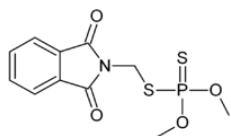
(b) Azamethiphos



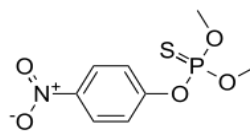
(c) Tetrachlorvinphos



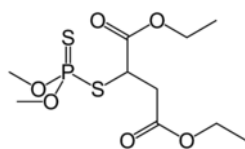
(d) Fenitrothion



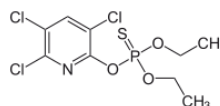
(e) Phosmet



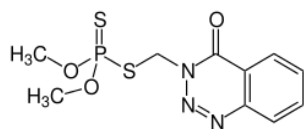
(f) Methyl Parathion



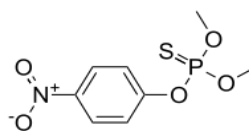
(g) Malathion



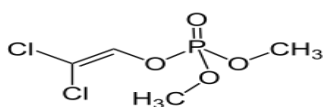
(h) Chlorpyrifos



(i) Azinphos-methyl



(j) Parathion



(k) Dichlorvos

Figure 2 (a-k): Chemical structures of organophosphates (OP) pesticides

In Nigeria, there are two seasons namely the dry and wet seasons. The wet season runs between April to October while the dry season starts in November and ends in March.

Earlier studies on Owena River basin did not report the effect these contaminants on the quality of the Owena River drinking water produced at the Ondo State Water Works. Hence, this current study intends to fill the knowledge gap. Ayesanmi *et al.*, [15] reported organochlorine

pesticide residues contamination in soils of cocoa farms in Ondo State Central Senatorial District, Nigeria where he discovered that the soil of those selected farms around the river basin were polluted with OCP residues. Others studies in Nigeria included the determination of the concentration of organophosphate pesticide residues in water and sediments from river Ilaje, Nigeria by Akinnawo *et al.*, [12]. Okoya *et al.*, [6] reported the presence of organochlorine pesticide residues in sediments and waters of rivers of cocoa producing areas of Ondo State Southwestern, Nigeria. They also reported that the concentrations of OCPs in the sediment from these rivers were higher than the surface water level. Nevertheless, literature survey revealed that there is little information on the levels and distribution of these pesticides in Owena River basin soil, the river water and treated water from the State Water works and their health implication. The theoretical basis for this study is based on the hypothesis that pollution from pesticide residues from cocoa producing soil could be detected via the monitoring of the pollutants in environmental matrices during dry and wet seasons. Therefore, the specific objectives of this study were to: (i) investigate the presence and the type of pesticide residues in the cocoa soil and monitor their seepage into Owena River water and sediments through runoff and other sources; (ii) assess the presence of these pesticide residues in the raw and treated water at the site of the State water works.

MATERIALS AND METHODS

Description of study area

The map of the study area and sampling sites were presented in Figure 3. The Owena River basin is located on geographical coordinates $7^{\circ} 12'$ and $5^{\circ} 5'E$ in Ondo East Local Government Area of the Ondo State. The study area is Owena town which lies along Ondo-Akure road. This area is an environmentally sensitive since water of the River Owena has to be processed to potable standards for human consumption. The areas for the consumption of this water include: Ifedore, Akure North, Akure South, Ondo West, Ondo East and Idanre local government areas. The study area is noted for cocoa farming around the river basin as well as fishing at the Owena river. Therefore, the people of the study area are mostly farmers and fishermen who sold their proceeds to the public for consumption. The villages around the study area are Kajola, Ijiziogba, Ago Eleshin, Aparere, Wasimi and Bolorunduro amongst others.

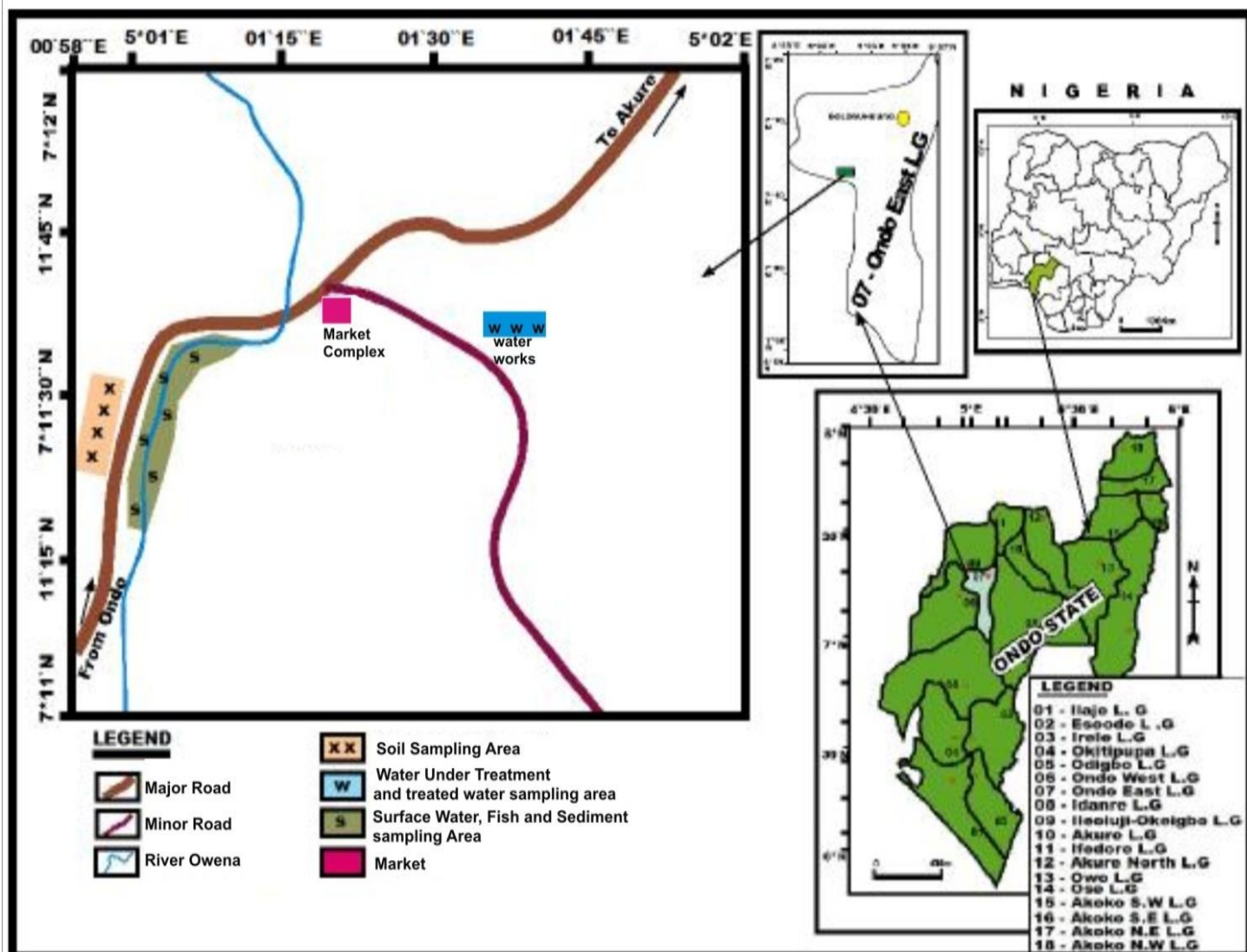


Figure 3: Map of the study area showing the Location of Owena River Basin, Ondo State, Nigeria [4].

Preparation of Stock, Intermediates and Calibration Solutions

All solvents used in this work were of pesticide grade and the reagents were of high purity in accordance with official analytical chemists' specifications. Standard stock solutions of the endosulfan external standard were made at 1000 ppm, by dissolving 0.0100 g of endosulfan pure standard provided by Sigma-Aldrich (UK) in hexane and diluting to volume in 10 mL volumetric standard flasks. The intermediate standard solutions were made at 5ppm. The endosulfan calibration standard was prepared at five different concentrations of 0.01ppm, 0.05ppm, 0.1ppm, 0.5ppm and 1ppm. The prepared standard solutions (stock, intermediate and calibration) were all stored in sealed PTFE containers in the dark.

Collection, Handling, Preservation and Storage of Soil Samples

Thirty soil samples were collected under each cocoa plant canopy from the depth of 0-15 cm by grab method using a soil auger to form a composite sample. The soil samples were collected in aluminum foils, air dried at room temperature and sieved through 2mm stainless sieve to remove coarse debris and stones [13-15].

Collection, Handling, Preservation and Storage of Sediment Samples

Thirty sediment samples were collected from 0-5 cm depth from the same spot in which the water samples were collected. The sediment samples were taken from the bottom surface of the river by metal grab and wrapped up in aluminum foils, air dried and sieved through 2.0 mm stainless steel sieve [16-19].

Collection, Handling, Preservation and Storage of Water Samples

Twenty composite surface, water under treatment and treated water samples were collected by grab method from the river, using pre-treated Winchester glass bottles with teflon lined screw caps. The winchester bottles stopper were removed just before sampling and the bottles were rinsed thrice with the river water. The bottom of each bottle was held with one hand while the neck held withheld with another hand and the bottle inserted into the river water at about 60 cm depth. The mouth was directed against the direction of the water current as the water flows into the bottle. The water samples were acidified with 10 mL (HPLC grade) H₂SO₄ to prevent degradation by microbes and 10 mL of extracting solvents were added to start the extraction process [12, 20, 21] and stored at 4°C in the laboratory prior to analysis.

Extraction of Pesticide Residues from the Soil and Sediment samples

The extraction of the pesticides from the solid samples was performed by EPA method 3550c. A super Scientific-100005(50W, 45 KHz) ultrasonic bath was used. Ten grams of the soil or sediment samples was weighed into a 50 mL glass beaker. Fifty gramme of Na₂SO₄ was added and the mixture covered with aluminum foil and extracted with 20 mL of the extracting solvent mixture (acetone/hexane 1:1v/v) [22, 23]. The temperature of the ultrasonic bath was set at 25°C and the extraction time was set at 30 minutes. The glass beaker was placed on the ultrasonic bath and a sufficient water quantity was deposited to cover three quarters of the beaker. The extractions were carried out thrice, combined and filtered prior to the cleanup [24].

Extraction of Pesticide Residues from the Water Samples

Pesticide residues extraction from the river, raw and treated water samples were carried out with EPA method 3510c [24]. Sixty mL of hexane were introduced into a separating funnel containing 1000 mL of the water samples and 5 g of NaCl for phase separation and shaken vigorously for about 30 minutes. The samples were allowed to settle to ensure separation of the phases. After separation, the organic layer was filtered into a 250 ml amber glass bottles that has been pre-washed with hexane and 5g Na₂SO₄ added to remove any residual water in the organic phase [Figure 5]. The extracts were filtered and extractions were repeated thrice using a 60 mL portion of hexane and later combined for cleanup.

Clean-Up of the Extract

The extracts were concentrated to 20 mL volume with a gentle nitrogen current and then added with 10mL of 0.1M Na₂CO₃ solution and shaken for 10 minutes. The aqueous phase which contains free fatty acids was discarded [16]. Two grammes of activated copper powder were added to the organic phase and shaken for 5 minutes to remove Sulphur interference that may likely be associated with sediment samples [16, 24]. The organic phase was separated by column chromatographic cleanup technique in which 10g of alumina in a slurry was placed in the chromatographic column. The column was tapped to settle the alumina and 2 g of anhydrous Na₂SO₄ was added to the top of the column. The column was then pre eluted with 40mL of hexane at elution rate of 2 mL/min. Twenty mL sample extracts were then quantitatively transferred into the column using additional 2mL of hexane to complete the transfer. The column was finally eluted with 140mL ethyl ether/hexane (1:4v/v) and the eluate was concentrated to 2 mL with a gentle stream of N₂ current. The cleaned concentrated extracts were transferred into amber vials for analysis with GC/MS [24].

GC-MS Analysis

A gas chromatograph from Agilent USA hyphenated to a mass spectrophotometer (5975C) with triple axis detector equipped with an auto injector (10µL syringe) and helium as a carrier gas was used for the analysis of the cleaned extracts in triplicates. All the chromatographic separations were performed on capillary column having the specification: length; 30m, internal diameter (0.2µm), thickness; 250µm, treated with phenyl methyl siloxane. Other GC-MS conditions are ion source temperature (EI) 250 °C, interface temperature; 230 °C, pressure; 16.2 psi out time, 1.8 mm, 1µL injector in split mode with split ratio 1:50 with injection temperature of 300 °C. The total elution time was 47.5 minutes. The identification of the

compounds of interest was carried out by comparing the mass spectra obtained with those of the standards mass spectra from NIST library.

Calculation of OC and OP Pesticides Concentrations Using External Standard Method

The external standard is like the internal standard (known behaviour), but is not added to the unknown. Rather it is run alone, as a sample and usually at different concentrations in order to generate a standard curve [14]. Again, the peak areas are related to the known amounts of external standard run. In external standard quantitation, known data from a calibration standard and unknown data from the sample are combined to generate a quantitative report. It is called external standard because the standard or known material is separate or external to the unknown material. External standard calibration is one of the most common approaches to calibrations. It involves a simple comparison of instrument responses from the sample to the target compound responses in the calibration standards [16]. Sample peak responses are compared with calibration standard peak responses. The ratio of the detector response to the amount (mass) of analyte in the calibration standard is defined as the calibration factor. Starting from standard of lowest concentration each calibration standard is analysed and the response (peak height or area) versus the concentration in the standard is tabulated. The results can be used to prepare a calibration curve for each compound. The ratio of the detector response to the amount (mass) of analyte in the calibration standard is determined as the calibration factor. When external standard calibration is employed, the calibration factor for each analyte at each concentration will be calculated and the mean calibration factor, and their relative standard deviation (RSD) of the calibration factors for each analyte will be determined [4, 22].

For aqueous samples (Water)

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_x) (V_t) (D)}{(CF) (V_i) (V_s)} \quad \text{Equation 1}$$

where:

A_x = Area of the peak for the analyte in the sample.

V_t = Total volume of the concentrated extract (μL).

D = Dilution factor =1, since the extracts were not diluted prior to analysis.

CF= Mean calibration factor from the initial calibration

Vi = Volume of the extract injected (μL).

Vs = Volume of the aqueous sample extracted in mL.

Using the units given here for these terms will result in a concentration in μg/L.

For non –aqueous (Soil and sediment samples)

$$\text{Concentration } (\mu\text{g/g}) = \frac{(A_x) (V_t) (D)}{(CF) (V_i) (W_s)} \quad \text{Equation 2}$$

where:

Ax = Area of the peak for the analyte in the sample.

Vt = Total volume of the concentrated extract (μL).

D = Dilution factor =1 since the extracts were not diluted prior to analysis.

CF= Mean calibration factor from the initial calibration.

Vi = Volume of the extract injected (μL).

The Calibration factor (CF) of the endosulfan external standard was calculated as:

$$\frac{\text{Peak area of standard}}{\text{Total amount of standard Injected}} \quad \text{Equation 3}$$

Quality Assurance for GC/MS Determination

Several quality assurance steps were undertaken in this study. These important measures include but not limited to monitoring of gas chromatography every day during the period of the analysis by checking the range of response factors of the calibration standards, running of blanks. Other quality assurance measures include exhaustive cleanup of reagents, ensuring that pure solvents and clean glasswares were used to eliminate background phythalate ester contamination.

RESULTS AND DISCUSSION

Organochlorine pesticides in soil samples

The mean concentration of the OCP detected from the cocoa-producing soil samples is shown in Tables 1 and 2. These values ranged from 0.89μg/g to 21.09μg/g and BDL to 9.55μg/g respectively for dry and wet seasons. Their total mean concentration values were 5.92±6.56μg/g and 4.32±3.79μg/g for dry and wet seasons respectively. The OCP residues may affect the physicochemical properties of the soil [18]. The trend in the distribution of these pollutants as shown in dry season aldrin > chlobycyclen > lindane > trans-chlordane > cis-

chlordane > α endosulfan > β endosulfan > hexachlorobenzene (Table1). Their distribution trend in wet season is aldrin > lindane > α endosulfan > β endosulfan (Table 2). The higher occurrence of OCP residues in the soil samples in dry season could be due to their persistence in the environment through applications. Their low concentration in the soil surface in wet season could be due to leaching. These contaminants could have been leached down from the surface of the soil in wet season. Although, most of these halogenated pesticides are no longer approved for cocoa farming in Nigeria, yet they are still found in the environment. Their occurrence in the study area showed that probably pesticide formulation with organochlorine active ingredients were commonly used in the study area. Their presence could also be due to previous, or recent, usage probably under different trade names. OCP residues are known to be very toxic, persistent with a higher accumulation and bioaccumulation potentials in sediments and aquatic organisms respectively [28]. They have been banned at the Stockholm Convention in Sweden as they are known as persistent organic pollutants [10]. They are among the banned dirty dozen and nasty nine [10]. They have half-lives between six to more than ten years. Hence, they do not degrade easily in the environment [25-27].

However, despite their ban, this study revealed that they are still present in the environment. Farmers could be buying them, under different trade names ignorantly due to their high pesticidal efficiency. The result from this study was lower than the 0.013-350.100 mg/kg reported by Aiyesanmi and Idowu [15] on OCP residues in soil of cocoa farms in another location of Ondo State Central Senatorial District, Nigeria. This study was however in agreement with 0.01–0.05 mg/kg reported in a study by Fosu-Mensah *et al.*, [2] on the assessment of organochlorine pesticide residues from cocoa soils in Ghana. The mean concentrations of the OCP residues from this study were lower than the $37.67 \pm 0.33 \mu\text{g/g}$ reported by Kumar *et al.*, [28] in a study on persistent organochlorine pesticides and polychlorinated biphenyls residues in intensive agricultural soils in North India. However, the level of OCP in this study was lower than the 0.05mg/kg US maximum residue limit for slightly polluted and $8 \mu\text{g/g}$ limit [28] by the Food Agricultural Organisation of United Nations Maximum Residue Limit (MRL).

Table 1: Mean Concentration (\pm SD) and Range of Organochlorine Pesticide Residues in Cocoa-Producing Soil, Sediment, Surface Water, Water under Treatment and Treated Water Samples During Dry Season

Pesticide	Soil ($\mu\text{g/g}$)	Range	Sediment ($\mu\text{g/g}$)	Range	Surface water ($\mu\text{g/L}$)	Range	Water under treatment ($\mu\text{g/L}$)	Range	Treated water ($\mu\text{g/L}$)	Range
Aldrin	21.09 \pm 4.98	20.41-22.38	18.02 \pm 0.04	17.95-18.17	0.04 \pm 0.01	0.03-0.06	0.01	0.00-0.01	BDL	-
Lindane	6.25 \pm 2.92	6.50-6.98	3.46 \pm 0.04	3.28-3.88	BDL	-	BDL	-	BDL	-
AEndosulfan	2.04 \pm 0.56	2.46-2.86	0.29 \pm 0.06	0.23-0.30	BDL	-	BDL	-	BDL	-
β Endosulfan	2.05 \pm 0.28	2.34-2.65	0.27 \pm 0.03	0.26-0.32	BDL	-	BDL	-	BDL	-
Hexachlorobenzene	0.89 \pm 0.15	0.78-0.92	0.65 \pm 0.39	0.64-0.69	BDL	-	BDL	-	BDL	-
Chlobycyclen	6.67 \pm 2.19	6.59-7.14	0.44 \pm 0.10	0.42-0.47	BDL	-	BDL	-	BDL	-
Cischlordane	4.19 \pm 0.14	4.06-4.32	4.37 \pm 2.91	4.18-4.93	BDL	-	BDL	-	BDL	-
Trans-chlordane	4.20 \pm 0.95	4.08-4.28	3.89 \pm 0.68	3.78-3.96	BDL	-	BDL	-	BDL	-
Σ OCP	47.38	-	31.39	-	0.04	-	0.01	-	-	-
Total Mean	5.92	-	3.92	-	< 0.01	-	< 0.01	-	-	-
SD	6.56	-	5.57	-	-	-	-	-	-	-
CV	110.81	-	142.89	-	-	-	-	-	-	-
ANOVA	P \geq 0.05	-	P \geq 0.05	-	-	-	-	-	-	-
Remarks	NS	-	NS	-	-	-	-	-	-	-

Σ OCP= Total organochlorine pesticides residues; BDL = Below detection limit; SD = Standard deviation; ANOVA=Analysis of variance; NS = No significant difference. Detection limit = 0.0001($\mu\text{g/g}$) ($\mu\text{g/L}$)

**Means values are of triplicate analyses.

Table 2: Mean Concentration (\pm SD) and Range of Organochlorine Pesticide Residues in Cocoa-Producing Soil, Sediment, Surface Water, Water under Treatment and Treated Water Samples During Wet Season

Pesticide	Soil ($\mu\text{g/g}$)		Sediment ($\mu\text{g/g}$)		Surface water ($\mu\text{g/L}$)		Water under treatment ($\mu\text{g/L}$)		Treated water ($\mu\text{g/L}$)	
	mean \pm sd	Range	mean \pm sd	Range	mean \pm sd	Range	mean \pm sd	Range	mean \pm sd	Range
Aldrin	9.55 \pm 0.53	9.87-10.15	6.09 \pm 1.02	6.02-6.21	BDL	-	NS ¹	-	NS ¹	-
Lindane	4.67 \pm 0.37	4.20-4.68	3.29 \pm 1.13	3.22-3.79	BDL	-	NS ¹	-	NS ¹	-
AEndosulfan	1.64 \pm 1.07	1.60-1.72	1.21 \pm 1.02	1.19-1.32	BDL	-	NS ¹	-	NS ¹	-
β Endosulfan	1.42 \pm 0.97	1.39-1.46	0.95 \pm 0.76	0.89-0.98	BDL	-	NS ¹	-	NS ¹	-
Hexachlorobenzene	BDL	-	BDL	-	BDL	-	NS ¹	-	NS ¹	-
Chlobycyclen	BDL	-	BDL	-	BDL	-	NS ¹	-	NS ¹	-
Cischlordane	BDL	-	BDL	-	BDL	-	NS ¹	-	NS ¹	-
Trans-chlordane	BDL	-	BDL	-	BDL	-	NS ¹	-	NS ¹	-
Σ OCP	17.28	-	11.54	-	-	-	-	-	-	-
Total Mean	4.32	-	2.89	-	-	-	-	-	-	-
SD	3.79	-	2.38	-	-	-	-	-	-	-
CV	87.73	-	82.35	-	-	-	-	-	-	-
ANOVA	P \geq 0.05		P \geq 0.05		-	-	-	-	-	-
Remarks	NS		NS		-	-	-	-	-	-

Σ OCP= Total organochlorine pesticides residues; BDL = Below detection limit; SD = Standard deviation; ANOVA=Analysis of variance; NS=No significant difference; NS¹ = No sample. Detection limit = 0.0001($\mu\text{g/g}$) ($\mu\text{g/L}$).

**Means values are of triplicate analyses.

Organochlorine Pesticide Residues in Sediment Samples

Tables 1 and 2 showed the results of organochlorine pesticide (OCP) residues detected in the sediment samples in wet and dry seasons respectively. These values ranged from 0.27 $\mu\text{g/g}$ to 18.02 $\mu\text{g/g}$ for dry season and BDL to 6.09 $\mu\text{g/g}$ in wet season. Their total mean concentration was $3.92 \pm 5.57 \mu\text{g/g}$ (Table 1) and $2.89 \pm 2.38 \mu\text{g/g}$ (Table 2) respectively. These values were higher than the European Union (EU) maximum residue limit of 0.3 $\mu\text{g/g}$ for sediment samples. Aldrin, lindane, cis-chlordane and trans chlordane were the frequently occurring OCP residues in the sediment samples.

The trend in the distribution of these pollutants is aldrin > cis-chlordane > trans-chlordane > lindane > hexachlorobenzene > chlobicyclen > α endosulfan > β endosulfan (Tables 1 and 2). All the pesticide residues detected in the soil samples were also found in the sediment samples. Endosulfan with trade name Thiodan was a previously approved insecticide for cocoa farms in Nigeria [5]. Their detection in the soil and sediment matrices of the study area further confirmed the possibility of the farmers still using this chemical despite their banning or they may still be present in the environment due to their persistence [29]. Generally, these pollutants presence in the sediments indicate that they were washed into the Owena River possibly through runoff. OCP such as chlordane and endosulfan are known to have endocrine and estrogenic disrupting effects which may have adverse effect on the ecosystem [30]. The frequency of occurrence of aldrin, lindane, cis and trans chlordane in the sediment matrices show that they are being washed into the Owena River. This is as a result of their current or wide usage of the chemicals before the banning at the Stockholm Convention [31]. Studies have shown that OCP tend to accumulate on the sediments [32]. This study established that the concentrations of sediment samples were generally higher than their corresponding concentration in water samples. This could be due to the hydrophobic nature of these chemicals in water. Moreso. The specific gravities of these pollutants are higher than that of water. Therefore, they tend to sink into the sediments.

In this study, higher concentrations of OCP residues were detected in the sediment samples than the water samples (Figure 4). This observation was in agreement with other previous studies on OCP contamination which reported higher pesticide levels in sediment samples than in the water. This could also be due to the higher specific gravities of these pollutants; hence, they sink into the sediments and harm benthic organisms (33-38). Their contamination could result from varied uptake and toxicity by aquatic organisms. This observation is in agreement with a study

by Osesua *et al.* [4] on the distribution of pesticide residues in water and sediment samples collected from Lugu Dam in Wurno Irrigation Area of Sokoto State, Nigeria. The concentrations of these pollutants in the water samples from that study were lower than that of the sediment samples in this study. This showed that OCPs molecules were sparingly soluble in water. They adsorb on the sediment layer of the river (Fosu –Mensah *et al.*, [2]. The mean level of $3.92 \pm 5.57 \mu\text{g/g}$ and $2.89 \pm 2.38 \mu\text{g/g}$ for dry and wet seasons OCP pollution respectively from this study were higher than $(0.02-0.39) \mu\text{g/g}$ obtained in a previous study by Okoya *et al.*, [6] on the pollution level of rivers receiving runoff from Owena-Ondo River during dry season. This is a prove that the level of pesticide pollutants in Owena River has greatly increased over the years, as cocoa farmers of the river basin have continued to use these chemicals indiscriminately despite the government regulation against their use for agricultural activities.

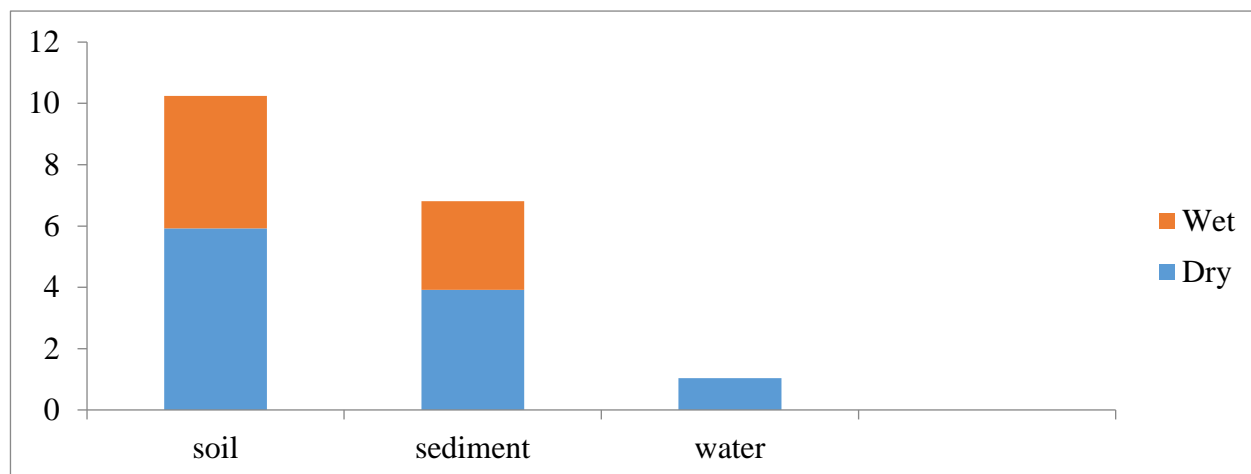
However, this study reported a higher level of OCP residues in dry season than the wet season (Figure 4). This observation could be due to dilution of aquatic ecosystem during wet season (Okoya *et al.*, [6]. Akan *et al.*, [1] reported a higher concentration of organochlorine pesticide residues in sediment samples from River Benue in Vinikilang, Yola, Adamawa State. Adir *et al.*, [30] reported lower concentration of $0.398-1,014 \text{ng g}^{-1}$ in a study of the presence of organochlorine and organophosphorus pesticide residues in urban lake Sediments in Cascavel City, Western Paraná State, Brazil. The value obtained from this study was higher than (EU) maximum residue limit of $0.3 \mu\text{g/g}$ for sediment samples by European Union [34]. The studies revealed that river waters all over the world were polluted with pesticide residues through runoff from agricultural crop protection practices.

Organochlorine Pesticide Residues in Water Samples

Tables 1 and 2 present the result of the values of mean concentration of organochlorine pesticide residues in the water samples. These values for surface water and water under treatment in dry season were $0.04 \mu\text{g/L}$ and $0.01 \mu\text{g/L}$ respectively. No organochlorine residues were detected in the treated water samples. The standard deviation of their mean values was less than $0.01 \mu\text{g/L}$. However, no contaminant was found in the surface water samples during the wet season. This could be as a result of their non-polar and hydrophobic nature. The only organochlorine pesticide residues detected in the surface water samples was aldrin. Exposure to aldrin could cause cancer to human [11]. The presence of aldrin, as the only detected OCP residues in the water samples could be due to its hydrophobicity. It could also be due to its higher specific gravity; hence it tends

to sink into the sediment where they can be toxic to benthic organisms. Generally, OCP are not easily degradable by biodegradation and hydrolysis. Therefore, they persist in the environment for years. The C-Cl bond in their structures makes them to be very toxic. This study reported higher concentration of 0.04-0.001 $\mu\text{g/L}$ (Table 1) in surface water for aldrin than 0.01 \pm 0.01 $\mu\text{g/L}$ reported by Okoya *et al.*, [6] in dry season in a study on OCP residues in rivers receiving runoff from Owena-Ondo River Ondo State, Nigeria. Ibigbami *et al.*, [35] reported a higher OCP mean concentration value of 9.10 $\mu\text{g/L}$ in surface water samples in a study of OC pesticide residues in water and sediment from Ero river, South Western Nigeria. This study is in agreement with a previous study by Akoto *et al.*, [19] on pesticide residues in water, sediment and fish from Tono Reservoir, Ghana where there were no OCP contaminants in the reservoir water. Kuranchie *et al.*, [36] reported mean concentration of 0.185 $\mu\text{g L}^{-1}$ in a study on the determination of organochlorine pesticide residue in sediment and water from the Densu river basin, Ghana. The reported concentration value was lower than 0.40 \pm 0.001 $\mu\text{g/g}$ (Table1) for surface water and higher than 0.00 $\mu\text{g/L}$ (Table 1) for treated water in this current studies. The concentration values of 5.12–39.66 ng L^{-1} reported by Shu Rui Cai *et al.*, [37] in the assessment of organochlorine pesticide residues in water, sediment, and fish of Songhua River, China were higher than the values obtained in the treated water from this study.

The level of aldrin in all the water samples, was lower than 0.05 $\mu\text{g/L}$ WHO [40], 0.1 $\mu\text{g/L}$ (EUC, [34] and 10 $\mu\text{g/L}$ MRL set by Nigerian Ministry of Environment [29]. This suggests that the water is safe for human consumption and aquatic lives.



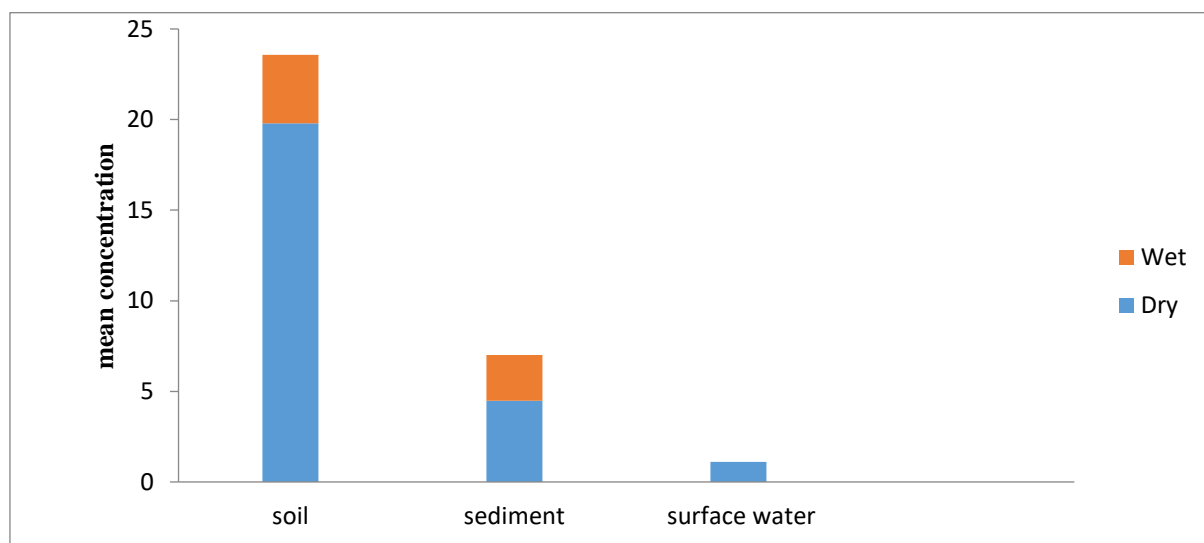
Note: The soil and sediment samples were expressed in $\mu\text{g/g}$ while the water samples were expressed in $\mu\text{g/L}$

Figure 4: Level of occurrence of compounds of organochlorine pesticide residues in cocoa-producing soil, sediment and surface water during wet season and dry seasons.

Organophosphate Pesticide (OP) Residues in Soil Samples

The mean concentration of the organophosphate pesticides detected from the cocoa-producing soil samples is shown in Tables 3 and 4. These values ranged from BDL to $57.34\mu\text{g/g}$ and BDL- $10.20\mu\text{g/g}$ for dry and wet seasons respectively. Their total mean concentration values were $19.79\pm 32.52\mu\text{g/g}$ and $3.78 \pm 5.56 \mu\text{g/g}$ for dry and wet seasons respectively. The mean concentration of chlopyrifos from this current study of $57.34\pm 15.904 \mu\text{g/g}$ (Table 3) in dry season was higher than the US and Nigerian Ministry of Environment MRL of 0.05mg/kg and 0.01mg/kg respectively for residues of pesticides in slightly polluted agricultural soils. However, their values in wet season were lower than these limits indicating the leaching of these contaminants from the topsoil during wet season. Chlopyrifos is a broad spectrum of OP pesticide [18]. It is sold under the trade name “Dursban 48EC” and registered for use in Nigeria [5]. This trend as shown in Tables 3 and 4 revealed comparatively higher level of chlopyrifos in the soil samples than the water and sediment matrices in dry and wet seasons. This is not surprising as chlopyrifos is currently approved by the Nigerian government for cocoa mirids control [5]. This study is in agreement with 0.01–0.04 mg/kg mean concentration reported by Fosu- Mensah *et al.*, [33] on organophosphorus pesticide residues in soils and drinking water sources from cocoa producing areas in Ghana. The result obtained from this study is lower than 0.12-0.24 mg kg^{-1} and 0.024 mg kg^{-1} mean

concentration reported for Chlorpyrifos and diazinon respectively by Wabel, *et al.*, [31] in a study on monitoring of pesticide residues (organophosphate) in soil samples collected from 15 regions around Saudi Arabia. Therefore, it can be deduced from this study that soil in Saudi Arabia is grossly contaminated with OPP residues than that of this study area. That has clearly shown that chlopyrifos was the predominant OPP compounds commonly used in that study area. The trend in the distribution of these contaminants in soil in dry and wet seasons is: Chlopyrifos > Diazinon > Methyl parathion (Tables 3 and 4). However, the wet season contamination was lower than that of the dry season (Figure 5).



Note: The soil and sediment samples were expressed in $\mu\text{g/g}$ while the surface water samples were expressed in $\mu\text{g/L}$

Figure 5: Level of Occurrence of compounds of organophosphate pesticide residues in cocoa-producing soil, sediment and surface water samples during dry and wet seasons

Table 3: **Mean Concentration (\pm SD) and Range of Organophosphate Pesticide Residues in Cocoa-Producing Soil, Sediment, Surface Water, Water under Treatment and Treated Water Samples During Dry Season

Pesticide	Soil ($\mu\text{g/g}$)	Range	Sediment ($\mu\text{g/g}$)	Range	Surface water ($\mu\text{g/L}$)	Range	Water under treatment ($\mu\text{g/L}$)	Range	Treated water ($\mu\text{g/L}$)	Range
Malathion	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-
Chlopyrifos	57.34 \pm 1.904	56.90-57.68	11.86 \pm 5.91	11.89-12.19	0.03 \pm 0.00	-	0.01	-	BDL	-
Fenithrothion	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-
Methyl parathion	0.82 \pm 0.28	0.80 - 0.88	0.76 \pm 0.16	0.72-0.84	BDL	-	BDL	-	BDL	-
Tetrachlovinphos	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-
Diazinon	1.22 \pm 0.96	1.20-1.28	0.85 \pm 0.52	0.79-0.89	BDL	-	BDL	-	BDL	-
Azimphos-methyl	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-
Dichlovos	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-
Σ OPP	59.38	-	11.54	-	0.03	-	< 0.01	-	-	-
Total Mean	19.79	-	4.49	-	-	-	-	-	-	-
SD	32.52	-	6.38	-	-	-	-	-	-	-
CV	167.80	-	142.09	-	-	-	-	-	-	-
ANOVA	P \geq 0.05	-	P \geq 0.05	-	-	-	-	-	-	-
Remarks	NS	-	NS	-	-	-	-	-	-	-

Σ OPP= Total organophosphate pesticides residues; BDL = Below detection limit; SD = Standard deviation; ANOVA=Analysis of variance; NS = Not detected. Detection limit = 0.0001($\mu\text{g/g}$) ($\mu\text{g/L}$).

**Means values are of triplicate analyses.

Table 4: Mean Concentration (\pm SD) and Range of Organophosphate Pesticide Residues in Cocoa-Producing Soil, Sediment, Surface Water, Water under Treatment and Treated Water Samples During Wet Season

Pesticide	Soil (µg/g)	Range	Sediment (µg/g)	Range	Surface water (µg/L)	Range	Water under treatment (µg/L)	Range	Treated water (µg/L)	Range
Malathion	BDL	-	BDL	-	BDL	-	NS ¹	-	NS ¹	-
Chlopyrifos	10.20±0.53	10.05-10.85	6.32±0.66	6.29-6.69	BDL	-	NS ¹	-	NS ¹	-
Fenithrothion	BDL	-	BDL	-	BDL	-	NS ¹	-	NS ¹	-
Methyl parathion	0.39±0.13	0.37 - 0.43	0.56 ± 0.26	0.54-0.61	BDL	-	NS ¹	-	NS ¹	-
Tetrachlovinphos	BDL	-	BDL	-	BDL	-	NS ¹	-	NS ¹	-
Diazinon	0.75±0.06	0.72-0.81	0.65±0.07	0.60-0.72	BDL	-	NS ¹	-	NS ¹	-
Azimphos-methyl	BDL	-	BDL	-	BDL	-	NS ¹	-	NS ¹	-
Dichlovos	BDL	-	BDL	-	BDL	-	NS ¹	-	NS ¹	-
∑OPP	11.34	-	7.53	-	-	-	-	-	-	-
Total Mean	3.78	-	2.51	-	-	-	-	-	-	-
SD	5.56	-	3.30	-	-	-	-	-	-	-
CV	147.09	-	131.47	-	-	-	-	-	-	-
ANOVA	P ≥ 0.05	-	P ≥ 0.05	-	-	-	-	-	-	-
Remarks	NS	-	NS	-	-	-	-	-	-	-

∑OPP= Total organophosphate pesticides residues; BDL = Below detection limit; SD = Standard deviation; ANOVA=Analysis of variance; ND = Not detected; NS= No Significant difference; NS¹ = No sample. Detection limit = 0.0001(µg/g) (µg/L).

**Means values are of triplicate analyses.

Organophosphate Pesticide (OPP) Residues in Sediment Samples

Tables 3 and 4 showed the results of Organophosphate pesticide (OPP) residues detected in the sediment samples in dry and raining seasons respectively. These values ranged from BDL to 11.86 $\mu\text{g/g}$ for dry season and BDL to 6.32 $\mu\text{g/g}$ in wet season. Their total mean concentrations for dry and raining seasons were $4.49 \pm 6.38 \mu\text{g/g}$ and $2.51 \pm 3.30 \mu\text{g/L}$ respectively. The individual mean level of the detected chlorpyrifos, methyl parathion and diazinon were $11.86 \pm 5.91 \mu\text{g/g}$, $0.76 \pm 0.16 \mu\text{g/g}$ and $0.85 \pm 0.52 \mu\text{g/g}$ for dry season. Their values for wet season were: 6.32 ± 0.66 , 0.56 ± 0.26 and 0.65 ± 0.07 respectively. These values were higher than the EU maximum residue limit of 0.3 $\mu\text{g/g}$ for sediment [34] indicating that these pollutants were concentrated in the sediment. All the detected organophosphate pesticide residues found in the soil samples in both seasons were also detected in the sediment samples (Tables 3 and 4). The lower level of methyl parathion indicates it was not frequently used in the study area. The presence of higher concentration of these pollutants in the sediment than the surface water could be as a result of their biodegradation and hydrolysis in water. They degrade in the environment between two to four weeks [2]. These chemicals are washed into the Owena River through runoff and are degraded. The mean concentrations of $0.104 \pm 0.052 \mu\text{g/g}$ of organophosphate pesticide residues recorded for sediment samples in a study by Akoto *et al.*, [19] on pesticide residues in water, sediment and fish from Tono reservoir were lower than the mean concentrations of $4.49 \pm 6.38 \mu\text{g/g}$ and $2.51 \pm 3.30 \mu\text{g/L}$ (Tables 3 and 4) observed from this study in both seasons. The higher concentration of OPP residues in the sediment from this study could be as a result of their indiscriminate or intensive use as approved organophosphate pesticide in the study area [5] which may not be the case in Ghana. Nevertheless, the level of contamination in dry season were higher than wet season (Figure 7). This could be as a result of the mass transport of these pollutants in wet season which led to their lower levels. Akan *et al.*, [1] reported a higher organophosphate mean concentration of $24.12 \pm 5.81 \mu\text{g/g}$ in a study on pesticide residues in sediment samples from River Benue in Vinikilang, Yola, Adamawa State, Nigeria. The mean concentration of $6.352 - 7.447 \text{ng g}^{-1}$ reported by Adir *et al.*, [30] on the presence of organophosphate pesticide residues in urban lake sediments in Cascavel city was higher than the values reported in this study. This could be as a result of their wide usage due to their potency. The distribution trend of compounds of the pesticide residues as shown in Figure 5 is in the order of soil > sediment > surface water. This study observed that chlorpyrifos was more predominantly present in the soil and sediment matrices. They were in

very trace quantities in the water samples. This suggested that chlorpyrifos could be the major organophosphate pesticide applied in the study area. The trend in their contamination in dry and wet seasons is similar to that of the polluted soil: chlorpyrifos > diazinon > methyl parathion (Table 3 and Table 4).

Organophosphates pesticide (OPP) Residues in Water Samples

Tables 3 and 4 present the values of mean concentration of organophosphate pesticides in the water samples in dry and wet seasons. These values for the surface water and water under treatment samples ranged from BDL-0.03 and BDL-0.01 respectively. Their mean values were less than 0.01µg/L respectively in dry season. There was no contaminant found in the surface water samples during the wet season as their concentrations were below detection limit. Treated water and water under treatment were not collected in the wet season due to the shutdown of the treatment plant at the time of wet season sampling. Organophosphate pesticides were not detected in the surface water samples in wet season as a result of the fact that the transport and dispersion of these pollutants in wet season are based on mass movement, mixing and diffusion [6]. The only organophosphates pesticides residues detected in the surface water samples in dry season was chlorpyrifos. Organophosphate compounds are hydrophobic and they accumulate more in sediment and fatty tissues than in water [1], [3], [7], [26]. Their low level in the water from the study area could also be attributed to their low persistence, chemical nature, usage and application level [13]. This study recorded a lower level of OPP for surface water than when compared to what was obtained in a previous study by Ibigbami *et al.*, [35] on assessment of organophosphorus pesticide residues in water and sediments from Ero river in South Western, Nigeria. However, this study is in agreement with a study by Akoto *et al.*, [19] which reported no pesticide contamination in Tono Reservoir, in a study of OC and OP residues in water, sediment and fish from Tono Reservoir, Ghana. This further proved that these pollutants are lipophilic and insoluble in water [36-39]. The 0.03±0.00µg/L (Table 3) level of chlorpyrifos in the surface water samples was lower than 0.05µg/L [40] and 10µg/L MRL set by Nigerian Ministry of Environment [29]. The contamination trend of OC and OP residues in the water samples as shown in Figure 6 revealed that surface water > water under treatment > treated water (Figure 6).

This shows the effectiveness of the treatment plant. Figures 7 and 8 give the representative chromatographic peaks of the detected OC and OP pesticides.

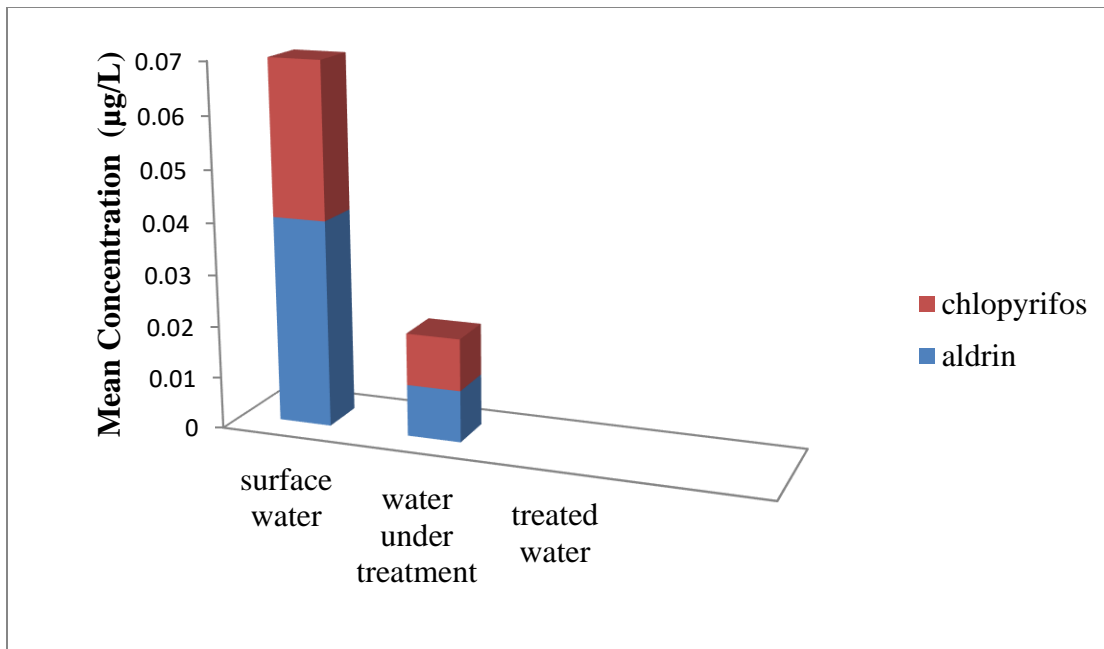


Figure 6: Level of occurrence of aldrin (organochlorine), chlopyrifos (organophosphate) pesticide residues in the surface water, water under treatment and treated water samples in dry season.

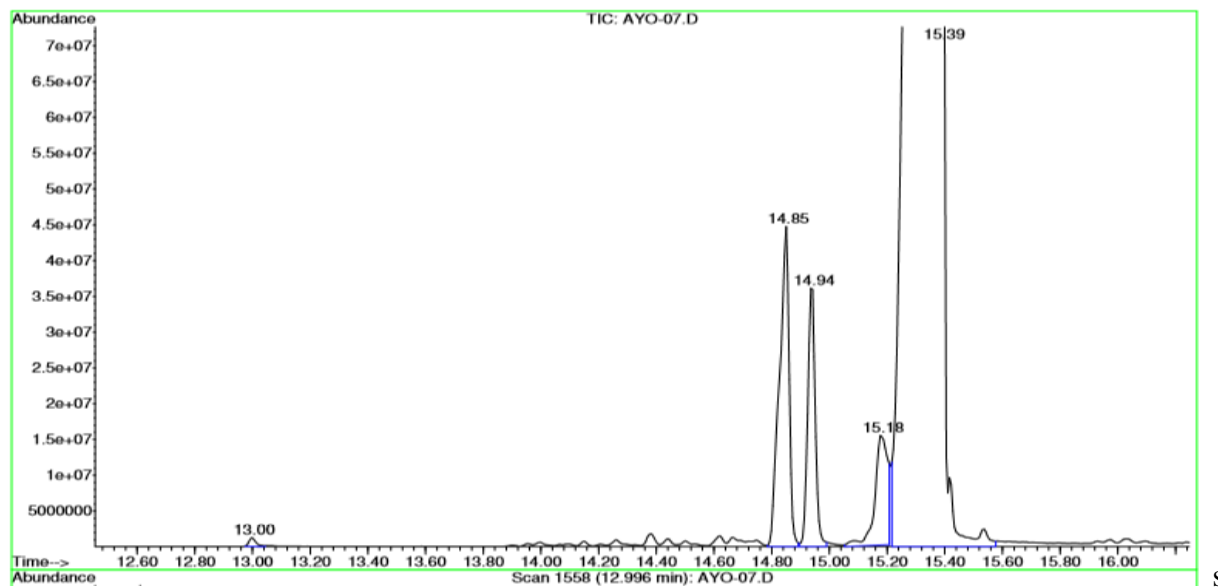


Figure 7: Representative chromatographic peaks of organochlorine pesticides

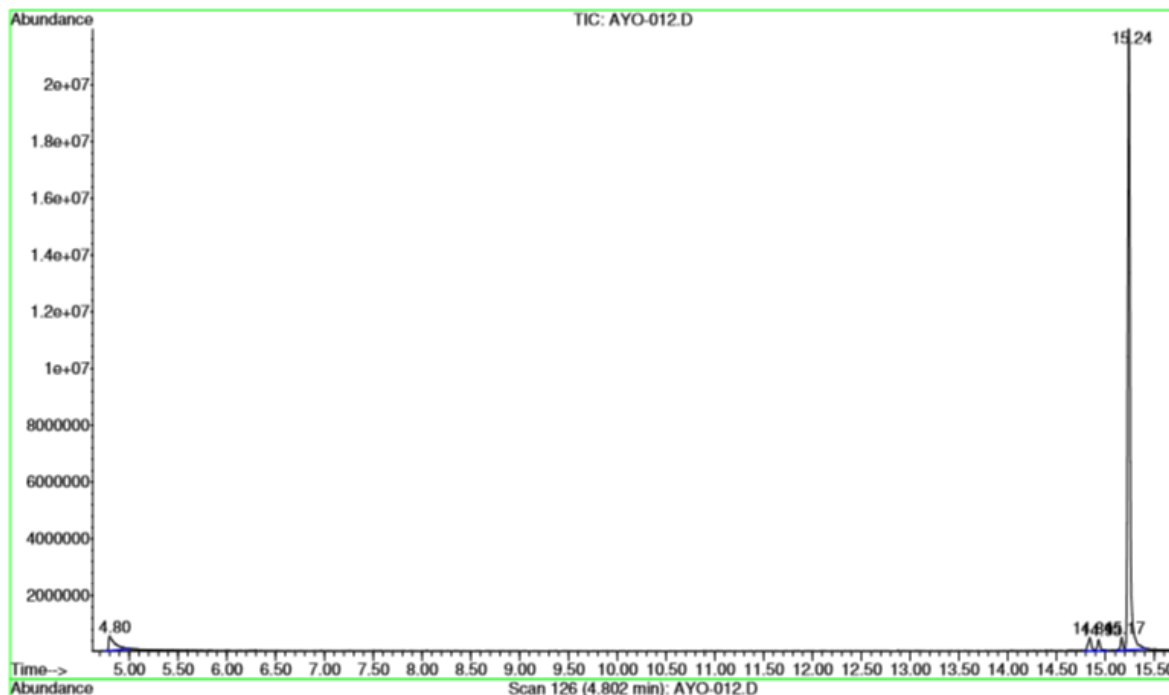


Figure 8: Representative chromatographic peaks of organophosphate pesticides

CONCLUSION

This study concluded that OC and OP pesticides were present in the cocoa producing soil, sediment and surface water of the investigated matrices in the study area. The study also established that these contaminants were more concentrated in the sediment than the water. However, the treated water from the Ondo State Water Works do not contain any of these contaminants and therefore, safe for drinking on the basis of non-chemical pollutants. The study further concluded that dry season contamination was higher than wet season. The data/information from this study could serve as baseline for future studies on organic pollutants in the study area.

LIMITATION OF STUDY

This study was limited with respect to the fact that treated water and water under treatment samples were not collected in wet season due to the closure of the Ondo State Water Works Treatment Plant for maintenance. Hence, the pollution level of these contaminants in the water under treatment and treated water was not determined for that season.

RECOMMENDATION

The study recommended that the global treaty signed at the Stockholm Convention in Sweden in 2001 on the eradication of POPs, especially the organochlorine pesticides, should be domesticated, signed into law and enforced in Nigeria and other developing world countries. Public enlightenment campaigns, should also be put in place for the control of the organophosphates which were also sold under different trade names despite their restrictions globally.

ACKNOWLEDGMENT

The financial support of the Analytical Chemistry Trust Fund of the Royal Society of Chemistry is appreciated, for the Developing World Scholarship awarded to Adegun, Ayodeji Oluwole, to conduct his Ph.D. benchwork in Kingston University, London, UK. This study forms part of his Ph.D. thesis.

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