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Organochlorine Pesticide Residues Levels in Cocoa Pods and Beans from Selected Cocoa Farms in Ondo Central Senatorial District

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Abstract: ***This Research project investigated the level of organochlorine pesticides (OCPS) residues in cocoa farms from three major cocoa producing Local Government Areas including: Akure south, Ifedore, and Idanre, in Ondo state Senatorial District. Cocoa seeds and cocoa pods were collected from three farms in Idanre, Oda and Ilara-mokin. All samples were analyzed for organo chlorine pesticide residues by Gas chromatography with Electron capture detector prior to the chromatography analyses,, extraction of samples was carried out using Ethyl Acetate (Et Ac) with the addition of sodium hydrogen carbonate ($NaHCO_3$). The sample extracts were then cleaned up by gel permeation chromatography (GPC) utilizing silica packed column, and a 1:1 mixture of cyclohexane /ethyl acetate ass eluting solvent. From all indication Endosulfan I occurred most frequently in the samples and at very high concentrations of 3.49mg/kg in pod sample from Ifedore farm 2. Endosulfan II was also detected in some of the sample at much lower concentrations compared to endosulfan I. The three isomers of Benzene hexachloride, α-BHC, β-BHC, and δ-BHC, were detected in some of the samples from the three Local Government Areas. Lindare was not detect in any of the samples. Heptachlor, heptachlor epoxide, aldrin and dieldrin were also measured in the various samples. The research thus, provides information on the current and health risk residue levels of organochlorine pesticides in cocoa fruits, as it is environmental performance on the use of pesticides on cocoa farms should be considered greatly.***

1. Introduction

Organochlorine Pesticides (OCPs) have a long history of wide spread use around the world. They are a class of moderately polar toxic chemical compounds containing Carbon, Hydrogen, and Chlorine. organochlorines are composed of five broad groups namely: the Dichloro-diphenyl-trichloro ethane (DDT) and analogues (e.g. dicofol, methoxychlor), the Hexacholrocyclohexane or Benzene hexachloride and their isomers (e.glindane, the – isomer), the cyclodienes (e.g. chlordane, heptachlor, aldrin, dieldrin, endrin, endosulfan, isodenzan), the Chlordecones (e.g. kelevan and murex), and the Toxaphenes (Pope *et al.*, 1994).

Organochlorine pesticide are ubiquitous environmental contaminants and also have been classified as a group of Persistent Organic Pollutants (POPs) due to their inability to breakdown in their environment; resisting degradation by chemical, physical, microbiological, and biological means (NCEH, 2005; Darko*et al.*, 2007; Swackhamer*et al.*, 1988.). Organochlorine pesticides have half –lives ranging from months to years, and in some cases decades (Cremlyn, 1991). They are toxic to humans and other animals, and very highly toxic to most aquatic life. Organochlorines can have serious short-term and long-term impacts even at low concentrations. In addition, non-lethal effects such as immune system and reproductive damages of most organochlorines may be very significant (Lemaire *et al.*, 2004). They also build up in the fatty tissues of humans, animals and plants. Most of them are attracted to fatty tissues and organs, and are accumulated significantly in animals such as fish (Bentzen *et al.*, 2008; Swackhamer*et al.*, 1988). Thus there is increase in the concentration of Organochlorine molecules up the food chain, with bioaccumulation and biomagnifications taking place in higher organisms including man (Ize-iyamu *et al.*, 2007; DEH, 1997).

One possible reason why organochlorine constitutes a great health risk to animals and humans is the ease with which they are absorbed both orally and by inhalation. A good number of them are also well absorbed transdermally and through the gastro-intestinal tract (Pope *et al.*, 1994).

Because of the multiple types and uses of organochlorine pesticides, exposure to these compounds occurs through diverse means. Rain and wind often move them (i.e. pesticide applied) from points of application, causing contamination of surface waters, ground waters, soil and sediment (Boumane*t al.*, 2002; Shomar *et al.*, 2005). Domestic use of the pesticides and staying close to where they are used or manufactured are also risk factors. The disposal of used household pesticides containers on dumpsite soils which are then carried by drainage is another source of organochlorine pesticides found in water bodies and the environment (Adeyemi*et al.*, 2008). Significant exposure also occurs through the consumption of contaminated agricultural products containing these pesticide residues or their degradation products (Hall, 1999). An estimated 3 million cases of pesticide poisoning occur each year world – wide with 95% of the fatal poisoning cases occurring in the developing countries (Pope *et al.*, 1994).

Despite the ban pronounced on most of these toxic organochlorine compounds, they are still being used in most developing nations both domestically and on agricultural crops. This continued use of organochlorine pesticides has remained a matter of international concern because of their persistence and long-distance carriage through oceanic currents and atmospheric transports (Bentzen *et al.*, 2008;

Caldas *et al.*, 1999). Osibanjo (1994) identified the high potency/efficacy and lower cost of organochlorinepersticides compared with alternative pesticides as the reasons for their continued use in most developing countries, including Nigeria.

Ondo state being the highest producer of Cocoa in Nigeria, with an estimated output of 45,004.5 Metric Tons in 2007, representing 40% of the total cocoa production in Nigeria for the year (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. A survey of the local markets within the region confirmed the sales of pesticides containing organochlorines; mainly lindane, endosulfan, and heptachlor, and this not undermining the sales and use of other toxic organochlorines not openly displayed on market stalls or not bearing labels about their chemical composition.

2. Aim and Objectives

The aim of this research project is to investigate the impact of pesticides used on cocoa farms in Ondo State and the attendant health risks involved with the following objectives:

a) To investigate the possible contamination of the cocoa pod and bean by organochlorine pesticides applied on the farms (Cocoa) and to know the level of such contaminations,
b) To determine the level of contamination in cocoa by organochlorine pesticides (OCPS),
c) To compare the measured organochlorine pesticide residues with maximum allowable limits in food and to evaluate possible contamination of the pods and beans.

3. Research Methodology

The cocoa pod, (Beans & Seeds) samples obtained from Idanre , Akure South and Ifedore were ultimately analyzed by Gas chromatography with electron capture detector to determine their contents of residues. Prior to the quantitative analysis by Gas Chromatography, important stages involving sampling, pretreatment, extraction, cleaning up, and standard preparation were all carefully carried out to obtain test samples which are representative of the entire bulk system being considered, and are suitable for injection into the chromatography system.

4. Materials and Equipment

All the reagents used were of analytical grade and they include n-Hexame, 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 analystes by adsorption on glass surface), all glass wares used for the organochlorine determination were cleaned as recommended by Method 1699 of USEPA (2007). The glass wares were washed with detergent solution and rinsed sequentially with methanol, warm water, another methanol portion, acetone and finally methylene chloride. They were then oven-dried, cooled and kept in inverted positions to avoid collection of dust particles pending their use. The USEPA Method 1699 (2007) was also adopted in preparing both the activated Silica gel for clean up procedure and the anhydrous Sodium sulphate used for drying the samples. This involved rinsing with methylene chloride, drying respectively at 180^0C and 400^0C for about 1 hour, cooling and storing in clean moisture-proof containers prior to their use.

Sampling

Three communities notable for coca production within the Ondo Senatorial District were selected for the study. They are Idanre in IdanreL.G.A, Oda in Akure South L.G.A. and Ilara-Mokin in Ifedore LGA. The total sampling region in each local government as geo-referenced by a Global Positioning System (Garmin 12 Channel GPS) lie within (Latitude : Longitude) (N. 07^0 19’ 52.0”- N 07^0 20’ 23.5” : - E 005^0 06’ 35.2” : - E 005^0 07’ 42.6”) for Ifedore, (N 07^0 04’ 43.2” - 07^0 04’ 43.6” : - E 005^0 12’ 20 8” - E 005^0 12’ 27..2”) for Idanre and (N 07^0 09’ 09.0” - N 07^0 09’ 45.8” - E 005^0 14’ 05.4 - E 005^0 14’ 23.3) for Akure South Local Government Area.

Figure 1: Map of Ondo State indicating the positions of the Local Government of the study Area

Three cocoa farm sites were randomly selected among the cocoa farms, in each of Idanre, Oda and Ilara-Mokin communities of Ondo State. In each of these farm sites, five Cocoa trees were randomly selected and four ripe pods (yellowish in colour) were plucked from each of the trees. These were gathered together to give a composite sample (for each farm site).

Samples Preparation

The cocoa pods in each case, were split open and the beans were removed. The coca beans obtained from each of the farm sites were fermented in boxes for fives days according to the local fermentation procedure. The fermentation procedure involves the removal of the beans from the pod and sealing in a water/air proof bag for five days before

airdried. The sundried fermented beans, was grinded to finer particles in order to have better contact with the extracting solvent. The pods obtained after removing the beans were gathered and cut manually into smaller chips and sundried for several days. The dry pods were also ground to fine particle sizes and were thus ready for extraction.

Extraction of the Analyte from the Samples (Bean & Pod)

Solid phase extraction of the sample was done by extracting about 20g of each sample with ethyl acetate solvent and sodium hydrogen carbonate using soxhletextractor. The mixtures were then sonnicated for 2 minutes in an ultrasonic water bath vibrating at a very high frequency. The ultrasonic vibration ensured further mixing and homogenization of the mixture which enhanced proper contact of the ethyl acetate solvent with the sample matrix to facilitate adequate extraction of the analyte. The mixture was then centrifuged at 2000 revolutions per minute for five minutes and filtered into a glass tube until the filtrate reached a 20ml mark on the collecting glass tube. The filtrate was concentrated in a rotary evaporator at 50^0C and using a nitrogen gas supply to enhance the drying of the evaporated solvent. The residue obtained after complete drying of the solvent was then cleaned up and ready for analysis with Gas chromatography coupled with Electron Capture Detector (GC-ECD).

The Clean Up Procedure

During extraction of pesticide residues, various components with high/large molecular size such as lipids, proteins, pigments, and resins are often present in the extract, especially when the original sample matrix involves a plant material (Tiryaki and Baysoyu, 2006). These substances referred to as 'dirt's may cause interference in the chromatographic system and detection, and may also damage the GC equipment. Thus, it is important to remove them before injecting the sample into the GC column.

The isolation of the pesticide molecules from the bulk extract was done by solid phase extraction in a normal phase mode. 2g of the activated silica gel was packed into a chromatographic micro-column of 10mm i.d. and approximately 10cm long (Ize-Iyamu, 2007; ASTM, 1979).

Separation of impurities from the analyte during clean up is achieved essentially based on the differences in molecular size between the pesticide molecules and the potential interferents, without any serious chemical interaction between the analyte and the porous column packing. This technique is named Size Exclusion Chromatography (SEC) or Gel Permeation Chromatography (GPC). The silica packing in the column has pores which are a little larger than the pesticide molecules, but much smaller than the interfering molecules. Thus, as the eluting solvent flows through the column, the pesticide molecules which are smaller than the pores diffuse in and out of the pores repeatedly and are therefore retained to a great extent by the pores. The impurity molecules, being larger than the pores, do not diffuse into/ or enter the pores at all and are carried very fast in the eluting solvent, thus emerging from the column first. The pesticide molecules which are retained by the pores emerge in the eluting solvent later and are thus separated from the interfering molecules.

Quantification of organochlorine residues

The method of internal standard was used to analyse both the standards used to prepare the calibration curves and the extracted samples. Standards containing a mixture of 13 organochlorine compounds; alpha-BHC, beta-BHC, Lindane, delta-BHC, Heptachlor, Aldrin, Heptachlor-epoxide, Endosulfan I, p,p-DE, Dieldrin, Endrin, p,p-DDT, and Endosulfan sulphate were prepared at concentrations of 0.100, 0.250, 0.500,1.000 and 2.000ppm respectively. The mixture also contained Permethrin, a pyrethroid compound added at varying concentration as for the organochlorine compounds, while Anthracene, PCB-153; and PF-38 were used as the internal standards.

The modern Shimadzu GC-MS QP-2010 was thereafter employed in analysing the standards and the calibration curve for each compound was prepared automatically. The extracted Bean and Pod samples were then analyzed under the same conditions as for the standards, and in the Selective Ion Mode (SIM) with m/z values ranging from 65 to 274.

5. Results

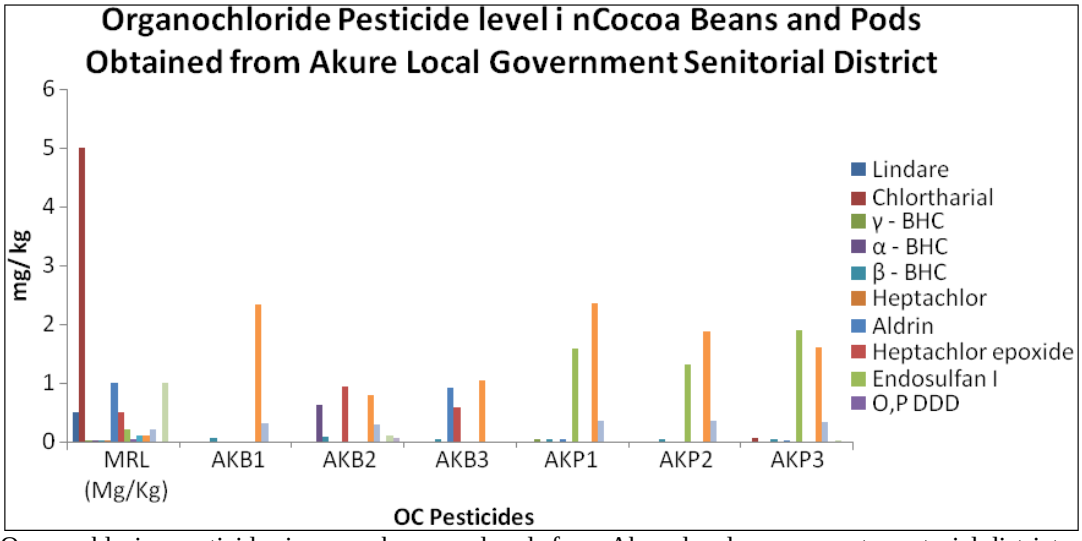

Figure 1.1: Organochlorine pesticides in cocoa beans and pods from Akure local government senatorial district of Ondo state

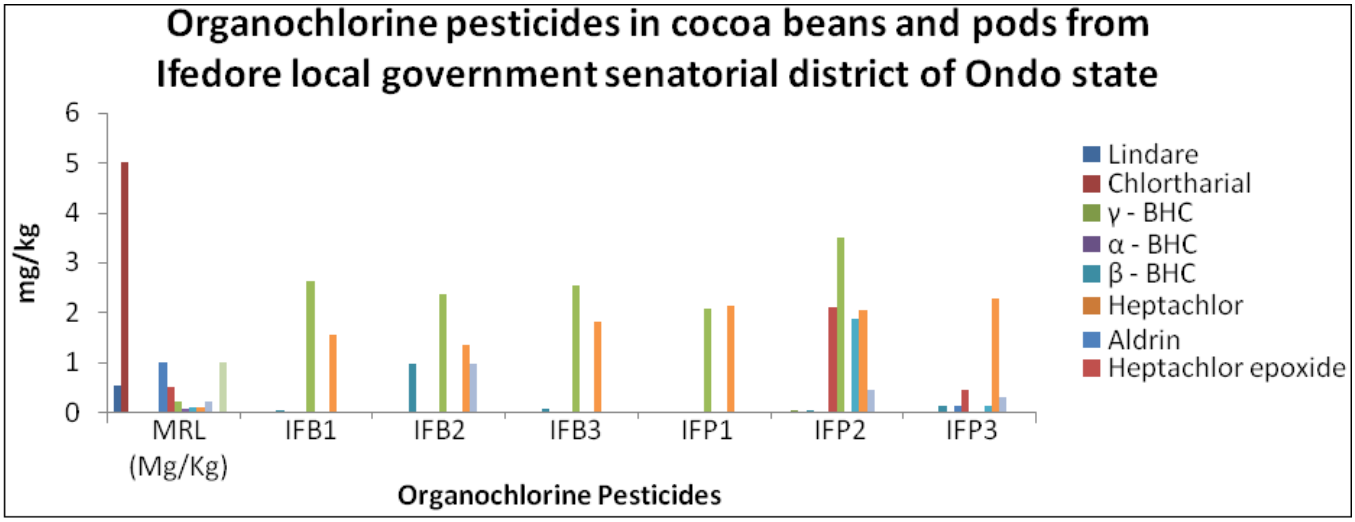

Figure 1.2: Organochlorine pesticides in cocoa beans and pods from Ifedore local government senatorial district of Ondo state

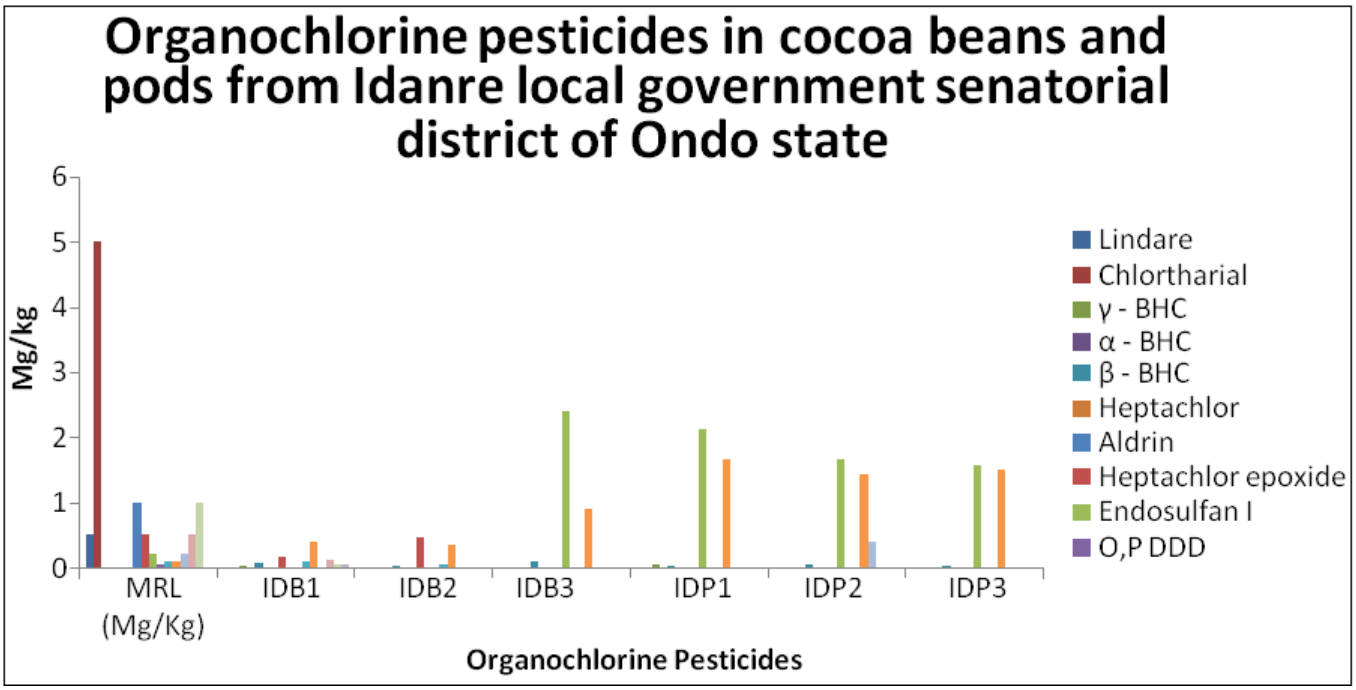

Figure 1.3: Organochlorine pesticides in cocoa beans and pods from Idanre local government senatorial district of Ondo state

Concentration of Organochlorine Pesticides Residues (mg/kg) in Cocoa Bean Sample from the Three Senatorial District of Ondo State

The concentration of the various organochlorine pesticides detected in the bean samples are presented in figure 1.0, 1.1and1.2 for the respective Local Government Areas.

The three isomers of Benzene hexachloride (BHC) or Hexa-chloro-cyclohexane (HCH), were detected in few bean samples from Akure South Area i.e. (AKB_1, and AKB_2) and it was detected in all bean samples from Ifedore and Idanrefarm site.

Some organochlorine compounds that belongs to the group of cyclodiene were also detected in the various samples, These include: heptachlor epoxide (B) and it was found in the following samples AKB_2 0.93 mg/kg, AKB_3 0.59 mg/kg, IDB_1 0.16 mg/kg, IDB_2 0.46 mg/kg, and it was not detected in any of the samples from Ifedore Area while heptachlor, aldrin and dieldrin were not detected from all the bean samples from the three Local Government Area. The metabolic product of heptachlor (heptachlor epoxide) appeared frequently in most of the samples from Akure South LG. The levels of heptachlor epoxide found in the samples may be directly related to the application of heptachlor on the farms, since heptachlor is only converted to heptachlor epoxide in the plant and insect tissues. The epoxide is more chemically potent than the heptachlor itself (Cremyln, 1991). Endrin was found in all the bean samples from the three Local Government Areas.

Dieldrin were detected only from Idanrefarm site with the following concentrations (IDB_1 0.098 mg/kg, IDB_2 0.052mg/kg and while aldrin was below detection limit from all the samples from the three Local Government Area. The two conformational isomers of endosulfan α – endosulfan (endosulfanI) and β – endosulfan (endosulfanII) occurred

most frequently compared to the other organochlorine except compounds in the bean samples from Akure South Area, where there was absence of endosulfan I in all the samples.

Also, much higher concentration of endosulfan I was found in the samples than the corresponding endosulfan II (endosulfan I appear in five samples from all the three Local Government Areas. While endosulfanII appear in four of the sample[s from all the three Local Government Areas.

From all indication, Highest concentration of endosulfan I were measured in the cocoa bean samples from Ifedore Area with the values ranging from 2.081mg/kg to 3.494mg/kg, while lower concentration of endosulfan II range between 0.304 mg/kg to 0.964mg/kg. The much concentrations of endosulfan I relative to those of endosulfan II in the samples may be attributed to two reasons.

Firstly, the manufactured technical endosulfan normally contains about 67% endosulfan I by mass of the total endosulfan content, while endosulfan II constitutes only 32% (WHO 1990). It is, therefore, not expected that more of endosulfan I would be found in its environment wherever the pesticide is applied.

Secondly, endosulfan I is thermally stable while endosulfan II is unstable and may be slowly converted to endosulfan I in the environment (Hapeman *et al*, 1997)

Moreover, the higher concentrations of endosulfan I and II detected in the samples may be an indication of recent application of the pesticides on some of the cocoa farms, as endosulfan is easily degraded and does not accumulate in the environment unlike the most other organochlorines (Cremlyn, 1991). This observation is further corroborated by the fact that endosulfan Sulphate, which is the primary (l^{O}) degradation product of endosulfan was not detected.

Finally, since multi residue method was adopted, most especially at the extraction stage, which is non-specific towards any class of pesticides and would normally extract all the pesticides molecules present, some levels of permethrin, a pyrenoid insecticide was also found in most of the cocoa beans samples in the three Local Government Area.

This is as a result of widespread use of this pesticide across the senatorial district due to the observation.

Organochlorine pesticides residue level in cocoa POD samples from the three senatorial district of Ondo state.

The concentration of the various organochlorine pesticides detected in the pod samples are shown in the figure too and their concentrations also differ markedly.

However, concentrations of each compound within the same phase of the environment appear to be of similar orders of magnitude.

From the result obtained the three isomer of hexa-chlorocyclohexane (HCH) or benzenehexachloride (BHC). α-BHC,β-BHC and δ-BHC were detected in most of the pod samples from the study Area with concentration ranging from 0.034 mg/kg + 0.058 mg/kg, while non o, and lindane was not found in any of the farm sites.

Some organochlorine compounds that belong to the group of cyclodiene were also detected in the various samples and these include:- heptachlor epoxide (B), hepthachlor, aldrin,endrin and dieldrin.

The hepthachlor epoxide (B) was found only at Ifedorefarm site 3 pod sample and it was not found in the remaining two farm site while hepthachlor was not found in any of the farm site. Aldrin was also found in Akure South farm site only ranging from 0.031mg/kg to 0.092 mg/kg while it was absent in the samples from Idanre and Ifedore farm sites.

Dieldrin was found in Ifedore and Idanrefarm siteswith this concentration ranging from 0.052-1.850 mg/kg, except in Akure South farm sites.

Endrin was found majorly in all the pod and bean samples from the study Area.

The two conformational isomers of endosulfan, i.e α-endosulfanI and β- endosulfan II occurred most frequently in all the pod and bean samples from the farm sites.

From the point of view, Highest concentration of endosulfan I were measured in the cocoa pod samples from Ifedorefarm site 2 with3.49mg/kg concentration values. The much concentration of endosulfan I relative to those of endosulfan II in the samples may be traced to these reasons.

1) The manufactured technical endosulfanI normally contains about 67% endosulfan content, while endosulfan II constitute only 32% (WHO, 1990). It is therefore, not amazing that more of endosulfan I will be found in the environment wherever the pescticide is being used or applied.
2) Endosulfan I is thermally stable while endosulfan II is unstable and may be slowly converted to endosulfan I in the environment (Hapeman,*et al*, 1997).

Moreover, the high concentrations of endosulfan I and II detected in the samples may be an indication of recent application of the pesticides on some of the cocoa farms, as endosulfan is easily degraded and does not accumulate in the environment unlike most other organochlorines (cremlyn, 1991). This observation also establishes the fact that endosulfan sulphate, which is the primary degradation product of endosulfan was not detected.

Lastly, since multi residue method was adopted most especially at the extraction stage which is non-specific towards any class of pesticides and would normally extract all pesticide molecules present, some levels of permethrin, and pyrethoid insecticide was also found in some of the cocoa pod samples from the study area.

O, P'-DDD and P,P' DDD was not found in any of the samples although they are minor insecticides called Rothane or TDEC (tetra-chloro di phenyl ethane). In certain circumstance, DDD is a metabolic product of DDT and is

inferior to DDT as an insecticide but it has proved particularly useful for the control of some horn worms and as mosquito larvicide. It is only about one-fifth as toxic as DDT to higher animals. (Cremlyn, 1991)

6. Conclusion

The use of chemical pesticides in crop protection is still at the moment inevitable, but the incidence of pesticides in food and environment in general, resulting from the use of these pesticides continues to be a matter of serious controversy, especially when attempt are made to strike a balance between the overall benefits derived from the pesticides and attendant adverse consequences resulting from their use. Analysis and result reveal the contamination level of pesticides residue of the cocoa out put (Beans and pods) from farms sprayed with pesticides chemicals contain residues. The study Area has provided information on the level of contamination of cocoa output by organochlorine pesticides applied on the cocoa farms within the central senatorial District of Ondo State.

The result revealed that, varied levels of the organochlorine compounds which includes:-α-BHC, β-BHC, Lindane (- BHC), chlorothalonil, δ-BHC, hepthachlor, Aldrin, Hepthachlor epoxide (B), Endosulfan I, Endosulfan II, Dieldrin, Endrin, O,P'-DDD, P, P' – DDD, CIS – Permethrin and Trans permethrin were found in the different samples Matrices.

Conclusively, the concentration of pesticides residues measured on cocoa pod is more than residues measured in cocoa bean in Akure farm 1 and 3, Ifedore farm 1and 2, Idanre farm 1 and 3, while in Akure farm 2, Ifedore farm 3 and Idanre farm 2 the concentration of pesticides residue measured in bean samples is more than the concentration in pod samples. The concentrations and the frequency of occurrence of endrin, endosulfan I, endosulfan II and beta – BHC in the cocoa samples (beans and pods) are the major concern because some pesticides have even been found to be bio-magnified (i.e. increase in concentration in the food chain as a result of food chain energetic and lack of degradation or elimination of the chemical pesticides). This further worsens the effect of the contamination of the food chain by such pesticides. Even man is not safe in this regard of contacting pesticides from the environment.

7. Recommendation

Based on the outcome of this study, the following recommendations among others are hereby made;-

1) Government, through the various agricultural research institutes, should develop practicable integrated pest management methods and educate the cocoa farmers, through the agricultural extension services, on the use of such methods, especially the biological control methods which is technical and may not be easily developed by the farmers themselves.
2) The cocoa farmers should adopt the integrated pest management technique in protecting their crops rather than depending entirely on chemical pesticides in general. Physical and cultural control methods are easy and affordable and can be conveniently incorporated by the farmers.
3) The farmers should try as much as possible to follow manufacturer's instruction regarding the quantity, the frequency, and the mode of application of pesticides. This would most likely reduce the incidence of organochlorine residues in cocoa.
4) Government should compel chemical pesticides manufacturers to carry out a thorough investigation of the tendency of their products to leave residues in crops and submit results of such analyses to the appropriate government agencies before their product are certified for use.
5) It is being claimed that organochlorine residues in harvested crops depreciates in storage and during processing but the rate of decay (especially in local products) has not yet been established. This should be an issue of concern for future research, and would involve daily or weekly analyses or stored products to determine how organochlorine decays with time.
6) The results of this research projects provides an estimate of the level of organochlorine pesticides residue contamination of the cocoa output of Akure South LG, Idanre LG and Ifedore LG, since only three selected cocoa farms were considered. Thus, future research should be conducted to obtain a more representative result by increasing the sampling site & site and local government area to ten or more; so that it can be uniformly spread across the Ondo Senatorial District.

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