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ORIGINAL RESEARCH PAPER

Pesticide pollution status in cocoa plantation soil

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ABSTRACT: Management of cocoa plantation field relied on the use of pesticides over the years; hence, the fate of such chemicals is one of the most debated issues among the stakeholders. Young and old cocoa plantation fields from 4 major cocoa producing States in Nigeria were selected as the study area. Eight composites soil samples collected from 3 portions of 6 transect measured area (100 x 50m) of the field were transported to the laboratory in sterile glass jar for analysis. A total of 19 organochlorine pesticides residues; (aldrin, α-hexachlorohexane, β-hexachlorohexane, γ-hexachlorohexane, δ-hexachlorohexane, α-chlordane, γ-chlordane, p,p'-dichlorodiphenyldichloroethane, p,p'-dichlorodiphenyldichloroethylene, p,p'-dichlorodiphenyltrichloroethane, dieldrin, endosulfan I, endosulfan-II, endosulfan sulfate, endrin, endrin aldehydes, heptachlor, heptachlor epoxide and metoxychlor) were analyzed with gas chromatography equipped with electron capture detector. The results revealed the variation in the number of residues detected among the study fields. Endosulfan-I had the highest value g organochlorine pesticides residue detected. Most of the residue concentrations were within the European Union regulatory standard of Czech Republic. Other-cyclodine group had the highest concentration value among the evaluated organochlorine pesticides groups. The significant ($P < 0.05$) higher concentration of total organochlorine pesticides were observed in old fields. Composition quotients values indicate that most of the observed organochlorine pesticides residues were products of historical usage. There were strong correlations among the total organic carbon contents of soils and the total organochlorine pesticides compounds. Government regulatory agencies are encouraged to vigorously embark in further monitoring and ensuring the safety compliance of farmers towards the use of pesticides in Nigeria farms.

Keywords: *Cocoa plantation fields; Composition quotients; Endosulfan-I; Gas chromatography; Organochlorine pesticides (OCPs).*

INTRODUCTION

The use of agrochemicals in modern farming is viewed as an integral part of the success of agricultural industry. Worldwide pesticide usage has increased dramatically during the last two decades, coinciding with changes in farming practices and increasing intensive agriculture practices. The widespread use of pesticide for agricultural and non-agricultural purposes has resulted in the presence of their residues in various environmental matrices (Dubey *et al*., 2012). The introduction of pesticide in agricultural system has some success in preventing, suppressing and eradicating the pest that reduced production quality and quantity in the sector. However, the increase and continuous application of pesticides may result in soil pollution (Cycon *et al*., 2006; Sturz and Kimpinski, 1999; Sebiomo *et al*., 2011; Tariq, 2015). In developing countries Nigeria agricultural practices still rely heavily on agrochemicals to prevent and/or control the crops threatening diseases (Emoghene and Futughe, 2016).

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Cocoa plants (*Theobroma cacao*) are tropical plant, belonging to the family Malvaceae and are usually cultivated for their beans, from which cocoa powder and butter are extracted (Adabe and Ngo-Samnick, 2014). It is one of the major cash crops in Nigeria and most especially the backbone of the economy of South-Western part of the country. The cocoa production is usually threatened by a number of problems which range from diseases (viral and fungal diseases), pest infestation to parasite invasion (Olujide and Adeogun; Adabe and Ngo-Samnick, 2014). Hence, the successful management and prevention of cocoa pests and diseases rely heavily on the use of pesticides (Asogwa and Dongo, 2009). In a consistent effort to combat the problem of pests, large metric tonnes of pesticides (about 125,000-130,000) were reported to be applied annually in Nigeria farms (Ndubuaku and Asogwa, 2006, Asogwa and Dongo, 2009). The reports have shown that many types of pesticides were used by Nigerian farmers in pest management and these include herbicides, insecticides, fungicides, rodenticides, acaricides and nematicides (Asogwa and Dongo, 2009; WAAPP, 2013). It has been reported in the previous research that practically no data exists on the issue of the pesticide contamination level and the extent of the pollution of agrarian communities can only be guessed in Nigeria (Asogwa and Dongo, 2009; Oyekunle *et al*., (2011). Oyekunle *et al*., (2011) also recognized that in developing countries like Nigeria, investigating and evaluating the occurrence and levels of pesticide residues on farm lands have not been an object of extensive research. Hence, there is scarcity of documented literature relating to the pesticide residues pollution status in Nigerian farm settlements.

Currently, most of the newly approved pesticide formulations were designed to have shorter half-life which could span within days or weeks (Camarata *et al*., 2006; Asogwa and Dongo, 2009). However, organochlorine pesticides (OCPs) compounds can remain in the environmental matrixes for many years following application (Jiang *et al*., 2009; Aiyesanmi and Idowu, 2012). Therefore, OCPs residues which were among the group of persistent chemicals with its metabolites that has the potential to pose a great threat to the environment were investigated from the soil samples of these areas. This study was carried out in the selected cocoa planation fields of four major cocoa producing States in Nigeria in 2016.

MATERIALS AND METHODS

Study area

Four major cocoa producing states in Nigeria were selected for this study. These states include; part of South-Western region (Ondo, Ekiti and Osun State) and a cocoa producing state in South-South Zone (Edo State) of the country (Fig. 1). The area lies between longitude 4^{o} 33' and 6^{o} 43' East and Latitude 5^{o} 44' and 8^{o} 05' North with a total land mass of about 46,906 km^2. The study area lies in the tropical rain forest zone and shared border

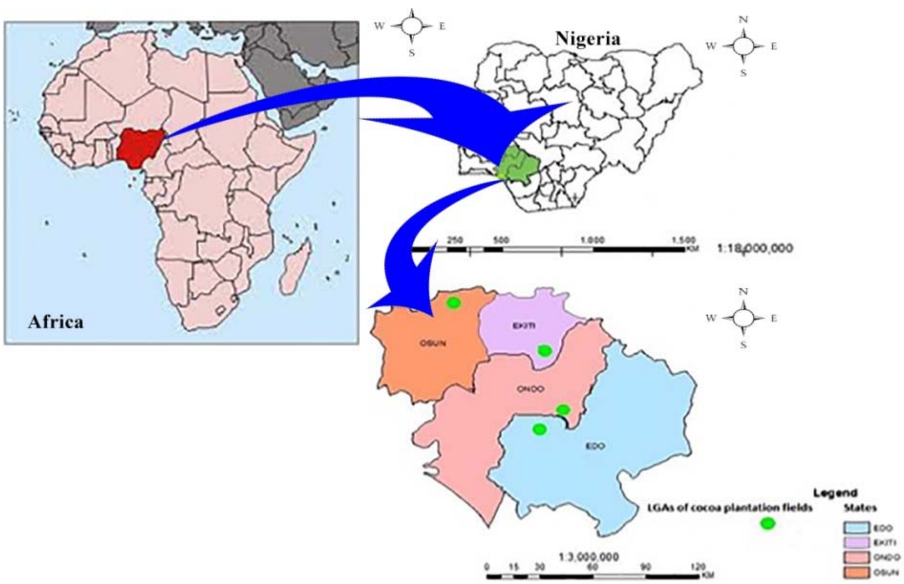


Fig. 1: Locations of the study area

with Delta state in the east, Kwara and Kogi states in the north, Oyo and Ogun states in the west and Gulf of Guinea in the south (Fig. 1). Cocoa is the major cash crop produced by these states. From each state, the selected farm settlements were "Egbute" camp, Okeluse, Ose local Government area, Ondo state; "General" camp, Okada, Ovia north-east local Government area, Edo state; "Afa" camp, Ise-Ekiti, Ise Orun local Government area, Ekiti state and "Isalegudu" camp, Aiyepe-Iragbiji, Boripe Local Government area, Osun state (Fig. 1).

Soil samples collection

Surface soils (0-15cm depth) as recommended by Organisation for Economic Cooperation and Development (OECD) from at least three portions of study area were collected and composited into one sample (Bishnu *et al*., 2009). The method of Bishnu *et al*. (2009) as modified by Moghaddam *et al*. (2011) was adopted. Soil samples were collected from two (2) different cocoa plantation farms in each selected cocoa producing state. The selected study areas were based on the farming history.

- Sampling site one 1) was an area presumed to be moderately contaminated by pesticide in each states (i.e. young plantation with farm history ≤ 10 years).
- Sampling site two 2) was an area presumed to be highly contaminated by pesticide application in the study state due to prolonged used of pesticide over the years of farming. (i.e. old plantation with farm history ≥ 20 years).

Soil samples were collected from each sampling area by dividing the site into six transects with area of 100 x 50m (Bishnu *et al*., 2009). Surface soils (0-15cm depth) from three portions of each transect were collected and all the samples from each sampling site were composited into one sample. Altogether, a total of 8 composites soil samples was collected and transported to the laboratory in tightly covered sterile glass jar for analysis. The soil samples were prepared as described by Estefan *et al*. (2013) before analysis. Visible plant debris and fauna hand-picked and removed from the samples. The soils were then gently sieved (<2mm fraction) and stored in sealed glass jars at 4^{o}C before analysis.

Soil Analysis

The relevant physicochemical properties of the soil samples that can provide an insight into the nature of the soils being investigated were analyzed by standard methods as described by Estefan *et al*. (2013). The parameter analyzed were the pH, particle size and the total organic carbon.

The pH was determined using pH meter. Ten grams of the soil sample was placed in a beaker, then 10 ml of distilled water was added and the mixture was stirred. It was allowed to stand for 30 minutes. A 0.1 M phosphate buffer solution was used to standardize the pH meter. Then the electrode of the pH meter was inserted into the mixture and the pH readings were taken.

Soil particle size distribution was determined by Bouyoucous's Hydrometer method (Estefan *et al*., 2013). Hydrogen peroxide (H_2O_2) was added to one hundred gram of air dried soil sample in 1000ml plastic beaker in other to digest the organic matter contents. Two hundred millilitres (200ml) of distilled water and 100ml of sodium hexa-metaphosphate solution were added to the treated soil sample and stirred with the help of glass rod. The plastic beaker was covered and kept for 4hours. The volume of the content was made up to 500ml and stirred for 10minutes. The whole contents were transferred to a suspension cylinder and the volume was made up to 1000ml with distilled water. The cylinder was tightly closed with stopper and shake for several times to allow the soil particles to disperse completely. The stopper was removed and hydrometer was immediately placed in the suspension. The first reading was taken exactly 40seconds after placement of hydrometer. The cylinder was closed with the stopper and inverted several times again to ensure complete dispersal of particles. The hydrometer was placed in the suspension exactly after 2hours and the second reading was noted. The blank was simultaneously run without soil and the room temperature was recorded. The soil textures were classified based on relative proportions of sand, silt and clay particles with the aid of United State Department of Agriculture (USDA) textural class automated software (nrc142p2_053196).

Total Organic carbon contents were determined by wet oxidation method of Walkely and Black as described by Atuanya *et al*. (2012). One gram of soil samples were weighed into a 500 ml conical flask, 10ml of 1N potassium dichromate (1 N $K_2Cr_2O_7$) and 20ml of concentrated sulphuric acid (conc. H_2SO_4) was added in order to oxidize the organic carbon. The flask was swirled carefully and allowed to stand for 30minutes. Two hundred millilitres

(200ml) of distilled water and 10 ml of concentrated orthophosphoric acid (conc. H_3PO_4) were slowly added. One millilitre (1ml) of diphenylamine indicator was added before titrated against 0.5N ferrous ammonium sulphate solution until green colour starts appearing indicating the end point. The blank was run simultaneously.

Pesticide residues' Analysis

The pesticide residues from the soil samples were analyzed chromatographically with a gas chromatography equipped with electron capture detector (GC/ECD) as described by Imane *et al*. (2015). Fifty gram (50g) of composite soil samples were placed separately into 500ml Erlenmeyer flask. One hundred milliliter (100ml) of acetone with 50ml of water, representing 2:1 acetone/water mixture was used for the extraction. The mixture was shaken overnight on shaker at 220 rpm. For liquid/liquid partitioning, appropriate amount of NaCl (15g) and cyclohexane (100ml) were added to the mixture before being subjected to additional shaken for another 1h.

The organic layer was decanted into 250ml Erlenmeyer flask and dried over 15g anhydrous sodium sulphate (Na_2SO_4). Then, 100ml of the extract were evaporated using rotatory evaporator and dissolved in 5ml of 1:1 n-Hexane and ethyl acetate mixture. The cleanup of the extracts was carried out in a chromatographic column packed with 10g deactivated silica gel and 1g of anhydrous Na_2SO_4. The non-polar fraction was transferred into the silica gel column and separated into three fractions; the first, second and third fractions were eluted with 50ml n-hexane, 50ml of 49:1 n-hexane/ethyl acetate and 50ml ethyl acetate respectively. After the cleanup procedure, each fraction was evaporated with rotatory evaporator and concentrated in a nitrogen stream to 1ml. The fractions were analyzed for pesticide residues.

The organochlorine residues concentrations were determined using a Hewlett-Packard (Hp) 5890 series II equipped with ^{63}Ni electron capture detector (ECD) with auto sampler. The chromatographic separation was achieved by using an HP-5 of 30mm x 0.25mm internal diameter (ID) fused silica cross-linked with 50% phenyl methyl siloxane stationary phase and 0.25μm film thickness. Helium (He) was used as a carrier gas, while nitrogen (N_2) was used as the make-up gas and maintained at a constant flow rate of 29ml/min. The chromatographic temperature program was kept at 60°C for 2min; increased to 300°C at 25°C/min for 5min and allowed to stay for 15min. The injection volume was 1.5μL.The detector temperature was maintained at 320 °C.

The efficiency of the analytical method was validated by recoveries studies of internal standards. The recovery of the pesticides ranged between 70.7% and 91.9% with maximum relative standard deviation (RSD) < 20%.

Data Analysis

The recorded data were further subjected to statistical analysis using Statistical Package for Social Sciences (SPSS) version 20. The unpaired t-test was used to establish significant differences between the total organochlorine pesticides levels in young and old cocoa plantation field samples at 5% level of significance. Correlation analysis was used to establish the relationship between the amount of OCPs residues groups and the soil physico-chemical parametres at 5% level of significance.

RESULTS AND DISCUSSION

Physico-chemical characterization of soil samples of the study areas

The physico-chemical parameters of the soil samples of the study areas were determined to assess the features of the soils under investigation. Result has shown that the pH values of the study areas ranged from 5.8 - 6.6 (Table 1) which indicates that the soils were slightly acidic in nature. The report has shown that the pH value of 5.5 – 7.0 was the preferred ranged of pH for most agricultural crops (Landon, 1991; Sharu *et al*., 2013). The soil samples were relatively rich in organic carbon contents with reference to Landon, (1991) mode of classification. He classified as low, any soil sample with organic carbon contents of ≤ 4. However, the organic carbon content has observed in this study ranged from 5.72 – 11.57. The soil particle size distribution shows the textural class of the soil as "sand clay loam" for Edo cocoa field planation soil type; while "sand loamy" type of soil texture was observed in other study areas. Generally, reports have shown that the soil pH, particle size distribution, organic carbon contents play a significant role in the dynamics and behavior of pollutants within the soil matrixes (Aiyesanmi and Idowu, 2012; Atuanya *et al*., 2012; Sharu *et al*., 2013).

Organochlorine pesticides residues profile of the study fields

A total number of 19 OCPs residues investigated were: aldrin, α-hexachlorohexane (α-HCH), β-hexachlorohexane (β-HCH), γ-hexachlorohexane (γ-HCH), δ-hexachlorohexane (δ-HCH), α-chlordane, γ-chlordane, p,p'-dichlorodiphenyldichloroethane (p,p'-DDD), p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE), p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehydes, heptachlor, heptachlor epoxide and metoxychlor (Figs. 2a-d). However, the total number of OCPs residue detected varied between and / or among the study sites (Fig. 2a–d). The total number of OCPs residue detected in young and old cocoa plantation soil samples from each location respectively in Edo (ED), Ondo (ON), Ekiti (EK) and Osun State (OS) were: ED (10, 15); ON (13, 18); EK (11, 16) and OS (11, 18). The variation in the OCPs residue profile of these study areas might be influenced by so many factors such as; differences in pattern of pesticide usage and variation in physicochemical parameters of the study sites that could determine the fate of the pesticide in the environment.

Results also showed that out of all the OCPs residue detected in the study areas, endosulfan 1 has the highest concentration value. This may indicates more recent uses of endosulfan products in these areas. Asogwa and Dongo (2009) listed endosulfan products (Thiodan and Decis-Dan / Cracker 282 E.C.) as some of the previously approved pesticide for use in cocoa farm in Nigeria, but were later banned due to potential negative impact on the environment.

In Africa continent, there had not been any standard limit set for minimum amount of pesticide residue in

Table 1: Physico-chemical properties of soil of the study area

Sampling area	Field	pH (in H_2O)	Organic carbon (%)	Sand (%)	Silt (%)	Clay (%)
ED	1	5.9	5.72	69.3	9.1	21.6
	2	6.2	8.26	65.7	13.3	21.0
ON	1	6.1	7.89	62.4	24.5	13.1
	2	5.8	11.57	66.8	21.7	11.5
EK	1	6.3	7.32	63.2	22.9	13.9
	2	6.7	9.66	65.1	21.3	13.6
OS	1	5.8	6.74	62.6	22.5	14.9
	2	6.1	9.53	61.2	26.5	12.3

1 = relatively young cocoa plantation field;
2 = old cocoa plantation field

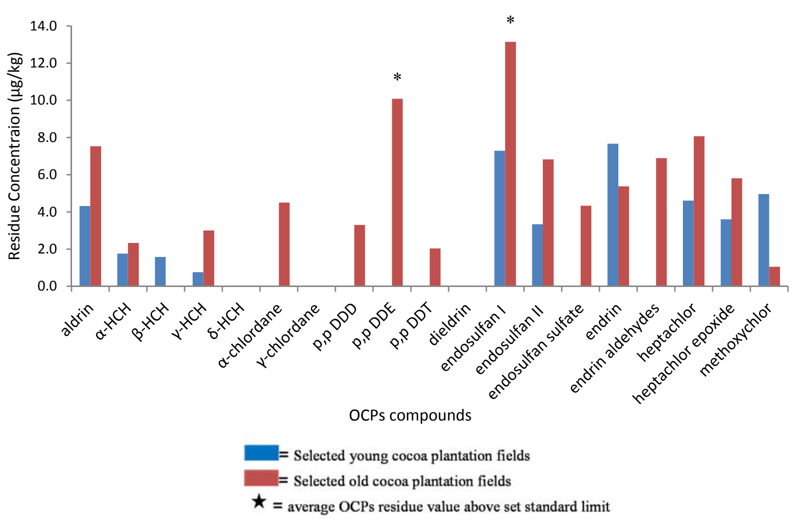


Fig. 2a**:** Organochlorine pesticides residue profile level in cocoa plantation soil of Edo State.

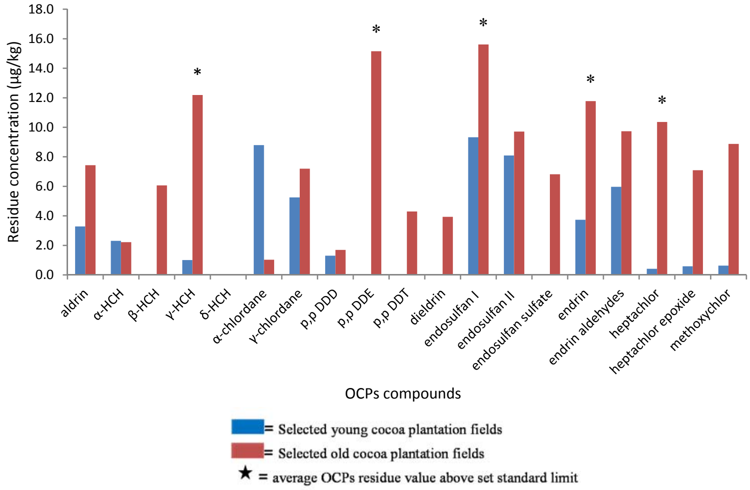


Fig. 2b**:** Organochlorine pesticides residue profile level in cocoa plantation soil of Ekiti State

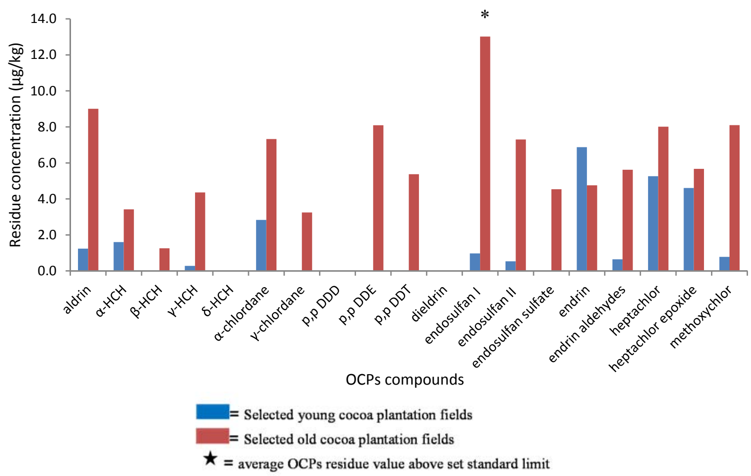


Fig. 2c**:** Organochlorine pesticides residue profile level in cocoa plantation soil of Ekiti State.

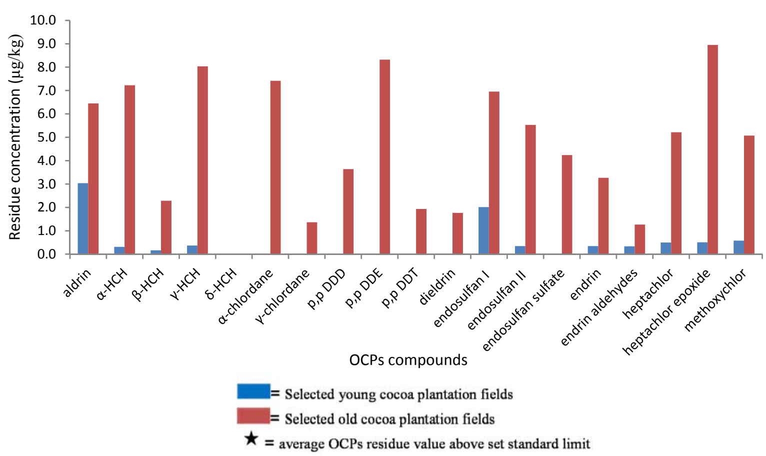


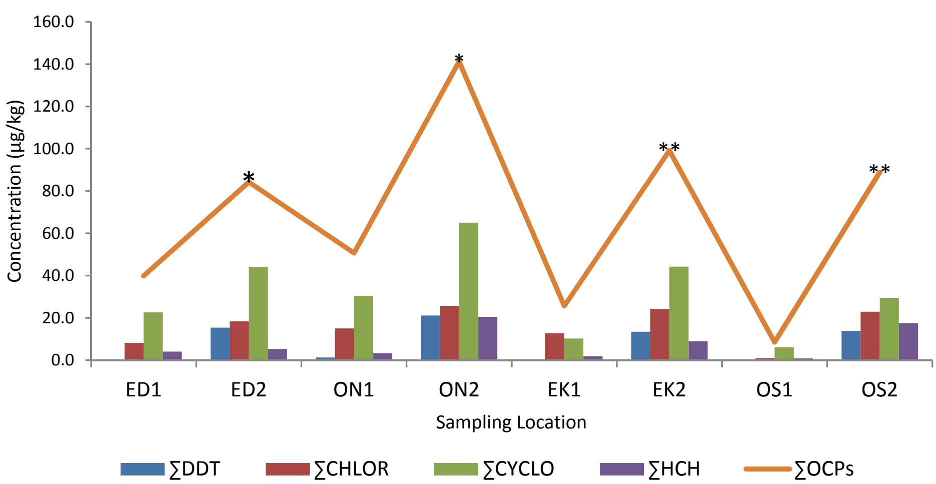
Fig. 2d**:** Organochlorine pesticides residue profile level in cocoa plantation soil of Osun.

the contaminated soils at a particular period; however, the results were compared with European Union regulatory standard of Czech Republic (i.e. 10µg/kg of soil for each of the residue) (IPEP, 2006). The study showed that most of the residue values obtained in the study sites was below the set standard limit. However, about 5.3%, 10.5% and 26.3% of the total number of residue obtained at Ekiti, Edo and Ondo State study fields respectively were above the set standard limit (Figs. 2c, 2a and 2b respectively). While, at Osun State study fields, all the value obtained were within the minimum set standard limit for contaminated soil (Fig. 2d). Although, the finding showed that most of the value obtained for analyzed OCPs residues from the various field samples were within the regulatory limits; however, the bioaccumulative potential of organochlorine pesticides give rise to serious health concern for human and the environment. The OCPs residue in the soil might be a potential threat not only to the soil organisms but also to the people who might get exposed to it through farming activities and consumption of crops that might have bioaccumulate some residues, thereby constituting serious health risks. Aiyesanmi and Idowu (2012) identified the intercropping as one of the farming systems usually practice in cocoa plantation in Nigeria, and emphasized that these plants have the potential to translocate the pollutant residue through their root system into other parts of plant. Researchers have reported the cases of presence of pesticide residues in vegetables and food products consumed in Nigeria (Benson and Olufunke, 2011; Erhunmwunse *et al*., 2012). The pesticide polluted farm land had been reported to be a potential contaminating source of surrounding water bodies (Mihale and Kishimba, 2004; Ogbeide *et al*., 2015).

Contamination level of OCPs group in the study area

The OCPs compound can be categorized based on their chemical compositions, metabolites and molecular weight characteristics (Miles *et al*., 2009). Therefore, the concentration levels of OCPs groups and the total OCPs values as evaluated from the data obtained from this study were presented in Fig. 3. The OCPs groups evaluated were; dichlorodiphenyl group (∑DDT), chlordane-cyclodiene related group (∑CHLOR), other-cyclodiene group (∑CYCLO) and hexachlorocyclohexane group (∑HCH) (Fig. 3).
At young cocoa plantation soil samples the ∑DDT level range from “not detected” as observe in ED, EK and OS sampling sites respectively to about 1.3µg/kg (ON). While ∑DDT were detected in all sampling sites at the old cocoa plantation soil samples with highest value (21.15µg/kg) obtained in Ondo State sampling site (Fig. 3).

Results showed that the level of ∑DDT obtained in study areas were obviously lower compared to few other reported cases in Nigeria agricultural farm. Oyekunle *et al*. (2011) recorded the ∑DDT value of about 228.60µg/kg during the month of August in Oke-Osun farm settlement, Osun State.



∑DDTs = Dichlorodiphenyl group; ∑CHLOR = Chlordane-cyclodiene related group; ∑CYCLO = other cyclodiene group; ∑ = hexachlorohexane group; ∑OCPs = sum of all OCPs residues; * = significant level at 0.05; ** = significant level at 0.01.

Fig. 3: Contamination level of OCPs group in the study area

Aiyesanmi and Idowu (2012) did not include the evaluation of dichlorodiphenyl group in their work on organochlorine pesticide residue in soil of cocoa farms in Ondo State Central District, Nigeria. Akan *et al*. (2015) also reported a very high ∑DDT value of 3.97µg/g (i.e. 3970µg/kg) in soil samples from Gashua, Bade Local Government Area, Yobe State. The lower concentration level of ∑DDT as shown in this study may suggest the decreasing level of DDT concentration in the soil and possibly the compliance of farmers in this area with regulatory bodies' directives on the use of banned pesticide in agricultural farm. Reports showed that DDT and its derivatives have been banned in Nigeria since 2008 (Asogwa and Dongo, 2009; Akan *et al*., 2015) but its tendency to persist in the environment for long period after used and bioaccumulate make it a pollutant of great concern.

Chlordane is a mixture of several components such as α-chlordane (~13%), γ-chlordane (~11%), heptachlor (~5%) and trans-nonachlor (~5%) (Jiang *et al*., 2009). It is generally used as insecticides and termiticide in agricultural feed. The level of chlordane-cyclodine related compound in young cocoa plantation soil samples of the study areas range from 1.01µg/kg (OS) to 8.21µg/kg; while, the old cocoa plantation soil samples have the value range of 18.37µg/kg to 25.68µg/kg. The level of chlordane-cyclodine group as obtained in this study, comparatively were almost in the same range as reported by Oyekunle *et al.* (2011). Other cyclodiene related group (∑CYCLO) has the range value of 6.07µg/kg (OS) to 30.41µg/kg (ON) in young cocoa plantation soil samples; while in old plantation, the level of ∑CYCLO range from 29.46µg/kg (OS) to 65.02µg/kg (ON). The result also showed that, among the evaluated OCPs group, the ∑CYCLO had highest concentration trend in all the study sites (Fig. 3). This could be attributed to the possibility of recent application of other cyclodiene related compounds on the study field and persistent nature of the group.

Dichlorodiphenyl compound was mainly used as pesticide and also for wood preservation (Jiang *et al*., 2009). ∑HCH was detected in relatively different concentration in all the soil samples of the study area (Fig. 3). At the young cocoa plantation, concentration value of ∑HCH range from 0.85µg/kg (OS) to 4.09µg/kg (ED); while relatively higher concentration was observed in old cocoa plantation soil samples with highest value of 20.47µg/kg (ON).

The observation shows that the soil samples in old cocoa plantation soil of Ondo State study site had the highest concentration level of total organochlorine pesticides (∑OCPs) (Fig. 2). This may indicate the prolonged used of OCPs product in the management of cocoa farm in this area and the capability of OCPs to persist in the soil. This was corroborated by Akan *et al*. (2015) who reported that soil may act as an important sink for persistent organic pollutants including many pesticides used in the past or presently. Several studies have confirmed the detection of synthetic organic pollutant in soils, most especially the OCPs which were reported to be more persistent, decompose very slowly and retained by soils for many years (Aiyesanmi and Idowu, 2012; Akan *et al*., 2015; Oyekunle *et al*., 2011). Statistical analysis indicates the significant differences in concentration level of ∑OCPs between the young and old cocoa plantation soil samples of the study area ($p < 0.05$) with highly significant differences observed in Ekiti and Osun State study sites ($p < 0.01$) (Fig. 3).

Composition quotients of Organochlorine pesticides residues in the study area

The composition quotient is the major method of evaluating the application status of pesticides used in the environment as it serves as good indicator of pollution status (Iwata *et al*., 1995; Wang *et al*., 2010). Based on the previous studies, the consensus of threshold value were used to distinguished between the current usage of banned / restricted pesticide and historical usage (Iwata *et al*., 1995; Wang *et al*., 2010; Wang *et al*., 2016). Therefore, OCPs residues composition quotients evaluated in this study according to Eq. 1.

$$\frac{(\text{DDE+DDD})}{\text{DDTs}}, \frac{\beta}{(\alpha+\gamma)}\text{HCH}, \frac{\alpha}{\gamma}\text{chlordane},$$

$$\frac{\text{endosulfan I}}{\text{endosulfan II}} \text{ and } \frac{\text{DDD}}{\text{DDE}}$$ (Table 2).

DDTs are organochlorine pesticide compounds that have a long persistence feature in the environment. The commercial grade dichlorodiphenyl (DDT) compounds was reported to contain 75% p,p'DDT, 15% O,P' DDD, 5% p,p'DDD (Wang *et al*., 2010). The ratio of $\frac{(\text{DDE + DDD})}{\text{DDTs}}$ in contaminated soil after a long period of application and several decades of

Table 2: Composition quotients of OCPs residues in the study area

Sampling Locations		$\frac{(DDE + DDD)}{DDTs}$	$\frac{DDD}{DDE}$	$\frac{\beta}{(\alpha + \gamma)}$	$\frac{\alpha}{\gamma}$	$\frac{\alpha}{\gamma}$chlordane	$\frac{endosulfan I}{endosulfan II}$
ED	1	-	-	0.63	2.32	-	2.19
	2	0.87	0.33	0.00	0.78	-	1.93
ON	1	1	-	0.00	2.29	1.67	1.15
	2	0.79	0.11	0.42	0.18	0.14	1.61
EK	1	-	-	0.00	3.72	-	1.83
	2	0.60	0.00	0.16	0.78	2.26	1.78
OS	1	-	-	0.24	0.85	-	5.87
	2	0.86	0.44	0.15	0.90	5.43	1.26

Keys: If $\frac{(DDE+DDD)}{DDTs}$ quotient value is >0.5 it indicate historical use of DDT; $\frac{DDD}{DDE}$ quotient value <1 signifies aerobic degradation; $\frac{\beta}{(\alpha+\gamma)}$ value <0.5 indicate aged used of hexacyclochlorohexen compounds; $\frac{\alpha}{\gamma}$ value ≤ 4 indicate the source of this compound to be lindane; $\frac{\alpha}{\gamma}$chlordane value <1 signifies recent input; $\frac{endosulfan-I}{endosulfan-II}$ value.

degradation; had been reported to usually be > 0.5 (Wang *et al*., 2010; Wang *et al*., 2016). However as shown in Table 2 above, the ratio for all the evaluated sites where DDT and its metabolites were detected were greater than 0.5; indicating the historical usage of DDT in these areas. This could be an indication that people engaged in cocoa plantation farming in this study areas have comply with the regulatory body's directives that banned the use of DDT in agricultural soil due to their negative impact on the environment. Furthermore, the ratio of DDD to DDE is an indication of degradation status of DDT compound under ambient conditions (Ma *et al*., 2010). In the surface soil under aerobic condition, the metabolism of DDT to DDE is usually favoured, while under anaerobic condition the DDD is usually the major by-product of DDT metabolism (Iwata *et al*., 1995; Ma *et al*., 2010). Therefore, at the surface soil, it is expected that DDE is much higher than DDD following long application of DDT. This is the case has shown in Table 2 above, which indicates the aerobic degradation of DDT compounds has taken place in all the study sites over the period of application. This further confirmed the possibility of DDTs residues obtained in this study to come from historical usage of DDT products in cocoa plantation in Nigeria.

Chlordane is a class of organochlorine pesticide that was majorly used as a contact insecticide for agriculture crops such as cutworms, white ants and termites (Boonyatumanond *et al*., 2002). It is a mixture of γ-chlordane, α-chlordane and heptachlor. The ratio of $\frac{\alpha}{\gamma}$ chlordane was reported to be 0.77 in commercial grade chlordane pesticide. Therefore, aged application and degradation of chlordane in the environment can increase the $\frac{\alpha}{\gamma}$ chlordane ratio to 1. The $\frac{\alpha}{\gamma}$ chlordane ratio has evaluated from this study was greater than 1 (except at site ON2), implying the possibilities of chlordane residue detected mostly derived from aged inputs.

Endosulfan-I or endosulfan II are the major representative the class of organochlorine called endosulfan. In terms of composition technical endosulfan was reported to contain 70% to 30% mixture of endosulfan I and endosulfan II respectively; while the endosulfan sulfate was the dominant product of endosulfan in the environment (Wang *et al*., 2016). Therefore, the recent input of technical endosulfan will increase the $\frac{endosulfan-I}{endosulfan-II}$ ratio which makes it a good indicator for the age of endosulfan (Ouyang *et al*., 2012). Because endosulfan-II is more stable in the environment than endosulfan I, the ratio of $\frac{endosulfan I}{endosulfan II}$ will be <1 if there is no endosulfan input. As shown in Table 2, the ratios of $\frac{endosulfan-I}{endosulfan-II}$ were greater than 1 for all the soil samples of the study sites, indicates the possibility of recent input of endosulfan.

Correlation of soil physico-chemical parameters with organochlorine pesticides groups

Soil physico-chemical properties such as the pH, organic carbon content, and particle size were among the major determinant of the fate of pesticide in the soil matrixes (Jiang *et al*., 2009). Results of correlation analysis between the analyzed soil parameters and the organochlorine pesticide compounds, showed a strong positive correlation only between the total organic carbon content and the OCPs compounds in all the study areas (Table 3). This indicates that the organic matter contents of these areas was closely associated with the amount of pesticide residue obtained and might have contributed to the persistent of OCPs compound in the study areas. Research has shown

Table 3: Correlation of soil physico-chemical properties with organochlorine pesticides groups of the study areas.

OCPs (µg/kg)		Soils parameters				
		pH (in H_2O)	TOC (%)	Sand (%)	Silt (%)	Clay (%)
∑DDT	1	-0.7827	0.7527*	-0.6404	-0.0742	-0.2654
	2	0.1350	0.8916*	0.1478	0.0878	-0.2363
∑CHLOR	1	-0.1230	0.9009*	0.0735	-0.7193	-0.4759
	2	0.4278	0.8823*	0.0279	0.2539	0.4636
∑CYCLO	1	-0.4160	0.6889	-0.8905	-0.2661	0.1642
	2	0.0987	0.8231*	0.3893	-0.0713	-0.1612
∑HCH	1	-0.6814	0.8394*	-0.1824	-0.7576	0.2497
	2	-0.1076	0.8666*	0.0524	0.2905	-0.4793
∑OCPs	1	-0.5426	0.9486*	-0.5754	0.2176	-0.2956
	2	0.1458	0.9119*	0.2508	0.0828	-0.3002

*significant positive correlation at $p < 0.05$; ∑DDTs = Dichlorodiphenyl group; ∑CHLOR = Chlordane-cyclodiene related group; ∑CYCLO = other cyclodiene group; ∑HCH = hexachlorobenzene group; ∑OCPs = sum of all OCPs; TOC = total organic carbon; 1 and 2 = young and old plantation respectively.

that organochlorine pesticides molecules usually have high affinity for the organic carbons in the soil because of their hydrophobic nature (Jiang *et al.*, 2009; Aiyesanmi and Idowu, 2012). The other soils' physico-chemical parameters showed no significant correlation with OCPs compounds as observed in this study, indicating little or no influence on the OCP level.

CONCLUSION

This study confirmed the occurrence of several organochlorine pesticide (OCP) residues in different concentration in the study areas despite the report that OCPs products have been banned since 2008 in Nigeria. However, the significant higher concentration of OCPs at old cocoa plantation compared to young cocoa plantation soil sample indicates the persistence nature of OCPs and its capability to accumulate, adhere or adsorbed to soil matrixes after long period of continuous application. The levels of OCPs in soil samples of old cocoa plantation were significantly higher than the relatively young plantation soil samples. The highest concentration of OCPs was recorded from the composite soil sample of Ondo State study site. Contrary to reports that the uses of banned agrochemical products such as pesticide compound was the common practices in Nigeria agricultural system; this results showed that most of the pesticide compound detected were not the product of recent application of such pesticide compound as confirmed by their metabolite quotients value. However, the detection of relatively higher levels of endosulfan 1 in all the soil samples of the study area couple with its metabolite quotient indicates more recent uses of endosulfan products in the study sites and called for a great concern. The Government regulatory agencies that are saddled with responsibility to regulate and enforce the use of chemicals in the environment are encouraged to vigorously embark in further monitoring and ensuring the safety compliance of farmers towards the use of pesticides in Nigeria farms.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

ABBREVIATIONS

α	*Alpha*
β	*Beta*
∑CHLOR	*Chlordane-cyclodiene group*
Conc.	*Concentrated*
^oC	*Degree Celsius*
δ	*Delta*
∑DDTs	*Dichlorodiphenyl group*
DDD	*dichlorodiphenyldichloroethane*
DDE	*Dichlorodiphenyldichloroethylene*
DDT	*Dichlorodiphenyltrichloroethane*
ED	*Edo*
EK	*Ekiti*
ECD	*Electron capture detector*

E.C.	*Emulsifiable concentrates*
Eq.	*Equation*
Fig.	*Figure*
γ	*Gamma*
GC	*Gas chromatography/*
g	*gram*
He	*Helium*
Hp	*Hewlett-Packard*
∑HCH	*Hexachlorobenzene group*
HCH	*Hexachlorohexane*
H	*Hour*
H_2O_2	*Hydrogen peroxide*
ID	*Internal diameter*
^{63}Ni	*Isotope of Nickel*
LGA	*Local Government Area*
m	*Metre*
µg/g	*Microgram per gram*
µg/kg	*Microgram per kilogram*
µL	*Microliter*
µm	*Micrometre*
ml/min	*Mililiter per minute*
ml	*Milliliter*
mm	*Millimeter*
Min	*Minute*
M	*Molar concentration*
µg/kg	*Microgram per kilogram*
N_2	*Nitrogen*
n-	*Normal (linear and unbranched)*
N	*Normality*
NaCl	*Sodium chloride*
ON	*Ondo*
OECD	*Organization for Economic Cooperation and Development*
OCPs	*Organochlorine pesticides*
H_3PO_4	*Orthophosphoric acid*
OS	*Osun*
∑CYCLO	*Other cyclodiene group*
p,p'-	*Para position (isomer)*
%	*Percent*
$K_2Cr_2O_7$	*Potassium dichromate*
pH	*Potential of hydrogen (i.e. a measure of acidity or alkalinity)*
P	*Probability value*
RSD	*Relative standard deviation*
Rpm	*Revolution per minute*
NaCl	*Sodium chloride*
Na_2SO_4	*Sodium sulphate*
SPSS	*Statistical Package for Social Sciences*
H_2SO_4	*Sulphuric acid*
∑OCPs	*sum of all OCPs*
USDA	*United State Department of Agriculture*
H_2O	*Water*
WAAPP	*West Africa Agriculture Productivity Programme*

REFERENCES

Adabe, K.E.; Ngo-Samnick, E.L., (2014). Cocoa production and processing. Pro-Agro Collection, Netherlands, **(44 pages).**

Aiyesanmi, A.F.; Idowu, G.A., (2012). Organochlorine pesticides residues in soil of cocoa farms in Ondo State Central district, Nigeria. Environ. Nat. Res. Res., 2(2): 65-73 **(9 pages).**

Asogwa, E.U.; Dongo, L.N., (2009). Problems associated with pesticide usage and application in Nigerian cocoa production: A review. Afr. J. Agric. Res., 4(8): 675-683 **(9 pages).**

Atuanya, E. I.; Aborisade, W.T.; Nwogu, N.A., (2012). Impact of plastic enriched composting on soil structure, fertility and growth of maize plants. European J. App. Sci., 4(3): 105-109 **(5 pages).**

Benson, N.U.; Olufunke, A.I., (2011). Assessment of contamination by organochlorine pesticides in Solanum lycopersicum L. and Capsicum annum L.; a market survey in Nigeria. Afr. J. Sci. Tech., 5(6): 437-442 **(6 pages).**

Bishnu, A.; Saha, T.; Ghosh, P.B.; Mazumdar, D.; Chakraborty, A.; Chakrabarti, K., (2009). Effect of pesticide residues on microbiological and biochemical soil indicators in Tea gardens of Darjeeling Hills, India. World J. Agric. Sci., 5(6): 690-697 **(8 pages).**

Boonyatumanond, R.; Jaksakul, A.; Puncharoen, P.; Tabucanon, M. S., (2002). Monitoring of organochlorine pesticides residues in green mussels (Perna viridis) from coastal area of Thailand. Environ. Pollut., 119(2): 245-252 **(8 pages).**

Camarata, M.; Wistar, G.; Rosenberg, M., (2006). Guidance for evaluating residual pesticides on land formerly used for agricultural production. Oregon, US, (**21 pages**).

Cycon, M.; Piotrowska-Seget, Z.; Kaczynska, A.; Kozdroj, J., (2006). Microbiological characteristics of a sandy loam soil exposed to tebuconazole and λ-cyhalothrin under laboratory conditions. Ecotoxicol., 15: 639-646 **(8 pages).**

Dubey, V.; Singh, D.; Shukla, A.; Shukla, S.; Singh, N., (2012). Effect of application of different pesticides to leguminous crops on soil microflora of Sidhi District. Int. J. Eng. Res. Dev., 3(12): 01-03 **(4 pages)**

Emoghene, A.O.; Futughe, A.E., (2016). Fungal applications in sustainable environmental biotechnology. Springer International Publishing, Switzerland. 43-62 **(20 pages).**

Erhunmunse, N.O.; Dirisu, A.; Olomukoro, J. O., (2012). Implications of pesticide usage in Nigeria. Tropical F. Bio., 21(1): 15-25 **(11 pages).**

Estefan, G.; Sommer, R.; Ryan, J., (2013). Method of soil, plant and water analysis: A manual for the West Asia and North Africa region. Third edition, International Centre for Agricultural Research in Dry Areas (**244 pages**).

Imane, E.; Rabea, T.; Smail, O.; Rakan, A.; Mufeed, B.; Mohammed, E. A., (2015). Multiresidue analysis of pesticides in soil profile from the Loukous valley using GC-ECD. Res. J. Pharm. Bio. Chem. Sci., 6(4): 1463-1472 **(10 pages).**

IPEP, (2006). Establishing the prevalence of POPs pesticide residues in water, soil and vegetable samples and creating awareness about their ill-effects. International POPs Eliminating Project. Janhit Foundation, India, **(13 pages).**

Iwata, H.; Tanabe, S.; Ueda, K; Tatsukawa, R., (1995). Persistent organochlorine residues in air, water, sediments, and soils from the Lake Baikal Region, Russia Environ. Sci. Technol., 29(3): 792–801 **(10 pages).**

Jiang, Y.F.; Wang, X.T.; Jia, Y.; Wang, F.; Wu, M.H.; Sheng, G. Y.; Fu, J. M., (2009). Occurrence, distribution and possible sources of organochlorine pesticides in agricultural soil of Shanghai, China. J. Hazard. Mater., 170 (2 – 3): 989-997 **(9 pages).**

Landon, J. R., (1991). Booker tropical soil manual. Longman Scientific and Technical Essex, UK. **(474 pages).**

Mihale, M.J.; Kishimba, M.A., (2004). Contamination of water and sediments by obsolete pesticides at Vikuge farm, Kibaha District, Tanzania. Tanzanian J. Sci., 30(2): 21-32 **(12 pages).**

Moghaddam, N.S.; Zakaria, M.P.; Omar, D.; Sijam, K.; Khakvar, R., (2011). Effects of imidacloprid on the biodiversity of soil microbes in selected soils of Malaysia. Env. Sci. Dev., 4: 7-10 **(4 pages).**

Ogbeide, O.; Tongo, I; Ezemonye, L., (2015). Risk assessment of agricultural pesticides in water, sediment and fish from Owan River, Edo State, Nigeria. Environ. Monit. Assess., 187: 654-670 **(7 pages).**

Olujide, M G.; Adeogun, S.O. (2006). Assessment of cocoa growers farm management practices in Ondo State, Nigeria. Spanish J. Agric. Res., 4(2): 173-179 **(7 pages).**

Ouyang, H.L.; He, W.; Qin, N.; Kong, X.Z.; Liu, W.X.; He, Q.S.; Wang, Q.M.; Jiang, Y.J.; Yang, C.; Yang, B.; Xu, F.L., (2012). Levels, temporal-spatial variations, and sources of organochlorine pesticides in ambient air of Lake Chaohu, China. Sci. World J. 1-12 **(13 pages).**

Oyekunle, J.A.O.; Ogunfowokan, A.O.; Torto, N; Akanni, M.S., (2011). Determination of organochlorines pesticides in the agricultural soil of Oke-Osun farm settlement, Osogbo, Nigeria. Environ. Monit. Assess., 177: 51-61 **(11 pages).**

Sebiomo, A.; Ogundero, V.W.; Bankole, S.A., (2011). Effect of four herbicides on microbial population, soil organic matter and dehydogenase activity. African J. Biotech., 10(5): 770-778 **(9 pages).**

Sharu, M.B.; Yakubu, M.; Noma, S.S.; Tsafe, A.I., (2013). Charcateristics and classification of soils on an agricultural landscape in Dingyadi District, Sokoto State, Nigeria. Nigerian J. Bas. App. Sci., 21(2): 137-147 **(11 pages).**

Sturz, A.V.; Kimpinski, J., (1999). Effects of fosthiazate and aldicarb on populations of plant-growth-promoting bacteria, root-lesion nematodes and bacteria-feeding nematodes in the root zone of potatoes. P. Patho., 48: 26-32 **(7 pages).**

Tariq, A.; Athar, M.; Ara, J.; Sultana, V.; Ehteshamul-Haque, S.; Ahmad, M, (2015). Biochemical evaluation of antioxidant activity and polysaccharides fractions in seaweeds. Global J. Environ. Sci. Manage., 1(1): 47-62 (**6 pages**).

WAAPP, (2013). Report of baseline study on status of use, registration and regulation of pesticides in Nigeria. West Africa Agriculture Productivity Program, Nigeria **(77 pages).**

Wang, G. L.; Ma, L. M.; Sun, J. H.; Zhang, G., (2010). Occurrence and distribution of organochlorine pesticides (DDT and HCH) in sediments from the middle and lower reaches of the Yellow River, China. Environ. Monit. Assess., 168: 511-521 **(11 pages).**

Wang, B.; Wu, C.; Liu, W.; Teng, Y.; Luo, Y.; Christie, P.; Guo, D., (2016). Levels and patterns of organochlorine pesticides in agricultural soils in an area of extensive historical cotton cultivation in Henan Province, China. Environ. Sci. Pollut. Res., 23: 6680-6689 **(10 pages).**

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