Hazard Characterization of Commonly Used Organochlorine Pesticide by Farmers in Upper Yedzaram Basin Adamawa State, Nigeria

Zira, S. P[1], Bwatanglang, I. B[1] and Tukur, S[2].

[1]Department of Pure & Applied Chemistry, Adamawa State University, Mubi-Nigeria
[2]Department of General Studies, College of Health Technology, Mubi Adamawa State

Corresponding Author: pstorspz@gmail.com

DOI: 10.29322/IJSRP.10.05.2020.p10186
http://dx.doi.org/10.29322/IJSRP.10.05.2020.p10186

Abstract
In this study, the levels of organochlorine (dichlorodiphenyl dichloroethylene (p,p-DDE), 4,4'-dichlorodiphenyldichloroethan (p,p'DDD), 2,4'dichlorodiphenyltrichloroethane (p,p'-DDT), alpha-BHC, beta-BHC, delta-BHC, lindane, heptachlor, heptachlor-epoxide, endosulfan I, endosulfan II, PF-38) pesticide residues were investigated in selected agricultural crops (cabbage, tomato, garden egg, guava, sweet potato and soya bean) produced in Upper Yedzaram Basin, Adamawa State, Nigeria. The concentrations of the pesticides in the samples were determined using Gas Chromatography/Mass Spectroscopy (GC/MS), equipped with electron capture detector (ECD). And the results showed endosulfan I as the most frequently detected organochlorine pesticide (OPCs) residue in the samples analyzed. The highest concentration of endosulfan I detected in sweet potatoes (5.027 mg/kg) and the least in cabbage (1.322 mg/kg). The DDT and its metabolites were not detected in the samples. However, isomers of BHC were detected in tomato samples. The results show the concentrations of the OPC detected in the samples exceeding the maximum residual limits (MRLs) allowed in edibles. Despite the ban and restrictions placed on OPC, the presence of endosulfan I and the isomers of BHC detected in samples could be due to their ability to persist in the environment. Further study to analyze the risk on consumption, shows the estimated daily intake (EADI) to be below the acceptable daily intake (ADI) for endosulfan I (0.006 mg/kg/day). The study shows higher potential health risk among children exposed to endosulfan I through the consumption of tomato (0.009 mg/kg/day) and sweet potato (0.007 mg/kg/day). The hazard quotient (HQ) values for endosulfan I in the same samples shows exposure risk slightly >1. Suggesting likely risk for non-carcinogenic related complications. The study therefore recommended proactive measures by the authority on prohibiting the sell and use of the legally banned pesticides. Clean up measures of major pesticide contaminated areas such as agricultural areas should be done by the ministry of environment.

Keywords: Organochlorine, Vegetable, Fruit, Crop, Pesticide Residue, DDT and Endosulfan.

Introduction:

The onslaught engineered by the indiscriminate use of agrochemicals is becoming alarming, observed to infringe on the right to health and quality food (Gerage *et al.*, 2017; Bwatanglang *et al.*, 2019a). And further reported to serve as causative factors to the pathogenesis of several diseases (Bwatanglang *et al.*, 2019b). High level of organochlorine pesticides (OPCs) in rivers or sediments found in agricultural areas (Zakaria *et al.*, 2003) often leaves behind destructive footprint, identified to contribute to the buildup of contaminants in soil and transfer dynamic in plants (Gerage *et al.*, 2017; Garba *et al*., 2018, Bwatanglang *et al*., 2019).

Dangerously classified organochlorine insecticides such DDT, are banned from circulation, while others specifically Dicofol, Lindane and Endosulfan are exceptionally allowed for limited and control uses only (Bouwman, 1990; WHO, 1990). The ban and restrictions is a fallout of its health-related complications and physiochemistry, having the propensity to metabolize and interfere with the central nervous system disrupting the electrophysiological properties and enzymatic neural membranes. Changing the chemistry and the kinetics of the flow of Na^+ and K^+ through the membrane of the nerve cell, leading to wide spread of multiple actions. Stimulating symptoms such as seizures, acute poisoning and death from respiratory arrest (Garcia *et al*., 2012).

The chemical stability of OPCs, their high lipid solubility and toxicity to humans and animals (Bouwman, 1990; Caldas *et al.*, 1999), leads to its outright ban by government and researchers globally. Sadly such a pronouncement were reported to exerts limited success in must developing economies as a number of studies reported traces of OPCs still in use in Nigeria (WHO, 1990, WHO, 2010; Akan *et al*., 2014; Ogah *et al*., 2018; Tongo, and Ezemonye, 2015; Bwatanglang *et al*., 2019a)**.** For these reasons, this study was engineered to look at farming related activities in Upper Yedzaram basin in Adamawa state, Nigeria in order to establish the level of widely used OPCs in the study location. Upper Yedzaram basin was selected due to its strategic contribution to the agricultural enterprise in Adamawa state. Thus, the study hypotheses possible use and applications of potentially toxic and banned pesticides in the study location which on the long run owed to their persistent nature will bio-accumulate and transcend across the trophic levels.

Material and Methods:

Study Area:

The main source of the river is the Hudu Hills, emanating south-east of Mubi, Adamawa state flowing northward toward Lake Chard in Borno state. With a total length of about 330 kilometer (Martins and Gadiga, 2015). Vegetable, fruit and crop samples were collected from Upper Yedzaram Basin, in Mubi North, Mubi South and Maiha Local Government Area in the Northeastern part of Adamawa State, Nigeria. Located between latitudes 10°11 '30” and 10° 22' 30”N and between longitudes 13°13' 00’’and 13° 30’ 00” 'E (Adebayo and Dayya, 2004). (Figure 1)

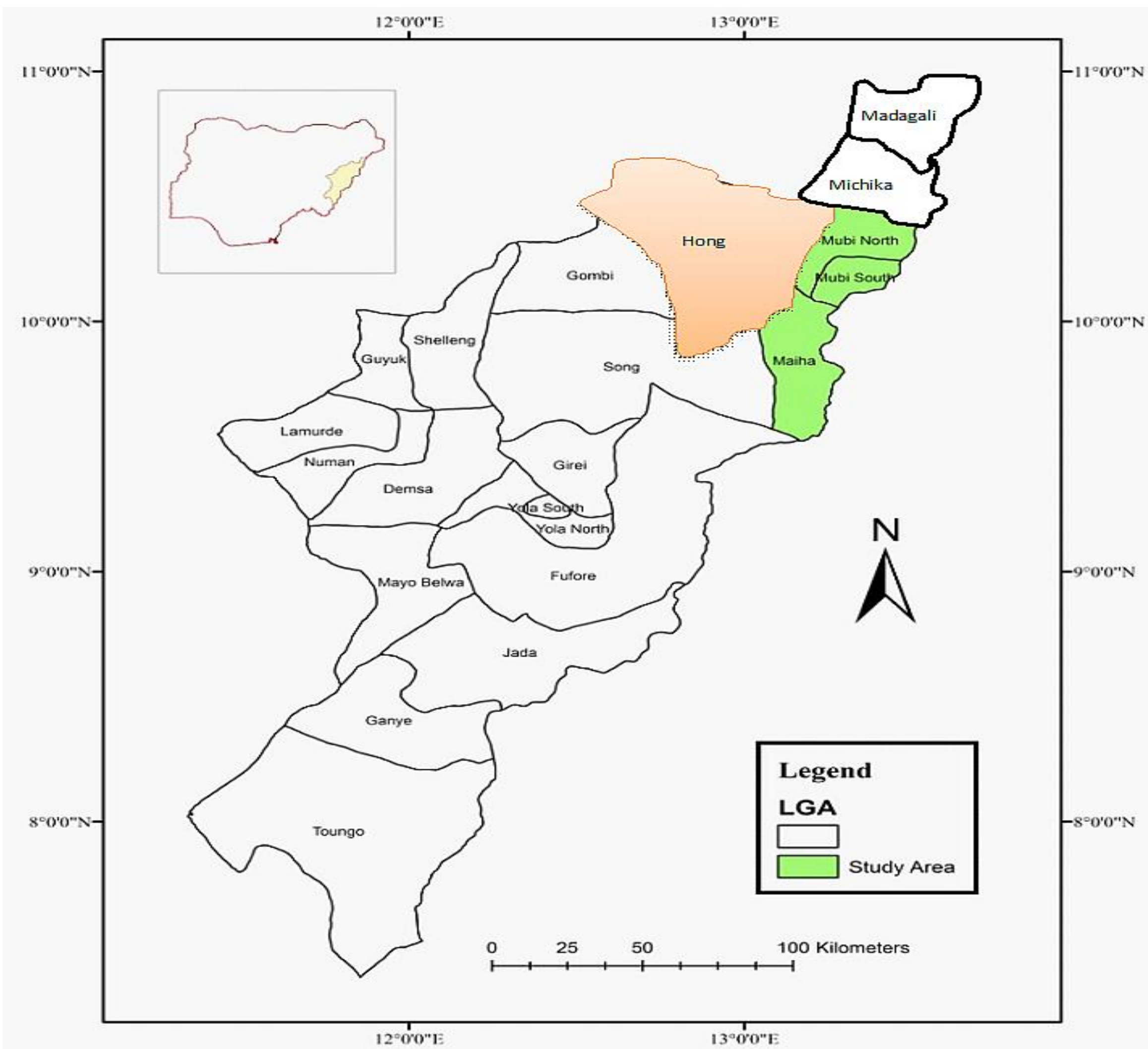


Fig. 1 Map of Adamawa state showing upper Yedzaram covering Mubi north, Mubi south and Maiha local government area of the state.

Samples Collection and Preparation:

Composite samples of the vegetables, (cabbage, tomato, garden egg), fruit (guava), and crops (sweet potato and soya bean) were collected from three different locations, Shuware, Wuro Gude, and Sabon Gari , along Upper Yedzaram Basin. In each location, samples were collected from six farmlands. The respective samples were washed thoroughly with distilled water and anhydrous sodium sulfate (Na_2SO_4) were used to remove water from the sample matrix. After weighing, the samples were washed thoroughly with distilled water and placed in a mortar and ground to a paste using a pestle. The paste was transferred into a conical flask and 40 ml of Ethyl acetate were added and shaken thoroughly. A 5g portion of sodium hydrogen carbonate ($NaHCO_3$) was added to the mixture followed by 20g of anhydrous sodium sulphate (Na_2SO_4) and the entire mixture was shaken vigorously for one hour. This process is to ensure that enough of the pesticide residue dissolved in the ethyl acetate. The procedure was repeated for the samples from each farmland and the mixture was filtered into a labeled container before being centrifuged at a speed of 1800 rpm for 5mins.The organic layer was decanted into a container and a 1:1 mixture of 5ml ethyl acetate and cyclohexane was added (USEPA, 2007).

Determination of Pesticide Residues in the Samples:

Prior to the elemental analysis, the respective sample extracts were cleaned up as follows; A 10 mm chromatographic column was filled with 3g activated silica gel and topped up with 2 to 3g of anhydrous sodium sulphate and 5ml of n-hexane was added to the column. The residue in 2ml n-hexane was transferred into the column and the extract was rinsed thrice with 2ml hexane. The procedure was repeated for all the samples. The sample was collected in a 2ml vial, sealed and placed in the refrigerator. The SHIMADZU GC/MS (GC-17A), equipped with fluorescence detector was used for chromatographic separation and was achieved by using a 35% diphenyl, 65% polysiloxane column. The oven was programmed as follows; initial temperature 40ºC, 1.5min, to 150ºC, 0.0min. 5ºC/min to 200ºC,7.5min, 25ºC/min to 290ºC with a final hold time of 12min and a constant column flow rate of 1ml/min. Detection of pesticides was performed using the GC-ion trap MS with optional MSn mode. The scanning mode offers enhanced selectivity over either full scan or selected ion monitoring (SIM). In SIM, at the elution time of each pesticide, the ratio of the intensity of matrix ions increased exponentially versus that of the pesticide ions as the concentration of the pesticide approached the detection limit, decreasing the accuracy at lower levels. The GC-ion trap MS was operated in MSn mode and performed tandem MS function by injecting ions onto the ion trap and destabilizing matrix ions, isolating only the pesticide ions. The retention time, peak area and peak height of the sample were compared with those of the standards for quantization. The data collected were analyzed and presented as Mean ±SD and the level of significance was set at $p<0.005$. The risk level of the pesticides concentration were assessed by comparing the obtained data for each sample with the maximum residual limits (MRLs) allowed in edibles (USEPA, 1996).

Risk Characterization:

The most commonly used pesticides established in the study were further subjected to health risk assessment, estimated using the Average Daily Intake (EADI), and the Hazard Quotient (HQ). The EADI (mg/kg/day) is drawn by multiplying the pesticides residue concentration in the samples (mg/kg) by the average daily consumption rate (Cri) for vegetables food, by the conversion factor and then divide by the body weight (Bw) for an adult and children respectively. The Cri of 0.35 and 0.23 mg/kg for adults and children were adopted in this study (Al-Hwaiti and Al-Khashman, 2014). The conversion factor 0.085 was used to convert fresh vegetable weight to dry weight, (Rattan *et al*., 2005). Body weights of 60 and 15 kg were adopted for adults and children in the study (Bwatanglang *et al*., 2019a). The Hazard Quotient (HQ), an index used in assessing risk associated with non-carcinogen is obtained by dividing the EDAI values with an established acceptable daily intake (ADI) values set by USEPA (1996).

Results:

The concentration of OPCs residues in the respective samples from the three different locations (Shuware, Wuro Gude, and Sabon Gari) are presented in figure 2-6. No residue of OPC detected in soya bean samples from all the sample locations. In cabbage samples, only endosulfan I was detected, with highest value of 0.755 mg/kg determined in farmlands from Shuware and the least concentration of 0.567 mg/kg in farmlands from Wuro Gude. The results are presented in figure 2.

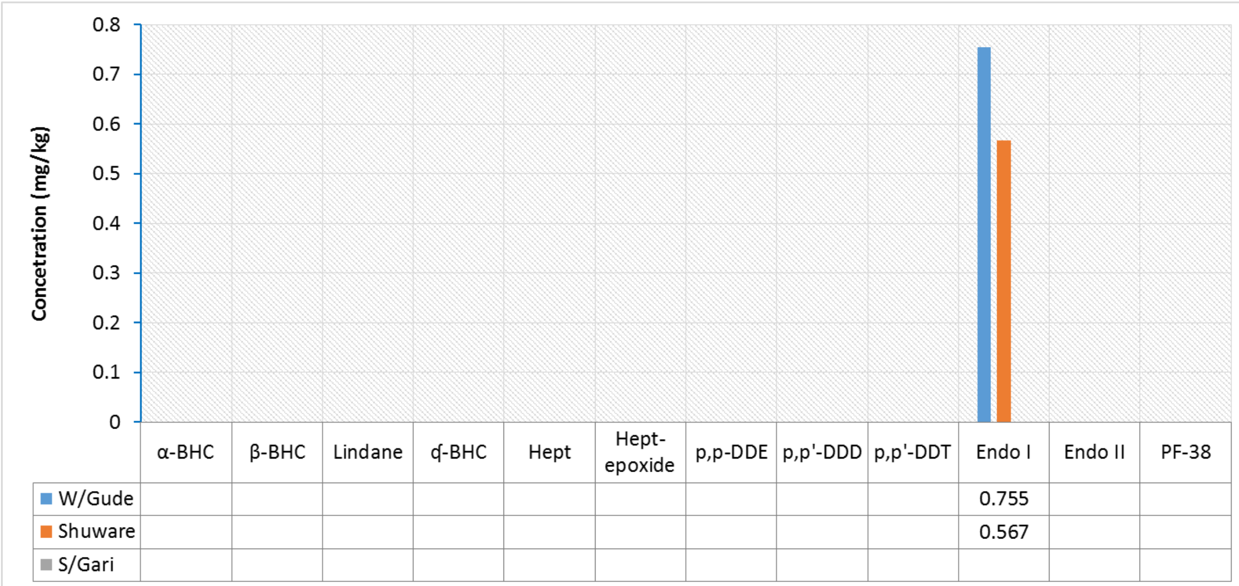


Fig. 2. Concentrations of OPCs Residues in Cabbage. Results presented in Mean ±SD of replicate values. Empty column signified Below Detection Limit.

Figure 3 presents the concentrations of the OPCs detected in tomatoes, in farmlands from Shuware, Wuro Gude and Jairi. Pesticides with highest concentration detected in Shuware is edosulfan (1.09mg/kg) followed by beta-BHC (0.270 mg/kg), delta-BHC (0.937 mg/kg), lindane (0.249 mg/kg), and Alpha-BHC (0.056 mg/kg). In Jairi, about 1.167 mg/kg of delta-BHC was detected. Similarly, in the same sample location about 0.462 mg/kg Heptachlor-epoxide was detected. Maximum concentrations of endosulfan I (3.341 mg/kg) were detected in tomato samples collected from W/Gude. The results further show the DDT and its metabolites occurring below detection limits.

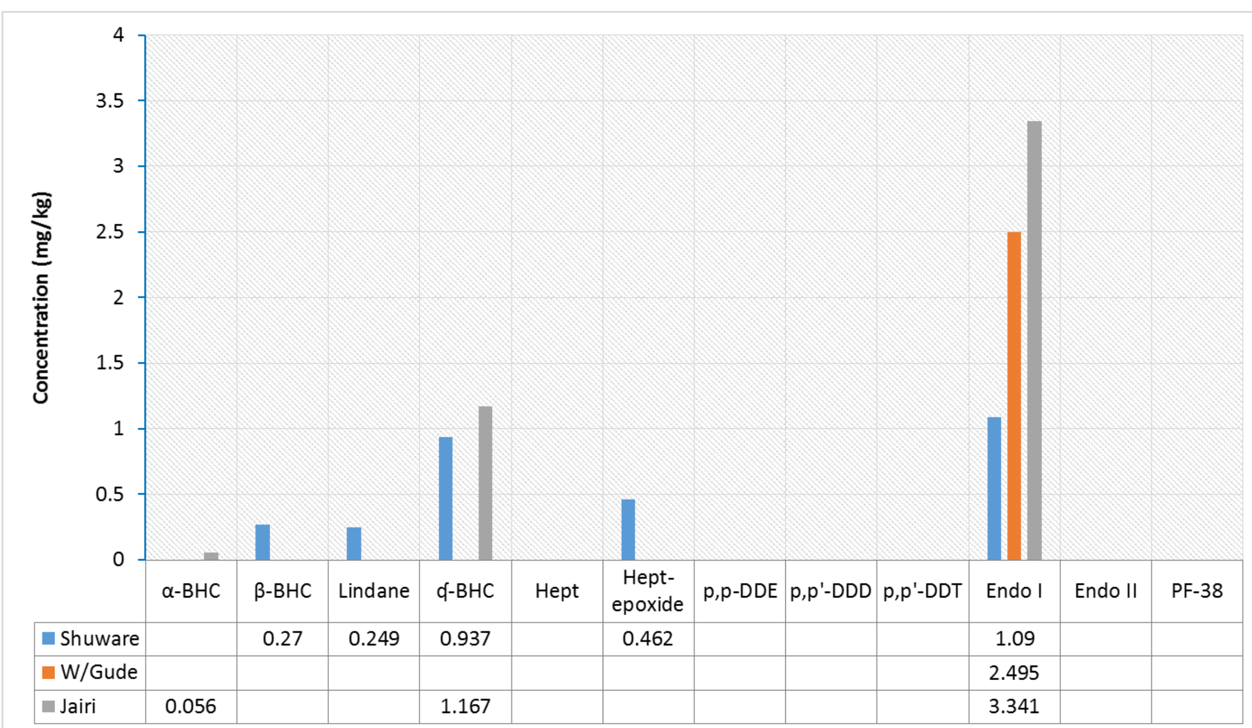
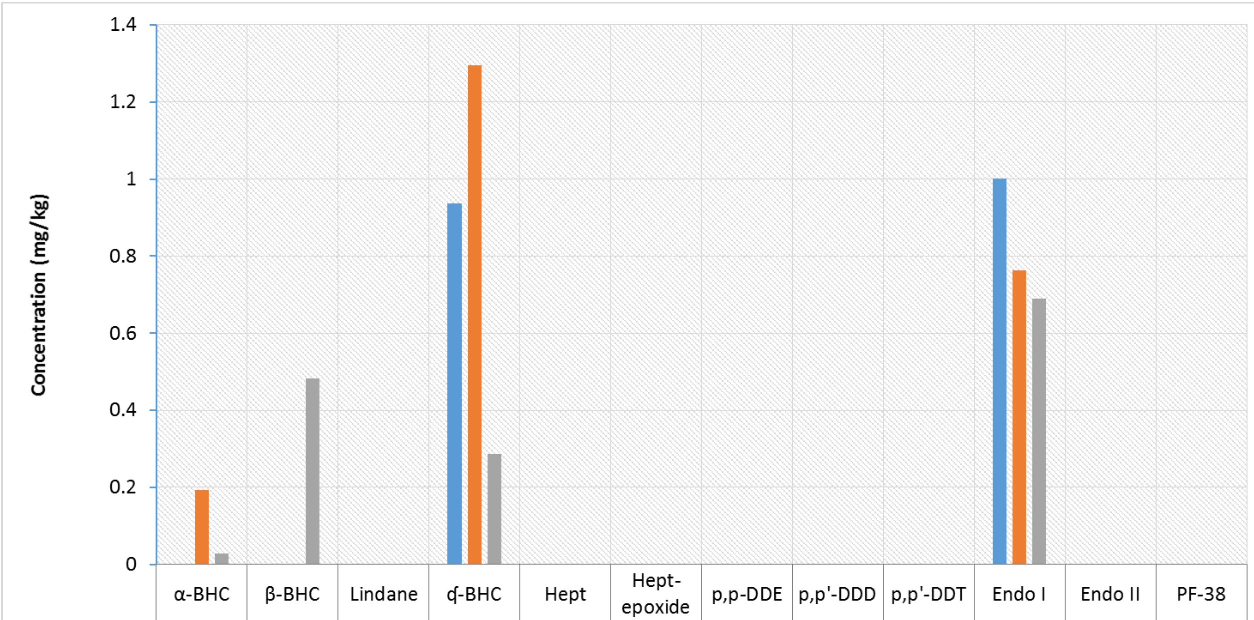


Figure 3. Concentrations of OPCs in Tomato. Results presented in Mean ±SD of replicate values. Empty column signified Below Detection Limit.

Figure 4 shows the levels of the OPCs residues in garden eggs collected from all the three sample locations. Highest concentration of alpha-BHC was detected in S/Gari (0.192 mg/kg) and the least in W/Gude (0.028 mg/kg). The level of beta-BHC and delta-BHC was observed to be higher in samples from W/Gude (0.483 mg/kg) and S/Gari (1.296 mg/kg). Heptachlor-epoxide is 2.102 mg/kg in W/Gude, endosulfan I with concentrations of 1.002 mg/kg, 0.763 mg/kg and 0.690 mg/kg were detected in W/Kondon, S/Gari and W/Gude respectively. Some levels of PF-38 (0.569 mg/kg) was also detected in W/Kondon. DDT and its metabolites were not detected in the farmlands under study.



	α-BHC	β-BHC	Lindane	ɗ-BHC	Hept	Hept-epoxide	p,p-DDE	p,p'-DDD	p,p'-DDT	Endo I	Endo II	PF-38
W/Kondon				0.937						1.002		
S/Gari	0.192			1.296						0.763		
W/Gude	0.028	0.483		0.286						0.69		

Figure 4. Concentrations of OPCs Residues in Garden Egg. Results presented in Mean ±SD of replicate values. Empty column signified Below Detection Limit.

The concentrations of the OPCs in guava samples collected from the three farmlands: Kwaja, Vimtim and Gella is presented in figure 5. From the figure, about 1.332 mg/kg, 1.225 mg/kg, and 1.115 of endosulfan I were detected in Kwaja, Vimtim, and Gella respectively. Furthermore, from the figure the following pesticides alpha-BHC, beta-BHC, lindane, delta-BHC, heptachlor, heptachlor-epoxide, p,p'-DDE, p,p'-DDDT, p,p'-DDT, ,endosulfan II and PF-38 were all found to be below the detection level..

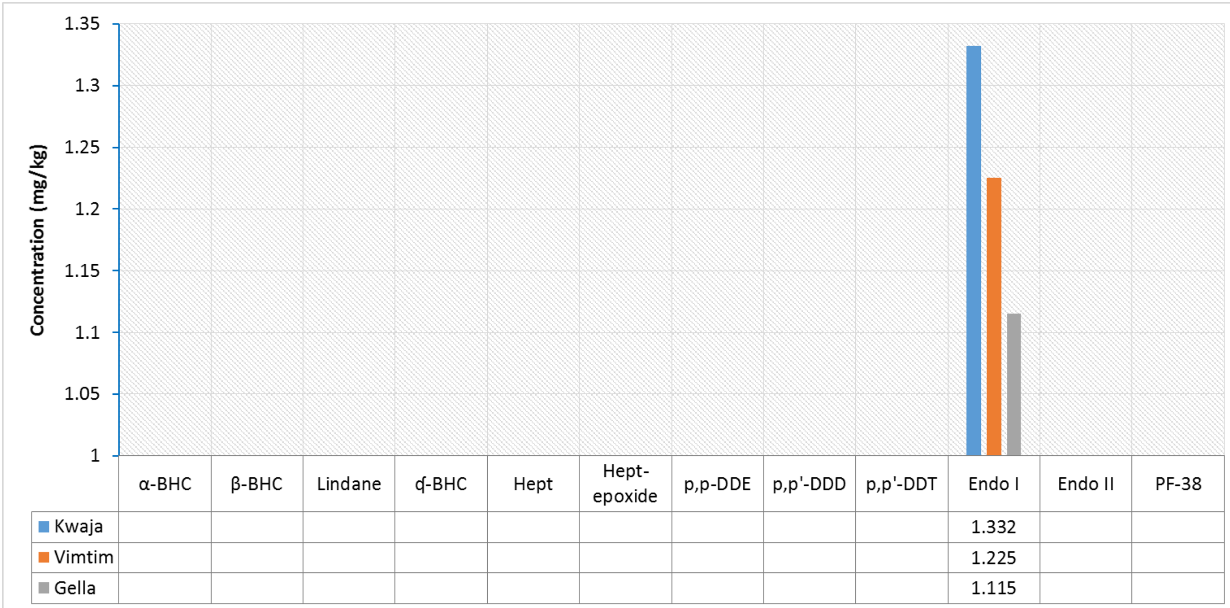


Figure 5. Concentrations of OPCs Residues in Guava. Results presented in Mean ±SD of replicate values. Empty column signified Below Detection Limit.

The concentrations of the OPC residues in sweet potato samples from Kwaja, Bwade and Duvu farmlands are presented in Figure 6. In the figure, Endosulfan I was the only organochlorine pesticide detected with concentrations of 2.973 mg/kg in Kwaja and 2.054 mg/kg in Duvu. DDT, its metabolites and the isomers of BHC were not detected in the samples.

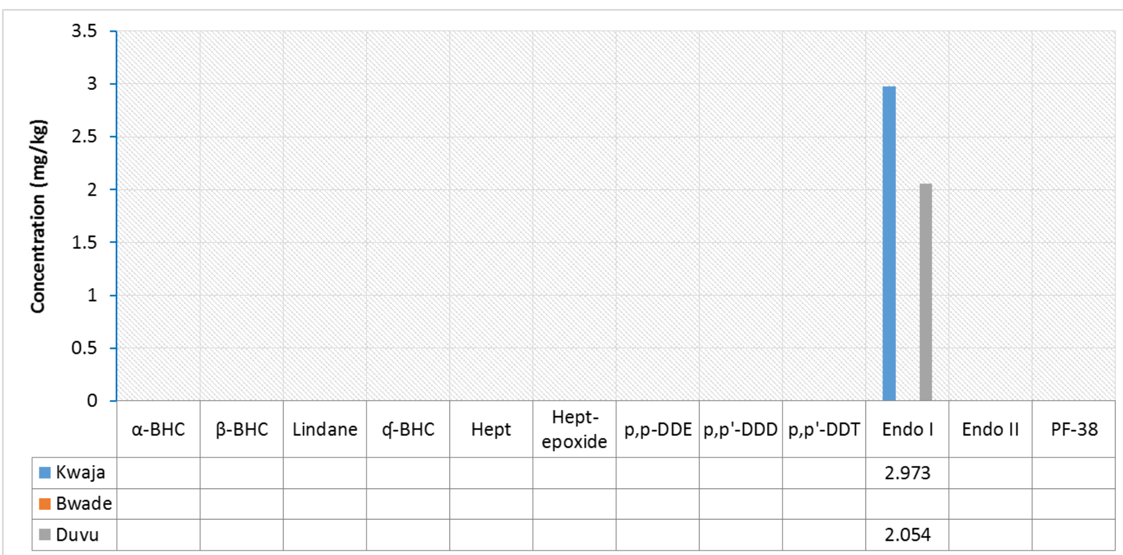


Figure 6. Concentrations of OPCs Residues in Sweet Potato. Results presented in Mean ±SD of replicate values. Empty column signified Below Detection Limit.

Discussions:

Organochlorine Pesticide Residues Detected in Vegetables, Fruit and Crops:

Among the OPCs analyzed in cabbage samples, only endosulfan I residue was detected, although its concentrations in the entire samples collected from the three different farmlands were not significantly ($p<0.05$) high (maximum of 0.755±0.02 mg/kg). Endosulfan II a metabolite of endosulfan I was not detected. This suggests fresh input of endosulfan I or lack of proper degradation of endosulfan I pesticide. The concentration of endosulfan I found in this study was generally lower than those found in cabbage samples from Alau Dam agricultural area by Akan *et a*l., (2014) which were up to 10.44 mg/kg and slightly above the 0.600 mg/kg concentration in cabbage samples from Dares Salam market by Mahugija *et al.,* (2017). The most frequent OPCs residue detected in tomato was endosulfan I which was detected in all the samples from the three different farmlands with concentration ranging from 1.09±0.03mg/kg to 3.341±0.1mg/kg. Endosulfan is an insecticide used in countries throughout the world to control pests on fruit, vegetables and tea and on nonfood crops such as tobacco and cotton. (Ogah *et al.*, 2018). Endosulfan contamination does not appear to be widespread in the aquatic, but the chemical has been found in agricultural runoff and rivers where it has been manufactured or on farmlands. Although endosulfan is among the list of pesticides banned or restricted in Nigeria by National Agency for Food Drugs Administration and Control (NAFDAC) (NLIPW, 2019) it is still being used either as single insecticide or in a mixture with cypermethrin by farmers in the study area. This and other reasons suggest the frequent detection of endosulfan pesticide residue in the analyzed samples. Several studies have shown that endosulfan alone or in combination with other pesticides, may bind to estrogen and perturb the endocrine system (Vega *et al*., 2007).

Lindane (gamma-BHC) was also detected in samples from one farmland with concentration of 0.249±0.04 mg/kg. Lindane is among the pesticides which use has been prohibited in Nigeria, but still use in storing beans. On the other hand, lindane and its metabolites are persistent organic pollutants (POPs) and they remain in the environment for long periods. It is therefore not surprising to find residues of these pesticides in this study. Other isomers of BHC including alpha-BHC, beta-BHC, and delta-BHC were also detected in some of the samples from the three different farmlands with mean concentration ranging from 0.056±0.001 mg/kg to 1.167±0.23 mg/kg. The alpha, beta and delta isomers are in many ways more problematic than lindane itself, alpha-BHC forms a major portion of technical BHC and the beta and delta-isomers are significantly more stable than gamma-BHC (Vega *et al.*, 2007). The result also confirmed the FAO 1998 inventory of obsolete , unwanted and or banned pesticides found unused stockpiles of both technical BHC and lindane (2,785 tons of technical BHC ,304 tons of lindane and 45 tons of unspecified BHC material) scattered in dump site in Africa and the near East (http://www.fao.org).

Heptachlor-epoxide, a metabolite of heptachlor used by farmers in killing insects was also detected in farmland, with concentration of 0.462±0.01mg/kg. Moderately persistent OPCs undergo significant photolysis, oxidation and volatilization in soil to yield different metabolites. It binds to soil particles and migrates slowly (Tsapko *et al.*, 1966; Fendick, 1990). This by implication suggested a residual remains of long time application in the farmland. Endosulfan I was the only organochlorine pesticide detected in sweet potato. From the result obtained for the analysis of pesticide residues in soya bean, no organochlorine pesticide residue was detected in the entire samples collected from the three different farmlands. The result reveals the absence or concentration below level of detection for all the OPCs. This suggested the non-application of the pesticide in planting the soya beans or the nature of the soil and temperature condition did not favor the persistency of the applied pesticide (Haffmans, 2008; ATSDR, 2013).

Though, endosulfan I and other pyrethroid pesticides were detected in guava, mango and sweet potato cultivated in some of the farmlands, the response by the farmers following an interview during the cause of study reopened another question as most of the farmers interviewed claimed not applying pesticide in mango, guava or sweet potato farming. The possible explanation as to the presence of these pesticides could be as a result of atmospheric transport and deposition (Haffmans, 2008) since the majority of the guava trees are planted in farmlands containing crops such as beans which require different kinds of pesticides. Furthermore, the volatile nature of the pesticides increase the atmospheric transport potential and hence its deposition. This may likely be the reason why endosulfan and cypermethrin residues were detected in guava despite the fact that the cross section of the farmers interviewed confirmed not applying the pesticide on the crop. Runoff and subsequent leaching are likely routes of pesticides enrichment in farmlands. This might be the reason why some of the pesticide residues were detected in sweet potatoes even though the majority of the farmers in the study area did not apply any pesticide both during planting and harvesting. This suggestion was confirmed by Ibrahim *et al*., (2007) who stated in his study that most of the pesticides were found to be reduced in the environment after they were banned except for lindane and endosulfan. All these findings were supported by the “grasshopper effect” in terms of mechanism of distribution of pesticide through air, plant and soil medium (Haffmans, 2008; ATSDR, 2013).

Maximum Residue Limits (MRLs) Compliance and Implications:

Food is considered adulterated and not safe for consumption if the residual level of pesticide in the food by implications exceed the Maximum Residue Limits (MRLs) established by the WHO and FAO (2018). In this study, the concentration of endosulfan I found in the cabbage samples from the three farmlands were observed to be above their MRLs of 0.5 mg/kg, which by implication means that some farmers did not observe the withholding periods. Violation of MRLs indicates hazard to human health (EFSA, 2009). The concentrations of alpha-BHC, beta-BHC, delta-BHC and gamma-BHC (lindane) detected in the tomato samples from the three different farmlands were all above their MRLs of 0.01mg/kg. Heptachlor epoxide residue detected in samples from one farmland was also above its MRL of 0.01mg/kg. The concentrations of endosulfan I in the entire sample analyzed from the three different farmlands were above their MRLs of 0.5 mg/kg. The highest concentration of 3.341mg/kg was up to 6.6 times higher than their MRL. In general most of the pesticide residues detected in tomato samples were having concentration above their MRLs. These findings suggest possible health threats to the consumers. The level of contamination found could be linked to improper agricultural practices by farmers or lack of knowledge on judicious use of pesticides (Barkat *et al.*, 2012).

The concentration of two isomers of BHC, alpha-BHC and delta-BHC in garden egg samples have all their concentration above their MRLs of 0.1mg/kg except the alpha-BHC residue from Wuro Gude with mean concentration of 0.028±0.02 mg/kg. The concentration of endosulfan I residues in all the samples were above their MRL of 0.2 mg/kg. Heptachlor-epoxide was detected with concentration of 2.119 mg/kg which exceeded the MRLs of 0.01mg/kg by 211times.The detected residue concentration of PF-38 was above its MRL concentration of 0.07mg/kg by 8.1times. Generally, the findings revealed that the majority of the pesticide residue were above the MRL. This by implication means they can be potential health hazards to the consumers (Ibrahim *et al*., 2007). The concentrations of the endosulfan I detected in guava samples analyzed from the three farmlands were all above their MRLs of 0.01mg/kg. The endosulfan I concentration in sweet potato samples from the two farmlands were above their MRLs of 0.05 mg/kg set by FAO and WHO.

Variation of Organochlorine Pesticide Residues among Vegetables, Fruit and Crops in farmlands at Upper Yedzaram basin:

In terms of occurrence, endosulfan was the most frequently detected organochlorine among all the pesticides. It was present in all the vegetables, fruits and crops with the exception of soya bean. All the isomers of BHC were detected only in some samples of tomato and garden eggs. Heptachlor epoxide was also detected in tomato and garden egg samples only. The compounds of DDT and its metabolites were not detected in all the samples. This suggests either they were not used for all the vegetables, fruits and crops studied or there was no significant contamination due to these compounds. There were slight variations in the concentration of endosulfan I among all the samples. The highest total mean concentration was observed in tomato (36%) while the lowest was found in cabbage (7%) samples as presented in figure 7.

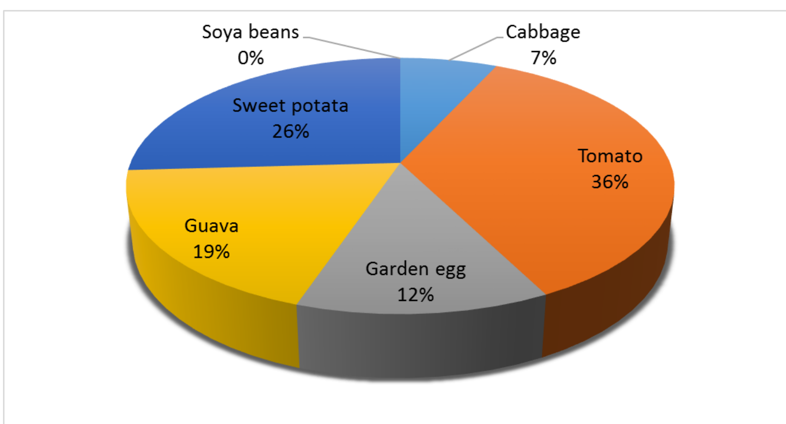


Fig. 7. Showing the percentage concentration of Endosulfan I in the samples across the farmlands in mg/kg

The EDAI and HQ established for the commonly used OPCs (Endosulfan I) is shown in table 1. The estimated ADI were observed to be below the ADI (0.006 mg/kg/day) values except in the children population exposed to the pesticides through the consumption of tomato (0.009 mg/kg/day) and sweet potato (0.007 mg/kg/day). The HQ values for endosulfan in the same samples shows exposure risk slightly >1. Non-carcinogenic risk, with an HQ value <1 signifies that population exposed to the endosulfan I through the consumption of the vegetables are unlikely to experience any adverse health hazard. A level of concern however exists, if the HQ is

>1, suggesting the likelihood of contracting non-carcinogenic risk (Sun and Chen, 2018). Based on the foregoing, it will suffice to say that the children population are more likely at risk for non-carcinogenic related complications due to exposure to endulsulfan I. The susceptibility of children to the non-carcinogenic risks compared to the adults couldn't be far from their higher intake rates per unit body weight, unintentional oral ingestion, and slow detoxification processes (Xiao *et al*., 2017; Sun and Chen, 2018). Though the risk of consumption of cabbage, guava, and garden eggs are of relative concern, the results however show a probability of this value increasing to a level of concern following prolonged consumption of the plants. Thus called for an immediate action to tame and restrain the use and application of endosulfan I in the cultivation of food for human consumption.

Table 1: The estimated daily intakes (EDAI), acceptable daily intake (ADI) and hazard quotient (HQ) of endosulfan I residues on consumption.

	EDAI (mg/kg/day)		HQ		ADI (mg/kg/day)
Plants	Adults	Children	Adults	Children	
Cabbage	0.001	0.002	0.11	0.29	
Tomato	0.003	0.009	0.56	1.50	
Garden egg	0.001	0.003	0.20	0.53	0.006
Guava	0.002	0.005	0.30	0.80	
Sweet potato	0.002	0.007	0.41	1.09	

Conclusion:

The findings of the research revealed the continuous application of the banned pesticides by some farmers in Upper Yedzaram Basin. The persistent nature of these pesticide residues in the environment is additional reasons behind the observed concentrations detected in the samples, even after they were seized to be used by the farmers in the study area. The study therefore recommended proactive measures by the authority on prohibiting the sell and use of the legally banned pesticides. Clean up measures of major pesticide contaminated areas such as agricultural areas should be done by the ministry of environment.

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