ECOLOGICAL AND HEALTH RISK ASSESSMENT OF ORGANOCHLORINE RESIDUES IN WATER, SEDIMENT, SOIL AND VEGETABLES IN BARKIN LADI LGA, PLATEAU STATE, NIGERIA

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ABSTRACT

The use of pesticides to curb recent menaces of 'tomato ebola', blights and insects' outbreaks have increased tremendously. This study investigated the levels of some of Organochlorine pesticides (OCPs) residues in the environment and in vegetables from Barkin Ladi Local Government Area (LGA), Plateau State, Nigeria, by GC-MS. b–endosulfan was the only OCP residue detected in water. b–endosulfan and b-BHC detected in Barkin Ladi sediment were below the threshold values. All the concentrations of the OCPs recorded in the soils were far above the World Health Organisation (WHO) and Federal Food, Drug, and Cosmetic Act (FFDCA) limits. The order of the concentrations of different isomers in the vegetables were: BHC: y-BHC>b-BHC>d-BH> a–BHC; DDT: p, p'-DDD> p, p'-DDT>p, p'-DDE; aldrin: dieldrin>aldrin; endosulfan: a–endosulfan>b–endosulfan > endosulfan sulphate; endrin:endrin ketone>endrin>endrin aldehyde. This indicated that y-BHC (lindane) and endosulfan were recently used or very slow in degradation. Health indices for y-BHC, b–endosulfan, endrin and endrin ketone in potato and green pepper exceeded one for both 32.7 kg (children) and 60 kg (adults) categories indicating potential health risk. The cancer ratio indices of b-BHC and γ-BHC, dieldrin, heptachlor and p, p'-DDT as estimated by US-EPA guidelines were above the acceptable risk levels 10E-06 in both children and adults.

Keywords: Ecological, Irrigated Vegetables, Organochlorine Residues, Risk Assessment

INTRODUCTION

Tomatoes (*Lycopersicon esculentum L.*), cabbage (*Brassica oleracea L. var. capatuta),* potatoes (*Solamuntu berosum*) are cultivated through intensive irrigation in Barkin Ladi LGA of Plateau

State, Nigeria and sold to consumers in other states of the federation and even to neighbouring countries. With the favourable weather and support of the government in procuring high yielding crop seedlings and pesticides, irrigation agriculture has received a boost in the locality in recent years. But the recent emergence of “tomato ebola”, cocoa yam, and potato blights and cabbage, green beans and pepper insects’ outbreak in the State had brought serious loses to farmers.

Blights devastated potatoes worth billions of Naira in the State in 2022. The emergence of a pest or disease outbreak constitutes perhaps the most significant threat to farmers across the world, yet it is widely seen as one of the most controllable threats. According to the Food and Agriculture Organisation (FAO), pests present a serious risk to agriculture, with global annual crop production losses falling in the range of 20% to 40% [1]. Thus, in order to meet the food demand of the world, it is essential to use plant protection strategies, based on various approaches including among others, the use of synthetic pesticides [2].

Pesticide is a damage control input to guard against insects and other pests and is considered to improve nutrition in food, has economic gains, labour-saving and efficient tool for pest management [3]. However, the irrational use and abuse of pesticide associated with inadequate irrigation system management contaminate ground water resources, degrade the environment and affect the biotic community negatively, bioaccumulate in food chains, poison food when use in post-harvest storage and contaminate global ecosystems [4-6]. The presence of pesticide residues in food samples may pose a deleterious effect on food safety and consequently compromise the health of consumers especially children, elderly, and pregnant women [7].

Organochlorine pesticides are characterized as persistent in the environment, high lipid solubility, carcinogenic, endocrine disruption in mammals, and causing arthritis, skin disease, developmental abnormalities, reproduction failure, bone and nerve disorders, biomagnificate through the food chain and highly toxic to wide range of animals including humans and other aquatic organisms [8-11]. They are the most prevalent pesticides in the environment, potentially dangerous as pollutants hence; most pest species have become resistant to these insecticides [12]. OCPs that are not even registered for use were also found in food and vegetables [13]. For humans, ingestion is the major pathway for exposure to OCPs [14]. Today, many OCPs have been banned or heavily restricted in most countries in response to public concern and increasing scientific evidence of their adverse effects on living organisms and the environment.

There is little documented information on human health risk of OCP residues from consuming irrigated vegetables in Barkin Ladi, Plateau State, Nigeria. For these reasons, this study aims to investigate pollution levels of OCP residues in water, sediment, soil and the human health risk of consuming five irrigated vegetables from the area. The outcome of the study could be used as guide in making policy towards regulating pesticides usage in irrigation and for the safety of consumers of vegetables in Barkin Ladi LGA.

EXPERIMENTAL

Study Area

Barkin Ladi is a Local Government Area in Plateau State, Nigeria with its headquarters in the town of Barkin Ladi at the latitude 9°32′00″N 8°54′00″E. It has an area of 1,032 km^2 and a population of 175,267 at the 2006 census.

Collection of samples

Soil samples were collected from irrigated areas in Barkin Ladi and in Foron of Barkin Ladi LGA, Plateau State, Nigeria. The agricultural soils were taken in triplicate at three depths (0-10 cm, 11-20 cm and 21-30 cm) using spiral auger of 2.5 cm diameter. The soil samples at each depth were then randomly selected and mixed together to form a composite sample before they were placed in clean labeled plastic bags and transported to the laboratory [15]. Sediments were collected from streams/ponds in the areas where water samples were fetched. Five vegetable samples: tomato (*Lycopersicon esculentum L*), potatoes (*Solamun tuberosum*), green beans (*Phaseolus vulgaris*), green pepper (*Capsicum annuum* L. cv. Lady Bell) and cabbage (*Brassica oleracea* L. Var. Capatuta) were collected from different irrigated farmlands. The samples of each vegetable were collected randomly from ten locations on the irrigated sites after which these samples were combined accordingly to create a composite sample for each vegetable crop species. The samples were sealed in polythene bags, labeled and stored at -4 °C for OCPs analysis [16].

Extraction of OCP residues from water, soil, sediment and vegetables samples

Liquid–liquid extraction method was used for the extraction of pesticide residue according to the procedure described by Akan *et al.* [17]. A 50 ml volume of n-hexane was introduced into a 2 liter separating funnel containing 1 liter of filtered water and was shaken manually for 5 min and allowed to settle. After complete separation, the organic phase was drained into a 250 ml conical flask, while the aqueous phase was re-extracted twice with 50 ml of n-hexane. The three extracted organic phases were combined and dried by passing through a glass funnel containing anhydrous sodium sulfate. The organic fraction was concentrated using rotary evaporator [15].

Pesticide residues from dried soil and sediment samples were extracted according to Akan *et al.* [17]. A 10 g portion of soil and sediment samples was transferred into an extraction thimble that had been previously washed with n-hexane and acetone and oven dried. The sample was extracted using 150 ml of n-hexane/acetone mixture 4:1 v/v for eight hours (8 hr) using soxhlet extractor. The extract was evaporated to dryness using a rotary evaporator at 40 ^{o}C. Each extract was dissolved in 10 ml n-hexane and subjected to clean-up procedure.

The method used for the extraction of the vegetables was the USEPA method 3510 for extracting pesticide residues in non-fatty crops, using ethyl acetate as the solvent. Sodium hydrogen carbonate ($NaHCO_3$) was used to neutralize any acid that may be present and the vegetable samples were washed thoroughly with distilled water. About twenty grams (20 g) of each of the samples was placed in a mortar and anhydrous sodium sulphate (Na_2SO_4) was 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 with the help of a spatula and 40ml of ethyl acetate was added and shaken thoroughly. A 5 g portion of sodium hydrogen carbonate ($NaHCO_3$) was added to the mixture followed by 20 g of anhydrous sodium sulphate (Na_2SO_4) and the entire mixture was shaken vigorously for an 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 area and the mixture was filtered into labeled containers before being centrifuged at a speed of 1800 rpm for 5min. The organic layer was decanted into a container and a 1:1 mixture of 5 ml ethyl acetate and cyclohexane was added [17, 18].

Sample clean-up

Silica gel was activated by heating at 130 °C for 16hr and stored in a desiccator. About 5 g of silica gel was packed in glass column. Exactly 1g of anhydrous Na_2SO_4 was added and the column was conditioned with 20ml n-hexane. Another portion of hexane was poured in the column to elute into a beaker labeled “waste”. The residue of the extraction step of each soil, sediment and vegetable extracts were dissolved in 2 ml of hexane from the top of the column. Sample vial was rinsed with additional hexane to complete quantitative transfer. Another 10 ml of n-hexane was added to the column and elute to waste. 10 ml of (1+1) DCM + hexane were added before the column head dries out, and the eluent collected. The eluent concentrated to approximately 2ml for analysis [15 – 18].

GC-MS determination of organochlorine pesticides (OCPs) residues

OCPs standard, 2000ppm (Catalog Number: M-8080) containing 18 OCPs components was purchased from AccuStandard by CTX- ION ANALYTICS Lagos. Five (5) point serial dilution calibration standards (0.10, 1.00, 5.00, 10.00, 100.00 ppm) were prepared from the stock and used to calibrate the GC-MS. Prior to calibration, the MS was auto-tuned to perfluorotributylamine (PFTBA) using already established criteria to check the abundance of *m/z* 69, 219, 502 and other instrument optimal and sensitivity conditions. Determination of the levels of OCPs in the sample was carried out using GC-MS by operating MSD in selective ion monitoring (SIM) and scan mode to ensure low level detection of the target constituents. Agilent 6890A gas chromatograph coupled to 5973C inert mass spectrometer (with triple axis detector) with electron-impact source was used. The capillary column used was HP-5MS (30.0 m × 0.25 mm × 0.25 μm). The carrier gas was helium at a flow rate of 1.2 mL/min at an initial nominal pressure of 026 psi and average velocity of 40.00 cm/sec. The injector was set at 250 °C. The oven temperature was programmed as follows: initially at 50 °C (equilibrium time 1.2mL/min).Exactly 1µL of the samples were injected in splitless mode at an injection temperature of 250 °C. Purge flow to spilt vent was 30.0 mL/min at 0.35 min with a total flow of 31.24 mL/min; gas saver mode was switched off. Oven was initially programmed at 50 °C (1 min) then ramped at 25 °C/min to 100 °C (3 min) and 5 °C/min to 300 °C (5 min). Run time was 51 min with a 3 min solvent delay. The mass spectrometer was operated in electron-impact ionization mode at 70eV with ion source temperature of 230 °C, quadrupole temperature of 150 °C and transfer line temperature of 300 °C. Acquisition of ion was via scan mode (scanning from *m/z* 50 to 500 amu at 2.0s/scan rate) and selective ion mode (SIM).After calibration, the samples were analyzed and corresponding OCPs concentration obtained [5, 17].

Health risk calculation of pesticide residues in water and sediment

The risk quotient (RQ) for each pesticide in water was calculated as the ratio between the measured environmental concentration and the predicted no effect concentration (MEC/PNEC)[19]. Many different sediment quality guidelines (SQGs) have been developed. The two levels of sediment quality guidelines used in the study are: the threshold effects level (TEL) and probable effects level (PEL). These two assessment values delineated three ranges of chemical concentrations as: rarely (minimal effect range; concentrations equal to and below the TEL), occasionally (possible effect range; concentrations above the TEL, but below the PEL), and frequently (probable effect range; concentrations equal to and above the PEL) associated with adverse biological effects [20].

Estimated daily intake of metals (EDIM, mg kg-1 day) of vegetables

The estimated or average daily dose (ADD) vegetable intake rate will be calculated by,

$$\text{EDIM} = \frac{CXIRXCf}{BW}$$

Where

C = Contaminant concentration in vegetable (mg kg-1); IR = Ingestion rate per unit time or event (kg day^{-1}); Cf= conversion factor; BW = Body weight.

The average body weight (BW) of 60 kg and 32.7 kg adult and child and the average daily intake for adults and children were set to 0.345 and 0.232 kg $person^{-1}day^{-1}$ (expressed as fresh weight) respectively,

Hazardous quotient (HQ)

Hazardous Quotient (HQ) for the locals (consumers) through the consumption of contaminated vegetables was assessed by:

$$\text{HQ} = \frac{EDIM}{RfDO}$$

Where, RfDo is the oral reference dose [21].

Hazard index (HI)

An exposure to more than one pollutant results in additive effects and is express as an arithmetic sum of the hazard quotients for each pollutant as shown. HI = ∑HQ [22, 23].

Carcinogenic risk and ingestion cancer slope factors (CSF_{ing})

The carcinogenic risk is expressed as:

$$CR = EDIM \times CSF_{ing}$$

$$TCR = \sum EDIM \times CSF_{ing}$$

Where CSF_{ing} is the cancer slope factor[24, 25]

TCR = Total cancer risk for multi contaminants

RESULTS AND DISCUSSION

The concentrations of OCP residues are presented in Table 1.

Table 1: Concentrations of OCPs residues (µg/kg) in water, sediment and soils with depth

Organochlorine residues	BLDW	BLDFW	BLDS	BLD1	BLD2	BLD3	BLDF1	BLDF2	BLDF3	WH0 MRL	∑OCP
a-BHC	ND	ND	ND	ND	ND	ND	104	64	ND	10	168
b-BHC	ND	ND	4	ND	16	8	40	48	ND	10	116
y-BHC	ND	ND	ND	ND	8	ND	80	80	860	10	1028
d-BHC	ND	ND	ND	ND	ND	16	148	4	ND	10	168
Heptachlor	ND	ND	ND	ND	ND	ND	64	52	8	10	124
Aldrin	ND	ND	ND	ND	ND	ND	44	4	12	10	60
Hept. epoxide	ND	ND	ND	ND	ND	ND	64	40	ND	10	104
a -Endosulfan	ND	ND	ND	ND	ND	ND	ND	ND	8	10	8
Dieldrin	ND	ND	ND	ND	ND	ND	ND	ND	12	10	12
p,p'-DDE	ND	ND	ND	ND	ND	ND	ND	ND	8	50	8
Endrin	ND	ND	ND	ND	ND	ND	ND	ND	104	10	104
b Endosulfan	36	20	16	24	ND	ND	124	4	32	10	256
p,p'-DDD	ND	ND	ND	156	28	ND	ND	ND	4	50	188
Endrin Aldehyde	ND	ND	208	ND	ND	ND	ND	ND	12	10	220
p,p'-DDT	ND	ND	ND	96	ND	ND	156	48	4	50	304
Endosulfan Sulfate	ND	ND	ND	ND	164	ND	60	52	4	50	280
Endrin ketone	ND	ND	ND	ND	ND	ND	ND	ND	192	10	192
Methoxychlor	ND	ND	ND	ND	ND	ND	56	52	4	10	112
∑ OCP (Location)	36	20	228	276	216	24	940	448	1264		

Key: BLD = BarkinLadi, BLDF = Foron, W= Water, S = Sediment, Subscripts 1 = 0 -10cm, 2 = 11 -20cm, 3 = 21 – 30, ND = Not detected predicted no effect concentration (PNEC) b – endosulfan = 0.028 [19] b – endosulfan was the only OCP detected in water of the two areas. The results agreed with a work reported by Onwona-Kwakye *et al*. [26] that organochlorine pesticide levels in water samples collected from a prominent vegetable-farming area in Ghana, showed that endosulfan sulfate was the most frequently (78%) occurring pesticide detected. Risk quotient (RQ) for b – endosulfan residues in water were greater than one for both areas showed that they are likely to cause adverse effect to biota.

b – endosulfan and b-BHC were detected in Barkin Ladi sediment. None of the OCP compounds detected in the sediment exceeded the threshold effects level (TEL) as well as probable effects level (PEL), meaning that their biological risk was negligible under the sediment quality guidelines [6].

The ranges of the levels of the pesticides at different soil depths were; 0-10cm, from ND to 156µg/g for both areas; 11 – 20, ND – 164 and ND to 80µg/kg for BLD2 and BLDF2 respectively and 21 – 30, ND – 8 and ND to 860 µg/kg for BLD3 and BLDF3 respectively. The highest level OCP residues recorded in this study was y- BHC (860µg/g) which was observed at depth of 21 - 30 at BLDF3 while the lowest concentrations were below the detection limits of the machine observed at different depths with different OCPs. The compositions of OCPs detected varied significantly with the OCPs and with the agricultural areas at $p<0.05$. The very high concentration of y – BHC at 21 – 30 cm could be due to the pesticide spillage at points of sampling or the spot where the empty containers had been dumped and could have seeped down to the level. All the concentrations of the OCPs detected were far above the WHO and FFDCA limits. According to Jorfi *et al*. [27], OCPs are strongly retained by soil due to their insolubility in water and they can be decomposed by environmental factors into metabolites which are more toxic compounds.

Vegetables are produced so much in these areas and their production could have led to the tremendous impacts upon the farms and the environment due to the excessive use of agrochemicals without regards to the local environmental conditions or according to the directives. These could have also led to the significant effects on the accumulation of agrochemical metabolites in soils and absorption by crops grown on such soil. It has been reported that anthropogenic activities aimed at enhancing food production, enormous economic development and rapid growth in many fields such as agriculture and industry could facilitate the accumulation of undesirable substances in plants and affect the qualities of both soil and water resources adversely [4, 28].

The rampant and uncontrolled use of pesticides in agriculture in most parts of developing countries could be attributed to poverty, poor policy governing agriculture and land use as well as the low level of awareness on sustainable land use, agriculture and environmental management. The decreasing order of the pesticide was; y-BHC>p, p'-DDT>endosulfan sulphate>b-endosulfan >endrin aldehyde>endrin ketone and according to sample; BLDF3>BLDF1>BLDF2>BLD1>BLDS>BLD2>BLDW>BLD1>BLDFW.

Hexachlorobenzene (BHC) is a fungicide that was widely used as a seed protection in Nigeria. The uses of hexachlorobenzenes are banned in many countries including Nigeria [29] but are still in use by farmers. Application and time of sampling both have higher probability of detecting these herbicide residues in vegetable samples. However, high concentrations of these herbicides in the vegetables indicated their inappropriate application as the most probable source of contamination.

Table 2: Concentrations of OCP residues (µg/kg) detected in vegetables from irrigated sites

Pesticide residue	BLDT	BLDFT	BLDP	BLDFP	BLDGB	BLDFGB	BLDGP	BLDFGP	BLDCa	BLDFCa	Total	*MRL	**MLR	*ADI
a-BHC	ND	ND	4	ND	ND	ND	ND	ND	ND	56	60	10	0.02	3
b-BHC	8	ND	12	4	40	8	ND	4	ND	80	156	10	0.02	3
y-BHC	ND	ND	1204	ND	ND	ND	ND	ND	ND	704	1908	10	0.02	3
d-BHC	ND	ND	28	24	ND	ND	20	24	ND	12	108	10	0.02	3
Heptachlor	ND	ND	28	16	ND	ND	ND	16	ND	40	100	10	0.01	0.1
Aldrin	ND	ND	24	ND	ND	ND	ND	ND	ND	8	32	10	0.01	0.2
Hept. epoxide	ND	ND	ND	ND	ND	ND	ND	ND	ND	24	24	10	0.01	0.1
a -Endosulfan	ND	ND	ND	3044	ND	ND	ND	3044	ND	40	6128	10	0.02	6
Dieldrin	ND	ND	92	ND	ND	ND	ND	ND	ND	68	160	10	0.01	0.2
p,p'-DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	64	64	50	0.02	20
Endrin	ND	ND	24	ND	ND	ND	ND	ND	ND	192	216	10	0.01	0.2
b Endosulfan	16	ND	16	48	60	20	24	48	32	68	332	10	0.02	6
p,p'-DDD	ND	ND	4	ND	ND	ND	104	ND	ND	12	120	50	0.02	20
Endrin Aldehyde	ND	ND	48	ND	ND	ND	84	ND	ND	88	220	10	1	0.2
p,p'-DDT	ND	ND	12	ND	ND	ND	72	ND	ND	4	88	50	0.02	20
Endosulfan Sulfate	ND	ND	8	ND	ND	ND	ND	ND	ND	28	36	10	0.02	6
Endrin ketone	ND	24	296	ND	ND	ND	ND	ND	ND	412	732	10	0.01	0.2
Methoxychlor	ND	ND	8	ND	ND	ND	24	ND	ND	56	88	10	0.02	5
Total	24	24	1808	3136	100	28	328	3136	32	1956				

*Vincent *etal*., (2018[30]), **Federal Food, Drug and Cosmetic Act (FFDCA, [31]

Key: BLD = BarkinLadi, BLDF = Foron, T = Tomato, P = Potato, GB =Green beans, GP =Green pepper and Ca = cabbage

Table 3: EDI estimations for OCP residues detected for Adult and Children in irrigated vegetables

	EDI Adults										EDI Children									
	BLDT	BLDFT	BLDP	BLDFP	BLDGB	BLDFGB	BLDGP	BLDFGP	BLDCa	BLDFCa	BLDT	BLDFT	BLDP	BLDFP	BLDGB	BLDFGB	BLDGP	BLDFGP	BLDCa	BLDFCa
a-BHC	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.32	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.30
b-BHC	0.05	0.00	0.07	0.02	0.23	0.05	0.00	0.02	0.00	0.46	0.04	0.00	0.06	0.02	0.21	0.04	0.00	0.02	0.00	0.42
y-BHC	0.00	0.00	6.92	0.00	0.00	0.00	0.00	0.00	0.00	4.05	0.00	0.00	6.37	0.00	0.00	0.00	0.00	0.00	0.00	3.72
d-BHC	0.00	0.00	0.16	0.14	0.00	0.00	0.12	0.14	0.00	0.07	0.00	0.00	0.15	0.13	0.00	0.00	0.11	0.13	0.00	0.06
Heptachlor	0.00	0.00	0.16	0.09	0.00	0.00	0.00	0.09	0.00	0.23	0.00	0.00	0.15	0.08	0.00	0.00	0.00	0.08	0.00	0.21
Aldrin	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.04
Hept. epoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.13
a -Endosulfan	0.00	0.00	0.00	17.50	0.00	0.00	0.00	17.50	0.00	0.23	0.00	0.00	0.00	16.10	0.00	0.00	0.00	0.00	0.00	0.21
Dieldrin	0.00	0.00	0.53	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.36
p,p'-DDE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.34
Endrin	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.00	0.00	1.10	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.00	1.02
b Endosulfan	0.09	0.00	0.09	0.28	0.35	0.12	0.14	0.28	0.18	0.39	0.08	0.00	0.08	0.25	0.32	0.11	0.13	0.25	0.17	0.36
p,p'-DDD	0.00	0.00	0.02	0.00	0.00	0.00	0.60	0.00	0.00	0.07	0.00	0.00	0.02	0.00	0.00	0.00	0.55	0.00	0.00	0.06
Endrin Aldehyde	0.00	0.00	0.28	0.00	0.00	0.00	0.48	0.00	0.00	0.51	0.00	0.00	0.25	0.00	0.00	0.00	0.44	0.00	0.00	0.47
p,p'-DDT	0.00	0.00	0.07	0.00	0.00	0.00	0.41	0.00	0.00	0.02	0.00	0.00	0.06	0.00	0.00	0.00	0.38	0.00	0.00	0.02
Endosulfan Sulfate	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.15
Endrin ketone	0.00	0.14	1.70	0.00	0.00	0.00	0.00	0.00	0.00	2.37	0.00	0.13	1.57	0.00	0.00	0.00	0.00	0.00	0.00	2.18
Methoxychlor	0.00	0.00	0.05	0.00	0.00	0.00	0.14	0.00	0.00	0.32	0.00	0.00	0.04	0.00	0.00	0.00	0.13	0.00	0.00	0.30

BLD = BarkinLadi, BLDF = Foron, T = Tomato, P = Potato, GB =Green beans, GP =Green pepper and Ca = cabbage, Adults DIR = 0.345 kg person-1 day, Children = 0.173, Adults Weight 60kg, children 32.7kg

Table 4: Hazard quotient of OCPs in five vegetables from BarkinLadi and Foron Districts

Health Index for Adults											Health Index for Children									
Pesticide residue	**BLD T**	**BLDF T**	**BLD P**	**BLDF P**	**BLDG B**	**BLDFG B**	**BLDG P**	**BLDFG P**	**BLDC a**	**BLDFC a**	**BLD T C**	**BLDF T C**	**BLD P**	**BLDF P**	**BLDG B**	**BLDFG B**	**BLDG P**	**BLDFG P**	**BLDC a**	**BLDFC a**
a-BHC	0	0	0.01	0	0	0	0	0	0	0.11	0	0	0.01	0	0	0	0	0	0	0.1
b-BHC	0.02	0	0.02	0.01	0.08	0.02	0	0.01	0	0.15	0.01	0	0.02	0.01	0.07	0.01	0	0.01	0	0.14
y-BHC	0	0	2.31	0	0	0	0	0	0	1.35	0	0	2.12	0	0	0	0	0	0	1.24
d-BHC	0	0	0.05	0.05	0	0	0.04	0.05	0	0.02	0	0	0.05	0.04	0	0	0.04	0.04	0	0.02
Heptachlor	0	0	1.6	0.9	0	0	0	0.9	0	2.3	0	0	1.5	0.8	0	0	0	0.8	0	2.1
Aldrin	0	0	0.7	0	0	0	0	0	0	0.25	0	0	0.65	0	0	0	0	0	0	0.2
Hept. epoxide	0	0	0	0	0	0	0	0	0	1.4	0	0	0	0	0	0	0	0	0	1.3
a - Endosulfan	0	0	0	2.92	0	0	0	2.92	0	0.04	0	0	0	2.68	0	0	0	0	0	0.04
Dieldrin	0	0	2.65	0	0	0	0	0	0	1.95	0	0	2.45	0	0	0	0	0	0	1.8
p,p'-DDE	0	0	0	0	0	0	0	0	0	0.02	0	0	0	0	0	0	0	0	0	0.02
Endrin	0	0	0.7	0	0	0	0	0	0	5.5	0	0	0.65	0	0	0	0	0	0	5.1
b Endosulfan	0.02	0	0.02	0.05	0.06	0.02	0.02	0.05	0.03	0.07	0.01	0	0.01	0.04	0.05	0.02	0.02	0.04	0.03	0.06
p,p'-DDD	0	0	0	0	0	0	0.03	0	0	0	0	0	0	0	0	0	0.03	0	0	0
Endrin Aldehyde	0	0	1.4	0	0	0	2.4	0	0	2.55	0	0	1.25	0	0	0	2.2	0	0	2.35
p,p'-DDT	0	0	0	0	0	0	0.02	0	0	0	0	0	0	0	0	0	0.02	0	0	0
Endosulfan Sulfate	0	0	0.01	0	0	0	0	0	0	0.03	0	0	0.01	0	0	0	0	0	0	0.03
Endrin ketone	0	0.7	8.5	0	0	0	0	0	0	11.85	0	0.65	7.85	0	0	0	0	0	0	10.9
Methoxychlor	0	0	0.01	0	0	0	0.03	0	0	0.06	0	0	0.01	0	0	0	0.03	0	0	0.06

BLD =BarkinLadi, BLDF = Foron, T = Tomato, P = Potato, GB =Green beans, GP =Green pepper and Ca = cabbage

The levels of OCP residues in vegetables are displayed in Table 2. The- BHC was detected only in BLDP and BLDFCa with concentrations of 4 and 56 µg/kg respectively; b – BHC was detected in almost all the samples with levels ranging from 4 – 80µg/kg except in BLDT, BLDFGP and BLDFCa. y – BHC presented the highest levels among the BHCs with concentration ranges from ND – 1204 µg/kg. The presence of y – BHC(lindane) in the samples may suggest the historical use or illegal use of technical BHC mixtures in the study area, since technical lindane have been officially discontinued as restricted chemical since 2002 [26].d – BHC had concentration ranging from ND – 28 µg/kg. The frequencies of OCP in this work are lower than that obtained in the work of Sulaiman *et al*. [33] but their lindane values obtained were lower than in this work. Hept. epoxide was only detected in BLDCa (24 µg/kg).

The levels of heptachlor were from 4 – 16 µg/kg. The concentrations of aldrin and dieldrin in vegetables samples were from ND – 24 µg/kg and ND – 92 µg/kg with the highest residues in BLDP. a- endosulfan, b – endosulfan and endosulfan sulphate presented residue levels of ND – 3044 µg/kg, ND – 68 µg/kg and ND -28 µg/kg respectively with b–endosulfan having higher frequency of occurrences in the study. The concentrations of a-endosulfan were higher than b-endosulfan in BLDFP and BLDFGP samples. This suggests recent inputs of fresh technical endosulfan or lack of significant degradation of the pesticide [34]. Endrin, endrin aldehyde, and endrin ketone presented the concentration ranges of ND – 192 µg/kg, ND– 88 µg/kg and ND–412 µg/kg respectively.

The levels of DDD, DDE and DDT in the vegetable samples were from ND-104 µg/kg, ND – 64 µg/kg, ND–72µg/kg in that order indicating aerobic, anaerobic and the likelihood of fresh application of the banned pesticides. Methoxychlor presented values from ND–56µg/kg. Most of the levels of organochlorine detected in the vegetables were above the WHO and the FFCDA limits. This could be due to unawareness and misuse of the use of OCPs pesticides in Nigeria especially at pre – harvest and during transport [33, 35].

Estimated Daily Intake (EDI) for y-BHC, b–endosulfan, endrin and endrin ketone (Table 3) in potato and green pepper from both Barkin Ladi and Foron exceeded the ADI for 32.7 kg (children) and the ADI for 60 kg (adults) categories. Conclusively, all pesticides with EDI higher than ADI had their HI (Table 4) far greater than 1 (>1) which indicated very high potential health risk through consumption. Hence, the results obtained from this study revealed potential health risk for the consumption of the five vegetables by the farmers for life time. Sosan et al. [36] in their work reported significant contamination in maize-based complimentary breakfast food products in Nigeria and their results also indicated the possibility of both systemic and cancer risks to infants and children that are consumers of the foods. However, the little or no data on pesticide's related poison on the population especially Nigerian workers in all agro-allied fields in Nigeria makes it difficult to ascertain the exact effects on human health in the country [35]. Effort should therefore be put towards establishing appropriate medical surveillance and record keeping of victims of pesticides affliction in Nigeria.

The combined health risks estimated for OCP residues in adults and children for the consumption of vegetables is shown in Figure 1 below. The combined health indices of less than 1 were obtained for adults and children for the consumption of tomato and green beans from BLD and BLDF. The hazard indices much greater than 1 were obtained for adults and children for the consumption of potato, green pepper and cabbage from the two areas with cabbage from Foron and potato Barkin Ladi having the highest concentrations. This could reduce the exportation of the farm produce. The use of pesticides varies from one country to another due to the objectives and the national needs of the country. Therefore, it is very important to consider the levels of pesticides of the farm produce to be exported which will be subjected to the rules and regulations of the importer country [37].

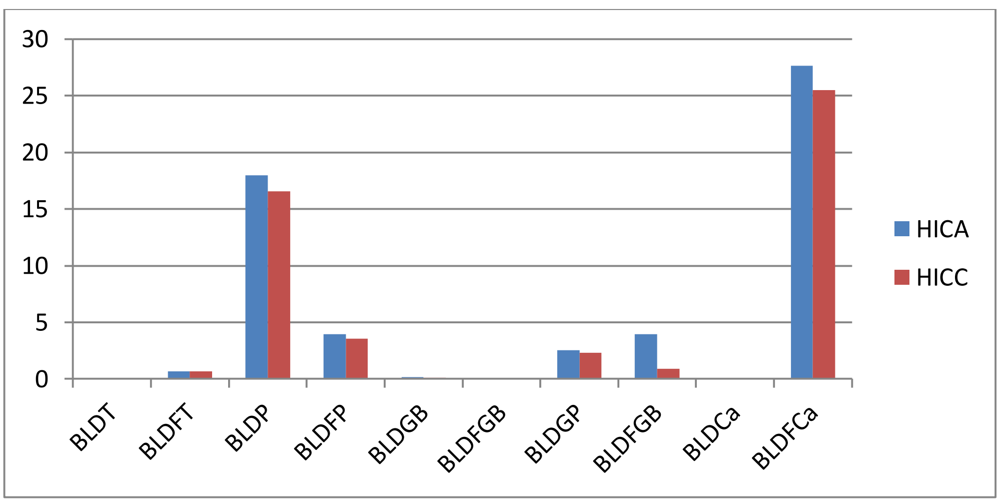

Figure 1: The combined Health indices of the samples for adults and children

The non-carcinogenic health risks obtained in study for children and adult were comparable with values obtained by Mazlan et al., [35]. Aldrin, dieldrin, endrin, heptachlor, hexachlorobenzeneare persistent organic pollutants (POPs) which resist degradation and thus remain in the environment for years. Some POPs have the ability to volatilize and travel great distances through the atmosphere to become deposited in remote regions. Such chemicals may have the ability to bioaccumulate and biomagnify and can bioconcentrate up to 70,000 times their original concentrations [38]. These can affect non-target organisms in the environment and increase risk to humans by disruption in the endocrine, reproductive, and immune systems. Other plant (branching habit, plant surface, plant species and varieties, plant maturity or age of the plant) as well as environmental (temperature and humidity, rain fall, wind, light) factors also influenced pesticides distribution in crops [31, 38]. Thorough washing of vegetables and cooking could help eliminate some of these residues [38, 40]. Mazlan *et al*. [35] reported higher levels of endosulfan (240-650 µg/m^3) and hexachlorobenzene from 120 to 2890 µg/m^3 (mean 790 µg/m^3) in the country. Much concerns have been raised about risks of pesticide residues in food as most pesticides show a high degree of toxicity. The European Union placed a ban on some agricultural commodities for some times now. Food items banned from Europe since June 2016 included beans, sesame seeds, melon seeds, dried fish and meat, peanut chips and palm oil. According to Onuwa*et al*., [38], the European Food Safety Authority prohibited Nigerian's beans because they were found to have concentration of dichlorvos ranging from 0.03 to 4.6 mg/kg whereas the acceptable maximum residue limit is 0.01mg/kg. Also, Mazlan *et al*. [36] reported that a total of 112 people in Bekwarra LGA of Cross River State, Nigeria, suffered from food poisoning and the deaths of two children due to ingestion of moi-moi and beans. According to the report, the moi-moi and beans from the homes of the victims and from open markets in Tarawa and Benue states in Nigeria were tested and revealed outrageously high levels of organophosphates, carbonates, fenithrothion, and chloropyrifos that are highly toxic pesticides. Another report has it that, over 120 students of Government Girls Secondary School, Doma, Gombe consuming a meal of beans suspected to have contained outrageously high levels of Lindane, an organochlorinated pesticide commonly called Gammallin [40].

Table 5: Carcinogenic risk of OCPs residues in vegetable for 45year Adult (Average weight of 60kg) and 15 year teenager(Average weight of 32.5kg)

	Carcinogenic risk of OCPs residues in vegetable for 45year Adult										Carcinogenic risk of OCPs residues in vegetable for 15year Teenager									
Pesticide residues	BLDT	BLDFT	BLDP	BLDFP	BLDGB	BLDFGB	BLDGP	BLDFGP	BLDCa	BLDFCa	BLDT	BLDFT	BLDP	BLDFP	BLDGB	BLDFGB	BLDGP	BLDFGP	BLDCa	BLDFCa
b-BHC	5.32E-05	ND	7.98E-05	2.66E-05	2.66E-04	5.32E-05	-	2.66E-05	-	5.32E-04	9.58E-05	-	1.44E-04	4.79E-05	4.79E-04	9.58E-05	-	4.79E-05	-	9.58E-05
y-BHC	-	-	5.79E-03	-	-	-	-	-	-	3.38E-03	-	-	7.52E-03	-	-	-	-	-	-	4.40E-03
Heptachlor	-	-	4.66E-04	2.66E-04	-	-	-	2.66E-04	-	6.65E-04	-	-	2.10E-03	1.20E-03	-	-	-	-	-	2.99E-03
Aldrin	-	-	1.51E-03	-	-	-	-	-	-	5.03E-04	-	-	2.56E-02	-	-	-	-	-	-	8.55E-03
Dieldrin	-	-	5.44E-04	-	-	-	-	-	-	4.02E-04	-	-	8.71E-04	-	-	-	-	-	-	6.43E-04
p,p'-DDE	-	-	-	-	-	-	-	-	-	8.04E-05	-	-	-	-	-	-	-	-	-	2.73E-05
p,p'-DDT	-	-	1.51E-05	-	-	-	9.05E-05	-	-	5.03E-06	-	-	5.13E-06	-	-	-	3.08E-05			1.71E-06
Total	5.32E-05	0.00E+00	8.40E-03	2.93E-04	2.66E-04	5.32E-05	9.05E-05	2.93E-04	0.00E+00	5.57E-03	9.58E-05	0.00E+00	3.62E-02	1.25E-03	4.79E-04	9.58E-05	3.08E-05	4.79E-05	0.00E+00	1.67E-02

The cancer risk values of the pesticide residues detected in the vegetables in the two areas (Table 5) showed that there is possibility for adversely contracting cancer for both the 15yr (32.7 kg) teenager and 45yr (60 kg) adult consumers of the vegetable via dietary exposure to these detected pesticides. b-BHC and γ- BHC (could cause Hepatic nodules and hepatocellular carcinomas), dieldrin (could cause Liver carcinoma), heptachlor could cause (Hepatocellular carcinomas), p,p'-DDE (Hepatocellular carcinomas, hepatomas) and p,p'-DDT (Liver tumours, benign and malignant) detected in all the vegetable were above the acceptable risk levels of 1 in 1 million people with higher risks on the younger [35]. The effects on younger (15yrs) to these pesticides are due to their high vegetable intake to body weight ratio, and immaturity of their defense systems against toxic chemicals [41]. Children younger than 15 and aged people may have immaturity of their defense and weaker immune system respectively which could be more susceptible to these OCP residues [8]. The order of contracting cancer according to the vegetables is Cabbage>Potato>Green beans>tomato>Green pepper and according to OCP residues is aldrin> y – BHC>dieldrin> b – BHC> heptachlor>p,p'-DDT>p,p'-DDE

CONCLUSION

OCP compounds are still detected in Barkin Ladi and Foron Districts of Plateau State, Nigeria. BHCs were the most abundant OCP compounds. The highest level OCP residues recorded in this study was y- BHC (860µg/g) which was observed at depth of 21 - 30 at BLDF3 while the lowest concentrations were below the detection limits of the machine observed at different depths with different OCPs. y – BHC presented the highest levels in the vegetables among the BHCs with concentration range from ND – 1204µg/kg. Most of the levels of organochlorine detected in the vegetables were above the WHO and the FFCDA limits. The combined health indices of less than 1 were obtained for adults and children for the consumption of tomato and green beans from BLD and BLDF but much greater than 1 were obtained for adults and children for the consumption of potato, green pepper and cabbage from the two areas with cabbage from Foron and potato Barkin Ladi having the highest concentrations in that order. Also, there are probabilities of contracting different types of cancers due to residues having cancer risk indices above the permissive limit.

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