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Assessment of hazard index of organochlorine pesticide residues in soil and fresh tomatoes from selected farmlands in Gusau, Zamfara state, Nigeria

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Abstract

In this research, organochlorine pesticide (OCP) residues in soil and fresh tomatoes samples from selected farmlands in Gusau, Zamfara State, Nigeria were studied. QuEChERS and GC-MS were used for sample preparation and analysis, respectively. The results obtained shows the presence of OCPs residues namely; α- lindane, endosulfan I, isodrin, heptachlor, DDMU, and dieldrin with concentration of 1.669 mg/kg, 1.183 mg/kg, 0.129 mg/kg, 0.032 mg/kg, 0.0067 mg/kg, 0.037 mg/kg, in fresh sample A, α-lindane, endosulfan I, and isodrin were above the maximum residual limits (MRLs) in the fresh samples, while δ- pent, α-lindane, β-lindane, endosulfan I and II, isodrin, dieldrine, and DDMU were detected in fresh sample B, with concentration of 0.012 mg/kg, 2.77 mg/kg, 0.010 mg/kg, 0.171 mg/kg,0.005 mg/kg, 0.129 mg/kg, 0.078 mg/kg, 0.273 mg/kg and 0.007 mg/kg, respectively. Concentration of α lindane, endosulfan I, and isodrin were above MRL in fresh samples B. α-lindane, β-lindane, endosulfan I and II, Isodrin, and DDMU were detected in fresh samples C with concentration of 2.160 mg/kg, 0.008 mg/kg, 0.168 mg/kg, 0.007 mg/kg, 0.187 mg/kg, and 0.031 mg/kg, respectively. α-lindan, Endosulfan I, isodrin and DDMU were above MRLs in fresh sample C. And beta lindane, DDMU, and heptachlor were detected in soil samples, α-lindan, isodrin, endosulfan I, and beta lindane were above MRL accepted in the environment except DDMU and dieldrin which are below MRL. On the other hand α lindane and heptachlor has hazard index of 2.737 and 1.012 respectively. Therefore,α lindane and heptachlor pose a potential health risk since the hazard index is equal and greater than 1.

Keywords: Organochlorine, Pesticide, Soil, Tomatoes, GS-MS

Introduction

Tomatoes are consumed raw in salads and also use to make juices. It is rich in essential nutrients such as vitamins, protein and minerals. It has high moisture content which makes it susceptible to pest and disease that result to loss of over 40-50% tomatoes annually during planting and post harvest season [12].

Tomato farmers use pesticides to combat pest and disease in order to obtain good and fresh tomatoes for consumption. Farmers may want to protect their crops from pests and diseases, therefore, they use this organochlorine pesticide indiscriminately in order to see their crops free and save from pest. The indiscriminate used of this pesticide leave harmful residues on the crops. Farmers consider organochlorine pesticides as most effective for pest and disease eradication and also their availability and low cost [48].

Mode of application of these chemicals to the vegetables increase residual deposits [3]. Some can stick to the soil, which the plant can pick up while some can wash into the soil by rain fall or volatilization by sun rays. Pesticides applied to the shoot of plants can moved down the circular layer through the lipoid and aqueous pathways [46].

Consumers such as children and adult are at immense risk of exposure to the residues of organochlorine pesticides deposited after used to control pests. Because of toxic nature of this chemical, they are banned or restricted in Nigeria and other countries [52]. Despite the positive impact of pesticide to increase the food production globally, pesticide residues contribute to food safety problem because of their potential harmful effects to humans and its environment. Many health problems associated with pesticide residues are reproductive disorder, cancer and endocrine disruption and respiratory disorder [52]

In Nigeria, the following organochlorine pesticides are ban, dichlorodiphenyltrichloroethane (DDT), aldrin, dieldrin, lindane, isodrin, heptachlor and endosulfan because of concerns on the human health and environment [44]. Several research shows that despite the ban on most of the organochlorine compounds, they are still been used in developing countries like Nigeria for pest control [48]. Poor education on the use of pesticide leads to wide spread of abuse in Nigeria [17]. Major processes of pesticide abuse include mixing of different classes of pesticides during spraying. Incorrect use of the nozzle for spraying, which makes it difficult to obtain the desired amount of the pesticide, and ignorance about the time of application, including incorrect formulation, are always causes of abuse [48].

Absorption of Organochlorine Pesticide Residues from Soil by the Target Plant

Soils in general have high affinity for organochlorine pesticides which might be taken up by crops, and grazing animals which in turn find their way into the human food chain. They can also wash into the river by drainage or emit into the atmosphere by volatilization, leading to atmospheric contamination [20], [21]. The retention and mobility of pesticides in soil is always depending on the strength of sorption reactions and the physiochemical properties of the soil such as organic component of the soil, the soil type which include clay, sand and pH of the soils [28].

Tomatoes assessments with regard to the content of toxic compounds such as pesticide residues are very important for correct information [57]. Determination of the banned toxic organochlorine pesticides residues level in Agricultural produces and soil farmland would provide information for regulatory agencies for strict control measures on the enforcement of the ban.

Materials and Methods

Chemicals/Reagents

The chemicals and reagents used in this research are of analytical grade. All the chemicals and solvents were purchased and used without any further purification.

Instruments

Centrifuge (30000Rpm, model number: AM-10607) and Gas Chromatograph couple with mass spectrometer Detector (GC-MS) (model 7890 Agilent technologies), weigh Balance (Electronic, model: ES225SM-DR), Oven (model: E028-280v), pH meter (Beckman model 72) , Thermometer, Platinum crucible, Petri Dish, Whitman No1 Filter paper, Disccicator, Precision Hydrometer.

Sample Collection

Samples of tomatoes and soil were collected from three major tomatoes farm lands in Wanke, Gusau, and Zamfara State. The three farmlands were in Unguwa Mallam Bawa. Wamke is located on the west region of Gusau in Zamfara State. Each sample were randomly collected from the farms into cleaned polythene bag and labeled. Total of six fresh samples were collected including three soil samples from each farm land.

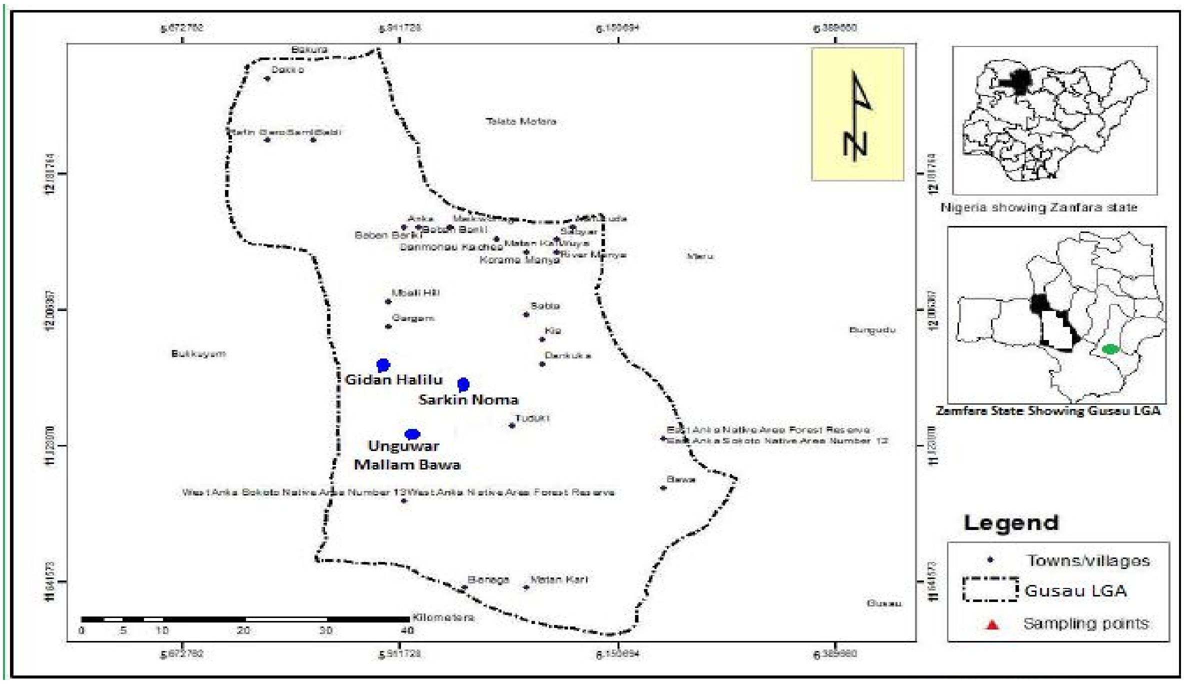

Figure 1 Map of samples collection sites.

Determination of Soil pH

The soil pH was determined using pH meter (Beckman model 72). 5g sample of the soil was weighed into a cleaned conical flask and 20 cm^3 of distilled water was added and shake vigorously for 30 minutes. Calibrated glass electrode was dipped into the solution and reading was taken [10].

Determination of the % Sand, Clay and Silt

The soil was air dried and sieved to remove coarse particles. Fifty grams (50g) of dried sieved soil samples were weighed and added 100 cm^3 of 25% sodium hexametaphosphate and shake for 16 hours using an electric shaker. The mixture was then placed in a bouyance blender cup and stirred for two minutes; the contents of the cup was placed in a 2000 cm^3 sedimentation cylinder and filled with dieionzed water. The suspended solid was measured with a hydrometer after 40 seconds of decantation. The first reading was estimated to be soil content, second as clay content while silt was calculated as the difference between the sum of sand and clay content [10].

Determination of Soil Organic Matter

Loss of ignition method as described in AOAC, [11] was used for the determination of soil organic matter. Ten grams (10g) of dried soil samples were weighed into crucible and ignited at 550^{o}C for 2 to 4 hours in muffle furnace until constant mass was achieved. Soil organic matter content was then calculated by difference before and after the ignition, using the equation below;

LOI is corresponding to the soil organic matter content: $$\text{LOI \%} = \frac{DM}{Ms} \times 100 \qquad (3.7)$$

Where; DM is loss of mass of the soil after ignition (g), Ms is mass of the soil dried at 105^{o}C and LOI is Loss of ignition [10].

Determination of Organochlorine Pesticides

The Quick, Easy, Cheap, Effective, Rugged and Safe (QuEchERS) method was based on a salting-out extraction with solvent mainly actonitrile and dispersive solid phase extraction. This method is very flexible, modifiable and has a growing popularity. This method was adopted by US Department of Agriculture for pesticide analysis for food and food product [11].

Extraction Procedure

Fresh tomatoes samples were homogenized using blender (Vitamix E310 Variable speed). Fifteen grams (15g) of the homogenized sample were weighed into a cleaned test tube and 20cm^3 of acetonitrile added and shake vigorously for 5 minutes. These was done to ensure the organic pesticides residues were dissolved in the solvent and separated from water. Six grams (6g) of anhydrous Magnesium Sulphate ($MgSO_4$) and 1.5g sodium chloride (NaCl) were added to remove the water and maintained the polarity respectively. The mixture was shaking vigorously for 10 minutes and centrifuged at 600 rpm for 10 minutes. The cleared extract was taken into a cleaned test tube for clean up [11].

QuEcHERS Extraction of Soil

After removing the coarse particles, the soil was sieved to obtain a homogenous sample and air dried at room temperature.10g of the sieved soil sample was weighed into a cleaned test tube and mixed with 15g anhydrous magnesium sulphate, 20 cm^3 of acetonitrte was added. The mixed was shaken for 20 minutes and allowed to stand for 2 hours. The mixed was centrifuge at 3000 r.m.p for 10 minutes. The cleared supernatant was transferred into 50ml test tube for clean up.

Cleanup of the Extract

Primary and secondary amine (PSA) is a weak anion exchange sorbent used to extract strong acid and poly-acidic compounds from aqueous samples. This was used to remove all the protein, lipid and sugar present in the extract. After centrifugation, the sample was clean up using solid-phase extraction cartridge. The extract was run through the dual pesticide extraction cartridge and eluted with acetonitrate. The process was repeated for all the samples [11].

Measurement and Condition of GC-MS

Using GC-MS model 7890 Agilent Technologies, equipped with auto sampler, capillary column HP5ms of length 30 mm and internal diameter of 0.320 mm and 0.25 micrometer thickness. The temperature program was 60^{O}C held for 5minutes at 8^{O}C per minute to the final temperature of 300^{O}C held for 0.5 minute and the MSD transfer line was held at 300^{o}C.

Splitless injection of 1µL was carried out at 300^{O}C injector temperature with a purge flow of 3ml/minute; the carrier gas used was helium at 99.9% purity and flow rate of 2.17ml/minute while the pressure was 150 kpa. The interface temperature was 300^{o}C.

The control and the extracts from sample were analyzed under the same condition as the standard and the residual level in mg/kg was calculated.

Health Risk Assessment

The health risk of organochlorine pesticide residues present in the tomatoes samples were estimated from the result of analysis and exposure assumptions. U.S environmental protection agency’s [8] data for health risk assessment of dietary pesticide intake in fruit used. The hypothetical body weight of 10 kg for children and 70 kg for adults and absorption rate of 100% was adopted [8].

It was assumed that the quantity of tomato consumed by an average person in day was 0.037 kg/day [26]. Maximum residue level (MRL) is the maximum concentration of pesticide residues in mg/kg that is legally permitted in fruit while acceptable daily intake (ADI) or reference dose [25].

Estimated acceptable daily intake (EADI) was obtained by multiply the residual of organochlorine pesticide concentration (mg/kg) in the tomatoes by consumption rate in (kg/day), and dividing by body weight in (kg) and hazard index (HI) for adult and children was calculated as shown in the following equation [13].

EADI =

$$\frac{Residual\ pesticide\ concentration\ mg/kg \times consumption\ rate\ in\ kg/day}{body\ weight\ in\ kg}$$

Hazard index (HI) =

$$\frac{EADI(mg/kg/day)}{Refrences\ dose\ mg/kg/day}$$

Results and Discussion

Table 1 Physicochemical Characteristics of Soil

	Physicochemical Characteristics				
Farmland	**Sand (%)**	**Clay (%)**	**Silt (%)**	**pH**	**O.M (%)**
A	28.80 ±0.164	51.0±0.78	17.18±10.17	6.45±0.082	3.15±0.0098
B	60.09 ± 0.001	25.79±0.755	19.01±0.861	6.39±0.156	3.09±0.303
C	32.30 ±0.059	56.35±0.399	13.6±0.56	6.29±0.734	5.44±0.592

Key: O.M = Organic Matter

From the Table 1, the result shows that soil sample B has sand content of 60.09 ± 0.001, clay content of 25.79 ± 0.755 and silt content of 19.01±0.861, while soil sample A has sand, clay and silt content of 28.80±0.164, 51.0±0.78 and 17.18±10.17 respectively. Soil sample C has sand content of 32.30 ±0.059, clay content of 56.35±0.399 and silt content of 13.6 ± 0.56 Soil sample C with highest clay content is expected to decrease the mobility of the pesticide and have a high water retention capacity because their small particle size. Therefore, the high content of clay in farmland A and C imply more retention of pesticide molecules and their metabolites [27]

Sample C has highest of organic matter content, 5.44±0.592 with pH of 6.29±0.734, while soil samples A and B has 3.15±0.0098 of organic matter and pH of 6.45±0.082 and 3.09±0.303 of organic matter and pH 6.39±0.156 respectively.

The soil pH and organic matter content determine the leaching and absorption capacity of the soil. Soil pH has a profound effect on soil organic matter preservation and decomposition. The degradation of organic matter is greater under acidic conditions than alkaline condition. Soil sample B was more acidic with low organic matter therefore; decomposition of organic matter is expected to be high. Soil pH is also a factor which influences the bio-availability and transportation of pesticide in the soil [27]

Organic matter of the soil has a positive correlation with organochlorine pesticide because organochlorine pesticides bind strongly with organic matter of the soil [27] Therefore, soil C with high organic matter is expected to retain more pesticide and it metabolites.

Pesticides are designed to adsorb onto organic matter, therefore, the more organic matter in the soil the greater chance that pesticides are being held in the soil and available for its intended use [27].

Table 2 GC-MS Result of Organochlorine Pesticides Residues in Soil

OCPS	A (mg/kg)	B (mg/kg)	C(mg/kg)	MLR
Deta pent	ND	ND	ND	NR
Alpha lindane	0.6 26	ND	0.050	0.04
Delta lindane	0.016	ND	ND	0.04
Endosulfan I	0.069	0.124	0.054	NR
Heptachlor I	ND	ND	ND	NR
Aldrin	ND	ND	ND	NR
Isodrin	0.148	ND	0.028	NR
Heptachlor II	ND	ND	0.006	0.03
DDMU	0.004	ND	0.003	NR
pp-DDE	ND	ND	ND	NR
Dieldrin	0.0031	0.023	0.006	0.02
Endrin	ND	ND	ND	NR
Endosulfan II	0.011	ND	0.014	0.02
Endrin keto	ND	ND	ND	NR
Methoxychor	ND	ND	ND	NR

Key: ND is not detectable, OCP is organochlorine pesticide, A, B, C is soil samples, MRL is maximum residual limit, NR is no record

From the table 2, seven OCPs residues were detected in sample A, including alpha lindane, beta lindane, isodrin, DDMU, Dieldrin, Endosulfan I and II, and heptachlor. But only Endosulfan I and Dieldrin were detected in sample B, while alpha lindane, Endosulfan, isodrin, DDMU, Dieldrin, Endosulfan II and Heptachlor were found in the soil of farmland C.

The concentration of alpha lindane in soil from farmland A and C were 0.626 mg/kg and 0.05 mg/kg respectively. Alpha lindane was higher in concentration compare to other OCPs residues in soils from all the farmlands and was higher than maximum residual limit (MRL) of 0.04 mg/kg acceptable in environment [22].

The presence of alpha lindane in soil samples A and C indicated that farmers are still using the chemical as an insecticide in Nigeria as it was also detected in a finding by [2], in the soil of Cocoa plantation in Ondo State of Nigeria. Alpha lindane was also reported in the findings of [27] in soils from a farmland in Ghana and was lower than MRL.

Alpha lindane is an isomer of hexachlorocyclohexane (HCH), which has been banned for agricultural insecticide because of its neurotoxic effect in human [58]

Deta lindane is also an isomer of hexachlorocyclohexane (HCH) and it was only detected in soil A at concentration of 0.016 mg/kg which is below acceptable MRL for agricultural soil [58].

The presence of lindane in the farmlands soil indicated the use of hexachlorocyclohexane for control of pest despite the banned. Farmers continue using these chemicals because it is readily available and cheap or it considered very active to eradicate pest.

Hexachlorocyclohexane (HCH) has eight isomer, but the common isomer used as an insecticide are α-,β-,γ- and δ-HCH. Their common name is lindane and it is partially soluble in water, but binds with organic matter of the soil and absorbed by the plant. Because of it persistence in the soil, it was banned worldwide for agricultural use [58]

Endosulfan I was detected in A, B and C but highest in soil B. Endosulfan II was found in soils A and C with the concentration been higher in farmland soil C than A but both are below the MRL set by FAO in agricultural soil.

The low concentration of endosulfan I and II in all the farmland soils maybe as result of long time use of the pesticide for pest control. [2] reported high concentration (above MRL) of endosulfan I and II in the soil of cocoa plant Ondo, Nigeria.

The concentration of endosulfan I in soil A was higher than endosulfan II in the same soil samples. This may be attributed to manufacturing of endosulfan which normally contained about 67% endosulfan I by mass of total endosulfan content while endosulfan II contained 33% by mass of endosulfan content. Endosulfan I are considered more thermal stable than endosulfan II, therefore, endosulfan I is expected to be more persistent in the environment [2].

Isodrin was detected in soil A and C with concentrations 0.148 mg/kg and 0.028 mg/kg respectively. The presence of isodrin in farmland soil indicated that farmers are using the isodrin pesticide for pest control despite the ban of the chemical for agricultural use.

Isodrin is chlorinated cyclodiene insecticide and isomer of aldrin and it is very stable in soil because of it low degradability as reported by [27].

Heptachlor was found only in farmland soil C with concentration of 0.006 mg/kg which is less than the MRL acceptable for agricultural soil. Heptachlor organochlorine pesticides are banned for agricultural use because of its health hazard. It has been associated with liver disease in animal and is suspected to be human carcinogenic [59].

The pesticide DDMU was present in farmland soils A and C with concentration of 0.004 mg/kg and 0.003 mg/kg respectively. The presence of DDMU in soils A and C maybe as a result of long time use of DDT, DDMU is a metabolite of DDT which has be banned for agricultural use, therefore, the detection of DDMU indicates the continued use of this dangerous pesticide. DDT was also reported in the findings of [27] with concentration of 0.03 mg/kg. It degrades to DDD, DDE and DDMU. All the degradation products pose health hazards to both human and animal, which was the reason these pesticide was banned worldwide for agricultural use [59].

Dieldrin was also detected in farmlands A, B and C, having concentration of 0.0031 mg/kg, 0.023 mg/kg and 0.006 mg/kg respectively. Dieldrin in Farmland C was higher than the concentration of dieldrin in farmland soil A, while dieldrin in farmland soil C has the lowest concentration with value of 0.0031 mg/kg. The higher concentration of dieldrin in farmland C could be as a result of recent used of the pesticide for pest control.

Dieldrin was also reported in the findings of [30] in the sediment of Cocoa producing area of Ondo State with mean value of 0.1507 mg/kg and it was higher than MRL.

Dieldrin is an extremely persistent pollutant which does not easily degrade in the environment but tend to biomagnified when it enters food chain. When ingested it causes headaches, dizziness, and vomiting. It was also found that this chemical can remain in the soil for decade and accumulate in agricultural produce and is unsuitable to humans. This is the reason dieldrin was banned worldwide [22].

Two organochlorine pesticides were detected in farmland B namely endosulfan and dieldrin. These may be attributed to the high sand content, low organic matter content and acidic value of farmland B. Seven organochlorine pesticide residues were found in farmlands sample A and C. this may also be attributed to the high clay and organic matter contents. [27] reported that negative correlation occurs between the soil with low organic matter and pesticide and positive correlation is observed between soil with high organic matter and pesticide.

Table 3 OCPs Residues in Fresh Tomatoes

OCPs	FT- A (mg/kg)	FT- B (mg/kg)	FT-C(mg/kg)	MRL mg/kg	WHO/ NAFDAC
Deta-pent	ND	0.012	ND		Banned
α-lindane	1.668	2.775	2.160	0.2	Banned
β-lindane	ND	0.010	0.008	0.01	Banned
Endosulfan i	1.183	0.171	0.168	0.05	Banned
Endosulfan ii	ND	0.005	0.007	0.05	Banned
Heptachlor I	ND	ND	ND	0.01	NR
Aldrin	ND	ND	ND	0.05	Banned
Isodrin	0.129	0.129	0.187	0.01	NR
Heptachlor II	0.032	ND	ND	0.01	NR
Trans-nonane	ND	ND	ND	NP	NR
P,p-DDE	ND	ND	ND	0.05	NR
Dieldrin	O.037	0.078	ND	0.01	Banned
Endrin ketone	ND	ND	ND	0.01	Banned
Methoxych	ND	ND	ND	0.01	NR
DDMU	0.0067	0.007	0.031	0.01	Banned

Key: ND- not detectable, FT=fresh Tomatoes A, B C, OCPs = organochlorine pesticide A,B,C=Farms, NP= No percentage, NR= No record

From Table 3 six organochlorine pesticide residues were detected in fresh tomatoes from farmland A, this including α- Lindane, Endosulfan I , isodrin, Heptochlor, DDMU, deildrin, with concentration of 1.668 mg/kg, 1.183 mg/kg, 0.013 mg/kg, 0.032 mg/kg, 0.168 mg/kg, and 0.037 mg/kg respectively. Eight organochlorine pesticides residues were found in fresh tomatoes from farmland B. They included deta.-Pentachlorocyclohexene, alpha-lindane, beta- lindane, endosulfan I and II, isodrin, diedrin and DDMU with concentration, 0.012 mg/kg, 2.775 mg/kg, 0.010 mg/kg, 0.171 mg/kg, 0.005 mg/kg, 0.129 mg/kg, 0.078 mg/kg, and 0.007 mg/kg, respectively. However, the following were detected in fresh tomatoes from farmland C, α-lindane, β-Lindane, Endosulfan I and II, isodrin and DDMU with concentration of 2.160 mg/kg, 0.008 mg/kg, 0.168 mg/kg, 0.007 mg/kg, 0.187 mg/kg and 0.031 mg/kg respectively. Alpha lindane found in fresh sample A, (1.668 mg/kg) is lower than the concentration of alpha lindane (2.775 mg/kg), found in fresh sample B.

It is important to note that, the concentration of alpha lindane found in fresh sample A, B, and C were higher than MRLs (0.2 mg/kg) set by WHO/FAO.

The detection of alpha lindane in the fresh samples is an indication that farmers are still using the pesticide for pest controlled despite the ban [22]. Alpha lindane is an isomer of hexachlorocyclorohexane which was banned by WHO and NAFDAC. The concentration of alpha lindane in fresh samples was higher compared to the findings of [16] which determined alpha lindane (0.001 mg/kg) in tomatoes samples from Mubi Adamawa in Nigeria. Alpha lindane was also detected in finding of [4] on fresh tomatoes with mean value concentration less than 0.2 mg/kg. [38] carried out assessment of OCP in vegetables' in Togo and find the mean concentration of alpha lindane determined in tomatoes to be 0.073 mg/kg.

The variation of concentration of alpha lindane in different finding at different areas can be attributed to the availability of the pesticide, and level of awareness on the health hazard.

Beta lindane was detected in fresh sample B and C with concentration of 0.0 1 mg/kg and 0.008 mg/kg, respectively. However, the concentration of beta lindane in sample B and C was lower than MRL set by the WHO/ NAFADAC in fruit and vegetables'.

The result of beta lindane in fresh sample B and C obtained in the present research is low compared to the finding by [38] who recorded 1.626 mg/kg in vegetables and fruits.

It is worthy of note that beta lindane is an isomer of hexachlorocyclorohexane which has been banned worldwide for agricultural use due to its persistent ability. Lindane has since been identified as a carcinogenic compound [58]

Endosulfan I was detected in fresh tomato sample A with concentration 1.183 mg/kg similarly, the concentration of endosulfan I in fresh tomato sample B, 0.71 mg/kg. However, endosulfan I in tomato sample C was 0.168 mg/kg. The identification of endosulfan I in the tomato indicated that farmers are still using the pesticide, or long time use of the pesticide because endosulfan I can persist in the soil more than other organochlorine pesticide [4].

Concentration of endosulfan I detected in fresh tomato sample was similar to the findings of [4] who detected endosulfan I in tomato sample with concentration of 0.16 mg/kg. [42] also established the presence of endosulfan I in tomato sample at a concentration of 0.015 mg/kg. Endosulfan I was also determined in finding of [57] in fruit and vegetable with mean concentration of 0.048 mg/kg. The results was higher than finding [16] who found 0.001 mg/kg endosulfan I in tomato sample from Mubi, Adamawa state.

0.00 5mg/kg endosulfan II was only detected in fresh tomato sample B, endosulfan II detected in fresh tomato sample C with concentration 0.007 mg/kg

Endosulfan I detected in three fresh tomato samples was higher than MRL set by the WHO/NAFDAC, (0.05 mg/kg). Endosulfan was recommended to be included among the banned organochlorine pesticide under the Stockholm Convention on Persistent Organic Pollutants (POP) [26].

In fresh tomato sample A, Isodrin was found with at a concentration 0.0129 mg/kg and 0.0129mg/kg in fresh sample B. However, for sample C, Isodrin detected was 0.187 mg/kg in fresh. The high concentration of isodrin in fresh sample C compared to fresh samples A and B may be as result of recent use of the pesticide by the farmer or due to the indiscriminate use of a combination of chlorinated cyclodiene insecticide such as aldrin, dieldrin and endrin because they are all endo-endo isomer of cyclodiene.

However, the isodrin detected in fresh tomato sample in A, B and C was higher than MRL set by WHO/FAO, 0.01 mg/kg accepted in fruits and vegetables. Isodrin organochlorine pesticide was developed after the banned of DDT worldwide as an alternative pesticide. It was later banned by FAO/WHO because of its persistent and slow degradation in soil and health hazard [58].

Heptachlor II was present only in fresh tomato sample A at a concentration of 0.032 mg/kg. Heptachlor has been banned by the WHO/FAO because the insecticide residues causes liver disease in animal and is also suspected to be carcinogenic in human [26]. The presence of heptachclor in fresh samples indicates that the pesticide is still in used for agricultural purposes despite been banned for potential health hazard. Heptachlor was detected in tomato sample by [4] with mean concentration of 0.003 which was lower than result obtained in this research and also lower than [13] who determined heptachlor, 0.00 6 mg/kg in fresh tomato from Ado Ekiti market. Indiscriminate use of this banned pesticide and lack of good agricultural practice (GAP) may result to high concentration of heptachlor in the fresh tomato sample. Environmental Protection Agency (EPA) classified heptachlor as possible human carcinogenic and it has long half life [8].

Deildrin (0.037 mg/kg), was detected in fresh tomato sample A and in fresh tomato sample B with concentration 0.078 mg/kg .The concentration of dieldrin was high in fresh tomato samples B compared to sample A. The result obtained was similar to the concentration of Deildrin, (0.024 mg/kg) from the findings of [49] in *solamium lycopersium* but lower than Deildrin detected in finding of [13] with concentration of 0.007mg/kg in tomato obtained from Ado-Ekiti.

Deildrin is a synthetic chemical used to kill insect but because of concerns about damage to the environment and potential risk to human health, U.S. Environmental Protection Agency (EPA) banned the use of this compound for agricultural use [22].

2,2-bis (chlorophenyl)-1-chloroethane DDMU was detected in fresh tomato sample A with concentration 0.0067mg/kg and 0.007 mg/kg was found in fresh sample B, while 0.031 mg/kg was found in fresh sample C The presence of DDMU indicated the use of DDT by the farmer for pest control, because DDMU is one of the degradation products of DDT. Dichlorodiphenyltrichloroethane (DDT) has been banned worldwide for agricultural application because of its health hazard and unfavorable environmental effect [58]. Concentration of DDT detected in fresh samples was similar to the findings of [49] with mean value of 0.006 mg/kg in fresh tomato. It was also similar to finding of [16] with mean value of 0.001 mg/kg in vegetable.

Nevertheless, the DDMU in all the samples is below the (0.01 mg/kg) MRL as set by WHO/FAO. Nonetheless, DDT and its metabolites such as DDD, DDE and DDMU have been identified as contributors to public health concern, and have been linked to cancer, asthma and growth disorder in children [58].
Deta pentachlorocychlorohexan (deta-pent) was found only in fresh sample B with concentration 0.012 mg/kg. The presence of deta pentachlorocychlorohexane in the sample was as result of used of lindane pesticide either in soil or applied directly to the crops as an insecticide, as pentachlorocychlorohexane is one of the metabolites of deta lindane.

All the OCPs determined in the samples have been banned in Nigeria by the National Food and Drugs Control [43], and in other countries according to FAO/WHO data for banned and restriction of organochlorine pesticide OCPs for agricultural pest control. Most of the organochlorine pesticide residues detected in the fresh tomato samples were also reported in most of the findings from different parts of Nigeria[2], [34],[16],[46]. This indicates the continued use of these toxic chemicals for pest control. Farmers may lack information about the potential health risk of OCPs residues in the vegetables and the dangers to the environment. The continued usage may not be far from the availability and low cost of these chemicals as reported by [2].

OCPS Residue in Fresh Tomato and Soil A (mg/kg)

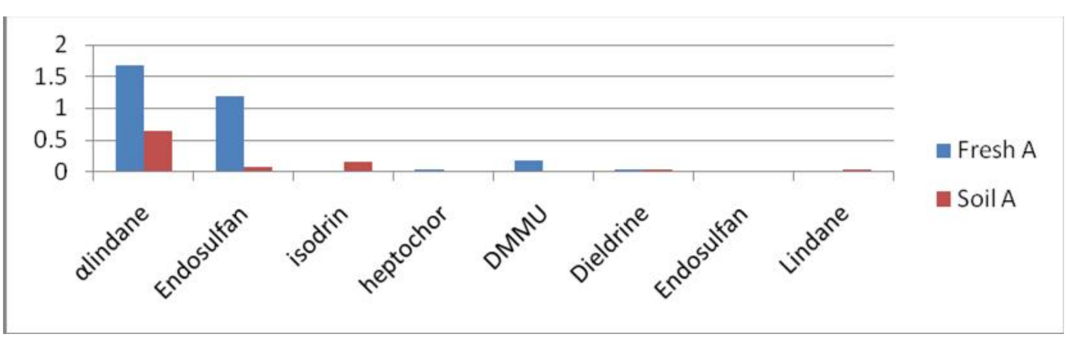

Figure 1 Comparison of OCPs Residues in Fresh, Dried Tomatoes and Soil Sample A

Figure 1, shows the comparison of concentration of OCPs residues in tomato fresh, and soil sample A. Organochlorine pesticide residues detected in fresh tomatoes sample A as shown in figure 1 namely; alpha lindane, isodrin, heptachlor, endosulfan I, dieldrin and DMMU, while in the same soil sample, lindane, Endosulfan, isodrin, DMMU,Dieldrin and endosulfan II were detected but heptachlor was not detected in the soil, but found in the tomato sample.

The concentration of alpha lindane (1.668 mg/kg), endosulfan I, (1.183 mg/kg), isodrin (0.013 mg/kg), DDMU (0.168 mg/kg), and dieldrin (0.037 mg/kg) in fresh tomato sample was higher than 0.626 mg/kg, 0.069 mg/kg, 0.148 mg/kg, 0.004 mg/kg, and 0.031 mg/kg for corresponding OCPs in the soil sample. This may be as result of absorption of the pesticide compound by crops from the soil and direct absorption after application.

There was on detection of heptachlor in the soil but detected in fresh tomato sample A while endosulfan II and beta lindane are detected in soil sample but not detected in the tomato sample A. This is because pesticide spray on vegetable and fruits accumulate on the outer peel, but the skin does not form an impermeable barrier. Some pesticide are actually design to be absorbed into the tissue of the vegetables or fruits and protect it from pests that penetrate through the tissue of the crops [34].

OCPS Residue in Fresh Tomato and Soil Samples B (mg/kg)

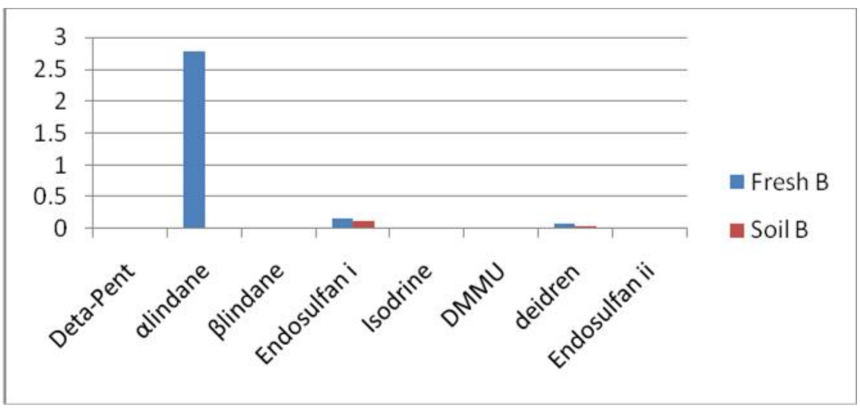

Figure 2 Comparison of OCPs Present in Fresh Tomatoes and Soil Sample

Figure 2 shows the comparison of organochlorine pesticide residues in Tomato, and the soil sample from farmland B. Pentachlorocychlorohehaxane, apha lindane, beta lindane, isodrin, DMMU, and endosulfan were detected in the fresh tomatoes sample B. but only endosulfan and Deildrin were detected in the soil sample B. The concentration organochlorine pesticide residues detected in fresh tomato sample B were higher than the concentration of organochlorine detected in the soil.

Soil sample B has a high sandy content and low organic matter as shown Table 1 Since the particles sizes of sandy soil are usually large, it does not hold water and pesticide molecules because pesticides bind with organic matter. These may be the reason of low organochlorine pesticide residues detected in soil sample B [27].

These indicated that plants did not only absorbed pesticide from the soil, but also absorbed pesticide mainly through their leaves and roots. After application of pesticide, it is taken up by plants and translocated to other parts of the plant to prevent pest feeding on any part of the plant.

OCPS Residue in Fresh Tomato and Soil Samples C (mg/kg)

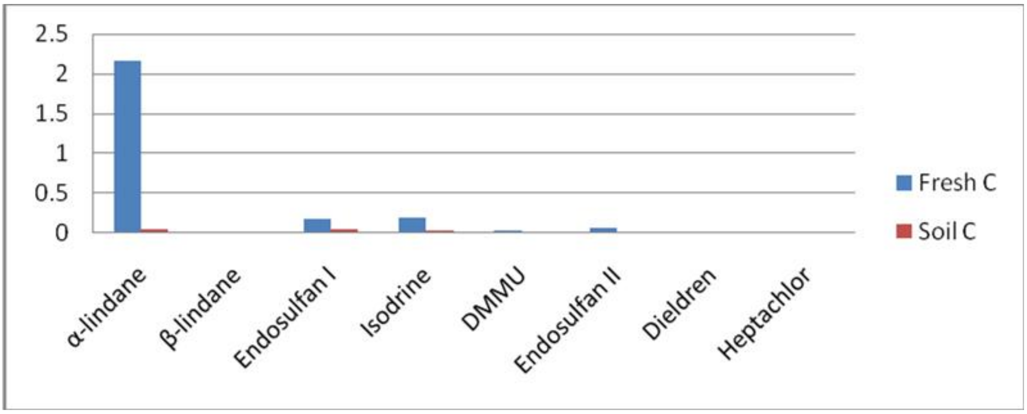

Figure 3 Comparison of OCPs Present in Fresh and Soil Sample C

figure 3 shows the comparison of the concentration of organochlorine pesticide residues present in fresh, dried tomatoes and soil samples from farmland C alpha lindane (0.05 mg/kg), endosulfan I, (0.054 mg/kg), Isodrin (0.028 mg/kg), DDMU (0.003 mg/kg), endosulfan (0.014 mg/kg), Deildrin (0.006 mg/kg), heptachlor (0.006 mg/kg) was detected in soil farmland sample C. Low concentration of organochlorine pesticide residues in the soil can also attributed to the higher absorption capacity of the soil because Soil sample C has high clay content as shown in Table 1 and therefore, has ability to hold water capacity and pesticide [27] . The quantity of pesticide absorbed depends on the nature of pesticide and how it was formulated, and its mode of application [45].

Table 4 Health risk Estimation of Organochlorine pesticide Residues in Tomato

OCPs	Reference .dose mg/kg/day	EADI of adult (mg/kg/day	EADI of children mg/kg/day	Hazard index	Health risk
αHCH	0.005	1.90×10^{-4}	$1.37\text{x}10^{-4}$	AD-0.399	N0
				CHD-2.737	YES*
βHCH	0.005	5.286×10^{-6}	$3.70\ \text{x}10^{-6}$	AD-7.6 $\text{x}10^{-8}$	NO
				CHD-7.4×10^{-4}	NO
Endosulfan I	0.05	9.059×10^{15}	$6.341\ \text{x}10^{-6}$	AD-2 $\text{x}10^{-3}$	NO
				CHD-1.3×10^{-5}	NO
Isodrin	0.01	6.824×10^{-5}	$4.777\ \text{x}10^{-6}$	AD-6.8 $\text{x}10^{-4}$	NO
				CHD-4.7 $\times10^{-4}$	NO
DDMU	0.01	3.541×10^{16}	$2.449\ \text{x}10^{-5}$	AD-3.5 $\text{x}10^{-5}$	NO
				CHD-2.4×10^{-6}	NO
Dieldrin	0.001	4.838×10^{-5}	$2.826\ \text{x}10^{-6}$	AD-4.0 $\text{x}10^{-4}$	NO
				CHD-2.8×10^{-4}	NO
Endosulfan II	0.05	2.854×10^{-6}	$1.778\ \text{x}10^{-6}$	AD-5.7 $\text{x}10^{-5}$	NO
				CHD-3.9×10^{-4}	NO
Heptachlor II	0.001	1.445×10^{-6}	$1.012\ \text{x}10^{-5}$	AD-0.144	NO
				CHD-1.012	YES*

KEY: AD is Adult, CHD is Children, and EADI is estimated average daily intake

The table 4above shows the calculation of hazard index estimated from dietary intake of adult children with respect their reference dose. This was calculated using U.S Environmental Protection Agencies data for health risk assessment of dietary pesticide intake in fruit and vegetables. Hypothetical body weight of 10 kg and 70 kg was adopted for children and adult, respectively while 0.037 kg/person as daily recommended consumption rate of tomato as stated by International Food Policy Research Institute.

α HCH, β HCH, Endosulfan I, Isodrin, DDMU, Dieldrin, and Endosulfan II did not pose health risk for adults because their respective hazard index is less than one while α HCH and heptachlor II with hazard index of 2.737 and 1.012, respectively pose health risk for children because each calculated hazard index was equal to one, According to [59] if hazard index is equal or greater than one such compound pose health risk and need further monitoring. The result was similar to [3] which Hazard index of heptachlor was 2.497 in leafy vegetables in south western Nigeria. Hazard index of DDD was also higher than 1.04 in the finding of [4] in cucumber. α-Hexachlorocyclohexane (α-HCH) is the isomer of hexachlorocyclohexane (HCH) and byproduct of lindane and it is found in commercial grade. (α-HCH) and (β-HCH) are classified as persistent organic pollutants (POPs) because they have ability to bioaccumulate, biomagnify, and exhibit long distance transport capacity. Exposure to these compound has a short time effects of causing dizziness, nausea,/vomiting , loss of appetite, and weakness of the body while the longtime exposure can result to brain disorder in children, reproductive defect. It was also indentified as human carcinogen by International Agency for Research on Cancer [26].

Conclusion

The results obtained from the present research shows that a number of organochlorine pesticide residues are present in the fresh and soil samples selected from the studied farmlands in Zamfara State. They include α HCH, β HCH, Endosulfan I, isodrin, DDM, dieldrin, and Endosulfan II in tomato sample A with concentration 1.668 mg/kg, 1.183 mg/kg, 0.129 mg/kg, 0.032 mg/kg, 0.037 mg/kg and 0.0067 mg/kg, respectively. α- HCH, endosulfan and isodrin in detected in tomato samples are higher than maximum residual limit (MRL) set up by FAO/WHO. Hazard Indexes (HI) of α-HCH and heptachlor are 2.737 and 1.012 which are equal and greater than one. According WHO, if HI equal or greater than one may pose health risk to children when exposed.

More also, the main sources of these residues in the tomatoes are more of direct application of pesticide by farmers than sorption from the soil.

Conflict of interest

The authors hereby declare that there are no conflicts of interest.

Author's contributions

The authors have equally contributed to the work.

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