



STUDY OF ORGANOCHLORINE PESTICIDE RESIDUES LEVEL IN FRESH AND DRIED TOMATOES FROM SELECTED FARMLANDS IN ZAMFARA STATE, NIGERIA

Momoh Shaibu, M.A.T. Suleiman, R.A.lafia-Araga, S.O. Salihu
Department of Chemistry, Federal University of Technology P.M.B 65,
Minna, Niger State, Nigeria

Abstract - In this study, organochlorine pesticide (OCP) residues level in fresh and dried tomato from selected farmland in Zamfara State, Nigeria were determined in fresh and sundried portion of the samples. QuEChERS and GC-MS were used for sample preparation and analysis respectively. The results obtained shows the presence of OCPs residues including; α HCH, β HCH, Endosulfan I&II, isodrin, DDM, deildrin, and mitotane with concentration of 3.669mg/kg, 0.0100mg/kg, 0.1714mg/kg, 0.129mg/kg, 0.0067mg/kg, 0.0054mg/kg, 0.2734mg/kg. The α HCH, endosulfan, isodrin and mitotane were above the maximum residual limit (MRL) in the fresh samples, below the MRL in dried samples, while endosulfan II, mitotane, and deildrine were below detection limit in dried tomato extracts. On the other hand α HCH and mitotane has hazard index of 2.737 and 1.012 respectively. It is therefore, recommended to the regulatory institutions in Nigeria for effective awareness and educates the farmers on the health effect of pesticides residues in our food and environment. Also encourage drying process when a high level of pesticide residues are suspected in the tomatoes.

Keynote: Organochlorine, Pesticide residues, Fresh Tomato, GC-MS.

I. INTRODUCTION

Tomatoes (*Lycopersicon esculentum*, *solanum Lycopersicon*.) belong to the *solanacea* family and correspond to one of the most widely grown vegetable in the world. The fruit vegetable is typically produced in the spring summer season, but in many country including Nigeria, it is produced throughout the years with the help of irrigation farming [5]. It is a basic ingredient of many meals in

Nigeria especially, the sauces and stews which accompany most traditional dishes. The fruit can also be consumed raw in salads or used to make juices [8]. Uncontaminated tomatoes play a vital role in human dietary intake; it help managing blood pressure, healthy hair, prevent cancer, maintained kidney, maintained sugar level in the blood, and provide essential antioxidant such as vitamin C and A. that is why tomato consumption is usually for healthy and balanced diet [4], [5] [8] The demand for tomatoes over shadows the supply, the challenge is attributed to the seasonality and lack of storage facility and inadequate post-harvest handling of tomatoes [3], [6].

Drying of tomatoes becomes the only way farmers can economically provide alternative to fresh ones, which are available in most vegetables, markets [4]. Drying is an important and traditional process of removing the moisture from the food. The basic principle of drying is to prevent microorganisms such as bacteria, and fungi, which required water for their growth and multiplication.

Tomato farmers used pesticide such as organochlorine to control pest and disease in order to protect the crops from pest attack and good yield. This pesticides are used indiscriminately by farmers to mitigate loses of tomato in the farm because they are cheap and readily available in market [25] [2].

In Nigeria, farmers and consumers of this vegetable fruits faces an immense risk of exposures to this toxic chemical use to controlled pest, some of these toxic chemicals are banned or restricted in Nigeria or in other countries [22]. Wrong application techniques and time of application of these chemicals to the vegetable, or the use of unsuitable equipment for application expose farmers and farm products to the



risks of residual deposition [15]. There are some pesticides residues that are unavoidable even when spraying are done in accordance with good agricultural practice. Organochlorine compounds are considered persistent organic pollutants, a category of chemicals that include: Dichlorodiphenyltrichloroethane (DDT), methoxychlor, Dieldrin, Chlordane, Toxaphene, Kepone, lindane, Benzene hexachloride, endrin, and mirex.

In Nigeria, the following organochlorine pesticides have been banned by NAFDAC dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexanes (HCHs), aldrin, dieldrin, endrin, and heptachlor) because of concerns on the environment and human health.

Despite the banned on most of the toxic organochlorine compounds, they are still in used in developing countries like Nigeria for pest control. This continues used of organochlorine pesticides has remained a matter of international concern because of their residual persistence in agricultural products [14],[22],[24],[15].

Maximum residual limit of organochlorine pesticide (MRL)

Residues is defined by [17] as any substance or mixture of substance in food for man or animals resulting from the use of pesticide and includes any specified derivatives, such as degradation and conversion products, metabolites, reaction products, and impurities that are considered to be of toxicological significance.

Each country setup it own maximum residue limit (MRL) and Acceptable Daily intake (ADI) of pesticide residues in their agricultural products. Nigeria used residual limits established by food and Agriculture organization of the United Nations (FAO) and world health organization (WHO) [23]. When the residues are more than MRL, it poses health risk to human and environment. Short term and long term impacts in human body are damage to reproductive system, and immune system [25]. WHO has reported that roughly three million pesticide poisoning occurs annually and results to 220,000 death worldwide. Farmers all over the world used both approved and banned pesticide to control pest and disease of tomato as reported [17].

II. MATERIALS AND METHODS

Reagents

Solvent, reagents and pesticides standard were of analytical grade and obtained from sigma and Co. The glass wares were cleaned with detergent and water, raised with distilled water and acetone before used. Centrifuge and Gas chromatograph couple with mass spectrometer detector (GC-MS) are used for the extraction and analysis respectively.

Sample collection

Tomatoes samples were collected from three major tomatoes farm land in Zamfara state. Part of each samples were cut and sun dried until it lost all water and moisture contents as it obtained in the traditional way of preserving tomatoes (dry tomatoes).

Samples extraction

QuEChERS was used for sample preparation as describe by [12].

The samples were grid to homogenized and increase the surface area. 15g of homogenized sample was weighed into a cleaned 50ml test tube; 15ml of acetonitrile was measured and added to the sample and shake vigorously for 5 minutes. This was done to ensure the organic pesticides residues were dissolved in the solvent and separated from water. 6g of $MgSO_4$ and 1.5g NaCL were added to remove the water and maintained the polarity respectively, before centrifuge for 10 minutes at 600rpm. The supernatants was transferred into cleaned test tube follow by adding 150mg of $MgSO_4$ and shake for 30 seconds and centrifuge for 1minute at 1500rpm, the cleared extract was used for GC-MS analysis. The process was carryout in all the samples and control.

III. INSTRUMENTATION

The analysis was carryout at Nigeria institute of Oceanography and Marine Research (NIOMR), Lagos State Using GC-MS model 7890 Agilent technologies, equipped with auto sampler, capillary column length HP 5ms of length 30m and internal diameter of 0.320mm and 0.25 micrometer. The temperature was program at 60°C held for 5minutes at 8°C per minute to the final temperature of 300°C held for 30 seconds and the MSD transfer line was held at 300°C.

Split injection of one microliter was carried out at 300°C injector temperature with a purge flow of 3ml/minute, the carrier gas used was helium, with



flow rate of 2.17ml/minute and the pressure was 150kpa. The interface temperature was 300°C. The mass spectrometer model 5975 agilent technologies ionization mode was electron impact with ion sources temperature of 230°C and in full scan mode ranges from 45-500M/Z.

Internal standard technique was employed to analyze the fresh and dried extracts. The organochlorine standard used are alpha lindane, delta lindane, endulfan I&II, heptachlor, aldrin, isodrin, trans-chloro, DDMU, DDT, P,P-DDE, dieldrin, endrin, mitotane, endrin keto, melhoxychlor and delta pent. The standards are prepare in different concentrations from 0.100ppm to 2.00ppm and was used to generate calibration curves for each compound. The efficiency of the method was validated with recoveries of references material without pesticide residues and with four organochlorine pesticide residues spiked 0.1ppm and 1.0 ppm.

The Estimated average daily intake (EADI) and hazard were calculated using equation 1&2 below:

$$\text{EADI} = \frac{\text{Residual pesticide conc.} \frac{\text{mg}}{\text{kg}} \times \text{consumption rate in kg/day}}{\text{body weight in kg}} \quad \dots\dots\dots 1$$

$$\text{Hazard index (HI)} = \frac{\text{EADI} \left(\frac{\text{mg}}{\text{kg}} / \text{day} \right)}{\text{references dose} \frac{\text{mg}}{\text{kg}} / \text{day}} \quad \dots\dots\dots 2$$

IV. RESULTS AND DISCUSION

The retention times of the analytes detected in the samples were the same as those of standards and the spectra has a very high match factor.

Table 1 Show the present and the concentration of organochlorine pesticides residue in the fresh and dried tomato extract. Almost all the OCPs determined in the samples are banned in Nigeria according to [23], and in other countries according to FAO/WHO data on banned and restriction of OCPs for agricultural pest control or eradication. α HCH, endosulfan, isodrin and mitotane are above the maximum Residual limit (MRL). However the concentration reduced significantly below the MRL in dried samples, while endosulfan II, mitotane, and deildrine are below the limit of detection in the dried tomato extracts.

Twenty OCPs standards were used for analysis as shown in table I and eight OCPs ; α HCH, β HCB,

endosulfan I and II, isodrin, DDM, deildrin, and mitotane were determined in fresh and dried tomatoes samples extract as shown in table II. Endosulfan II, mitotane and dieldrin are below the limit of detection in the dried tomato extracts, this may attribute to the volatility nature of the OCPs residues as reported by [27].

Most the organochlorine pesticide residues detected in the fresh tomato extract was also reported in a work of [1], [22], [19],[15]. This indicates that farmers may lack information about the potential health risk of OCPs residues in the food product and the dangers to the environments. The continued usage may not be far from the availability and low cost of these chemicals as reported by [1].

Statistical analysis shown significant reduction in concentration of OCPs residues in dried tomatoes compared to the concentration of OCPs residues in the fresh tomato samples at 95% degree of confidence.

Table 3 shown health risk assessment estimated from the results of eight OCPs residues obtained in this work, using US environmental protection agency data and guideline adopted on dietary pesticide intake on vegetables. Hypothetical body weight of 10kg and 70kg was adopted for children and adult respectively while 0.037kg/person for daily consumption rate of tomato as stated by international food policy research institute and FAO.

It appeared in the table 3.below that all the eight OCPs residues present did not poses health risk except α HCH and mitotane with hazard index of 2.737 and 1.012 respectively. According WHO if a hazard index is equal or greater than one, such pesticide residue poses a health risk. α HCH and mitotane pose health hazard to the children when exposed. α -Hexachlorocyclohexane (α -HCH) is an isomers of hexachlorocyclohexane (HCH) and byproduct of lindane (γ -HCH) and it is typically still contained in commercial grade lindane used as insecticide. As of 2009, the Stockholm Convention on Persistent Organic Pollutants classified (α -HCH) and (β -HCH) as persistent organic pollutants (POPs), due to its ability to persistence in the environment, bioaccumulate, biomagnifying, and long-range transport capacity. Exposed to this pesticide residues 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 blood disorder, reproductive defect and international agency for research on cancer and US-EPA has also classified them as possibly human carcinogen FAO/WHO 2015.



TABLE 1: Detectable and non detected OCPs residues in fresh and dried tomatoes (mg/kg)

OCPs	F-tomato A (mg/kg)	D-tomato A (mg/kg)	F-tomato B (mg/kg)	D-tomato B (mg/kg)	MRL mg/kg	WHO/NAFDAC
Delta-pent	0.0115	ND	ND	ND		Banned
α -lindane	3.6995	0.0227	2.1603	0.0012	0.2	Banned
β -lindane	0.0100	ND	ND	ND	1	Banned
Endosulfan i	0.1714	0.1014	0.1678	0.15194	0.05	Banned
Endosulfan ii	0.0054	ND	0.0074	0.00336	0.05	Banned
Heptachlor I	ND	ND	ND	ND	0.01	-
Aldrin	ND	ND	ND	ND	0.05	Banned
Isodrin	0.1291	0.0132	0.1866	0.04752	0.001	-
Heptachlor II	ND	ND	ND	ND	-	-
Trans-nonane	ND	ND	ND	ND	-	-
P,p-DDE	ND	ND	ND	ND	-	-
Dieldrin	0.0784	0.01252	0.0308	0.00576		Banned
P,p-DDE	ND	ND	ND	ND	-	-
Mitotane	0.2734	ND	ND	ND	0.01	
Endrin ketone	ND	ND	ND	ND	0.01	Banned
Methoxych	ND	ND	ND	ND	-	-
DDMU	0.0067	0.0290	0.0290	0.0029	0.01	Banned
Endrin	ND	ND	ND	ND	0.01	-

Key: ND- not detectable, F-fresh, D- dried and OCPs means organochlorine pesticide.

TABLE 2: OCPs residues (mg/kg) in fresh and dried tomatoes

OCPs	α HCH	β HCH	Endosulf	Isodrin	DDM	dieldrin	Endosulf	Mitotane
F-TSA	3.6995	0.0100	0.1714	0.1291	0.0067	0.0764	0.0054	0.2734
D-TSA	0.0227	0.00	0.1014	0.0132	0.029	0.01252	0.00	0.00
F-TSB	2.1603	0.00	0.1678	0.1866	0.0290	0.0308	0.0074	0.00
D-TSB	0.0012	0.00	0.15194	0.04752	0.0029	0.00576	0.00336	0.00

Key: F-TSA means fresh tomatoes sample A, D-TSB means dried tomato sample B,

Table 3: 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
α HCH	0.005	1.900×10^{-4}	1.37×10^{-4}	AD-0.399 CHD-2.737	NO YES
β HCH	0.005	5.286×10^{-6}	3.70×10^{-6}	AD- 7.6×10^{-8} CHD- 7.4×10^{-4}	NO NO
Endosulf I	0.05	9.059×10^{-5}	6.341×10^{-6}	AD- 2×10^{-3} CHD- 1.3×10^{-5}	NO NO
Isodrin	0.01	6.824×10^{-4}	4.777×10^{-6}	AD- 6.8×10^{-4} CHD- 4.7×10^{-4}	NO NO
DDM	0.01	3.541×10^{-6}	2.449×10^{-5}	AD- 3.5×10^{-5} CHD- 2.4×10^{-6}	NO NO
Dieldrin	0.001	4.838×10^{-5}	2.826×10^{-6}	AD- 4.0×10^{-4} CHD- 2.8×10^{-2}	NO NO
Endosulf II	0.05	2.854×10^{-6}	1.778×10^{-6}	AD- 5.7×10^{-5} CHD- 3.9×10^{-5}	NO NO
Mitotane	0.001	1.445×10^{-6}	1.012×10^{-5}	AD-0.144 CHD-1.012	NO YES



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

V. CONCLUSION

The result obtained from the present study shows that organochlorine pesticide residues are present in the fresh and dried tomato from selected farmland in Zamfara State, are α HCH, β HCH, Endosulfan, isodrin, DDM, dieldrin, mitotane and endosulfan with concentration of The α HCH, endosulfan, isodrin and mitotane higher than MRL setup by FAO/WHO. The concentration of OCPs residues in dried tomato samples are below the maximum residual limit. The HCH and mitotane hazard indexes are high; this may pose health risk to the children when exposed. The study also provides data on organochlorine pesticide residues in the dried tomato sample which shows significant reduction in concentration of the residues. Drying tomato should encourage whenever high level of pesticide residues is suspected in the tomato. Strict regulation and public awareness is also required by regulatory agency to educate the users on the health risk and environmental effect.

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