DETERMINATION OF ORGANOCHLORINE PESTICIDE RESIDUES IN SOIL, FRESH AND DRIED TOMATOES FROM SELECTED FARMLANDS IN GUSAU, ZAMFARA STATE, NIGERIA

BY

MOMOH, Shaibu
MTech/SPS/2017/7278

DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCE
FEDERAL UNIVERSITY OF TECHNOLOGY
MINNA, NIGER STATE

AUGUST, 2021

DETERMINATION OF ORGANOCHLORINE PESTICIDE RESIDUES IN SOIL, FRESH AND DRIED TOMATOES FROM SELECTED FARMLANDS IN GUSAU, ZAMFARA STATE, NIGERIA

BY

MOMOH, Shaibu
MTech/SPS/2017/7278

A THESIS SUBMITTED TO THE POSTGRADUATES SCHOOL FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA, NIGERIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR MASTER OF TECHNOLOGY (M.TECH) IN ANALYTICAL CHEMISTRY

AUGUST, 2021

ABSTRACT

In this study, organochlorine pesticide (OCP) residues in fresh, dried tomatoes and soils from selected farmlands in Gusau, Zamfara State, Nigeria were determined. 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 while endosulfan I, isodrin and dieldrin with concentration of 0.027 mg/kg, 0.003mg/kg and 0.025 mg/kg were detected in dried sample A. α- lindane, endosulfan I, and isodrin were above the maximum residual limits (MRLs) in the fresh samples, all below the MRLs in dried samples A, 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. Only α lindane, endosulfan I, isodrin, dieldrin, and DDMU with concentration 0.023 mg/kg, 0.102 mg/kg, 0.013 mg/kg, 0.013 mg/kg and 0.001 mg/kg were detected in dried sample B. Concentration of α lindane, endosulfan I, and isodrin were above MRL in fresh samples B, below the MRLs in dried 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-lindane, endosulfan I and II, isodrin and DDMU with concentration of 0.01 mg/kg, 0.0152 mg/kg, 0.003 mg/kg, 0.048 mg/kg and 0.003 mg/kg were detected in dried samples C. α-lindan, Endosulfan I, isodrin and DDMU were above MRLs in fresh sample C, but below the MRLs in dried samples C. All the OCPs detected in the soil samples are below the MRLs except α- lindane and endosulfan I, with concentration of 0.626 mg/kg and 0.069 mg/kg, which are above the MRLs in soil sample A. On the other hand α- lindane and heptachlor has hazard index of 2.737 and 1.012 respectively. Therefore, the level of OCP residues were lower in the dried tomato samples compared to the fresh samples, while α- lindane and heptachlor pose a potential health risk since the hazard index is equal and greater than 1.

TABLE OF CONTENTS

Contents		Pages
Title Page		i
Declaration		ii
Certification		iii
Dedication		iv
Acknowledgments		v
Abstract		vi
Table of Contents		vii
List of Tables		xi
List of Figures		xii
Glossary of Abbreviation		xiii
CHAPTER ONE		
1.0	**INTRODUCTION**	**1**
1.1	Background of the Study	1
1.2	Pesticide Misuse and Abuse	3
1.3	Organochlorine Pesticide Residues	3
1.4	Exposure to Organochlorine Pesticide	4
1.5	Effect of Organochlorine Pesticide Residues in Human	4
1.6	Absorption of Organochlorine Pesticide Residues from Soil by Target Plan	5
1.7	Statements of the Research Problem	6
1.8	Justification of Research Problem	6
1.9	Aim and Objectives of the Study	7

CHAPTER TWO

2.0	**LITERATURE REVIEW**	8
2.1	Food Safety	8
2.2	Maximum Residual limit	9
2.3	Tomatoes Cultivation in Nigeria	10
2.4	Tomatoes Processing and Storage	11
2.5	Chemical Structure and Degradation of Organochlorine Pesticide	11
2.5.1	Endosulfan	12
2.5.2	Dichlorodiphenyltrichloroethane	12
2.5.3	Dieldrin and Aldrin	13
2.5.4	Hexachlorocyclorohexan	14
2.6	Working Principle of Gas Chromatography Couple with Mass Spectrometer	14

CHAPTER THREE

3.0	**MATERIALS AND METHODS**	33
3.1	Materials	33
3.1.1	Chemicals /reagents	33
3.1.2	Pesticide standard	34
3.1.3	Instruments	34
3.1.4	Sample collection	34
3.1.5	Proximate analysis of fresh and dried tomatoes	35
3.1.5.1	Moisture contents	35
3.1.5.2	Ash content determination	36
3.1.5.3	Determination of fat/lipid content	36
3.1.5.4	Determination crude protein	37

3.1.5.5 Determination of crude fibre 38

3.1.5.6 Total carbohydrate content 38

3.1.5.7 Soil pH 38

3.1.5.8 Determination of percentage of sand, clay and slit 38

3.1.5.9 Determination of soil organic matter 39

3.2 Determination of Organochlorine Pesticides 39

3.2.1 Extraction procedure 40

3.2.2 QuEcHERS extraction of soil 40

3.2.3 Cleanup of the extract 40

3.3 Condition of GC-MS 41

3.4 Sample Analysis for Organochlorine Pesticides Residues 41

3.5 Health Risk Assessment 42

CHAPTER FOUR

4.0 Results and Discussion 43

4.1 Proximate Analysis of Tomatoes 43

4.2 Physicochemical Characteristics of Soil 45

4.3 Organochlorine Pesticides Residues Analysis 48

4.4 Organochlorine Pesticide Residue in Soil, Fresh and Dried Tomatoes from Farmland A 62

4.5 Organochlorine Pesticide Residue in Soil, Fresh and Dried Tomatoes from Farmland B 64

4.6 Organochlorine Pesticide Residue in Soil, Fresh and Dried Tomatoes from Farmland 67

4.7 Health Risk Estimation of Organochlorine Pesticides Residues 69

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion 71

5.2 Recommendation 72

REFERENCES 73

APPENDICES 80

LIST OF TABLES

Tables		Pages
2.1	Related literatures	19
3.1	Chemicals and reagents	33
4.1	Proximate analysis of fresh and dried tomato	43
4.2	Physicochemical characteristic of soil farmland	45
4.3	GC-MS Result of organochlorine pesticides residues in soil	48
4.4	OCPs Residues in fresh and dried tomato	54
4.5	OCPS Residue in fresh, dried sample and soil A (mg/kg)	62
4.6	OCPS Residue in fresh, dried and soil samples B (mg/kg)	64
4.7	OCPS Residue in fresh, dried and soil samples C (mg/kg)	67
4.8	Health risk estimation of organochlorine pesticide residues in tomato	69

LIST OF FIGURES

Figures		Pages
2.1	Chemical structure of DDT	13
2.2	Chemical structure of Dieldrin	13
2.3	Chemical structure of lindane	14
2.4	Techniques used by previous researchers	31
2.5	Sample matrix used by previous researchers	31
3.1	Map of Samples Collection Sites	35
4.1	Comparison of OCPs Residues in fresh, dried tomatoes and soil sample A	62
4.2	Total of OCPs Residues in fresh, dried tomatoes and soil sample A	63
4.3	Comparison of OCPs present in fresh, dried tomatoes and soil sample B	65
4.4	Total OCPs Residues in fresh, dried tomatoes and soil sample B	65
4.5	Comparison of OCPs Present in fresh, dried tomatoes and soil sample C	67
4.6	Total OCP Residues in fresh, dried tomatoes and soil sample C	68

GLOSSARY OF ABBREVIATIONS

FAO	Food and Agricultural Organization
NAFDAC	National Agency for Food, Drug Administration and Control
SON	Standard Organization of Nigeria
MRL	Maximum Residual Limit
WHO	World Health Organization
OCP	Organochlorine Pesticide
GAP	Good Agricultural Practice
ARFD	Acute Reference Dose
ADI	Acceptable Daily Intake
JMPR	Joint Meeting on Pesticide Residues
PSA	Primary Secondary Amine
SPE	Solid Phase Extraction
FPD	Flame Photometric Detector
ECD	Electron Capture Detector
NPD	Nitrogen Phosphorus Detector
MS	Mass Spectrometry
POPs	Persistent Organic Pollutant
P,P-isomer	Para, Para-isomer
ND	Not Detected
HCH	Hexachlorocyclohexane
EPA	Environmental Protection Agency
DDT	Dichlorodiphenyltrichloroethane
CAC	Codex Alimentarous Commission

Mg/kg	Microgram per kilogram
Deta-pent	Deta pentachlorocychlorohexan

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the Study

Tomatoes (*Lycoperiscum esculentum, solanum Lycoperiscum.*) belong to the *solanacea* family and are one of the most widely grown vegetables in the world. The vegetable is usually grown in the summer season, but in many countries including Nigeria, it is produced throughout the year with the help of irrigation (Arah *et al*., 2015).

It is a basic ingredient of many meals in Nigeria especially, the sauces and stews which accompany most traditional dishes. Tomatoes can also be consumed raw in salads or used to make juices. It is rich in essential nutrients such as vitamins, protein, dietary fibers 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 (Ugonna *et al.,* 2015). As a result, drying of tomatoes becomes the only way farmers preserve and provide alternative to fresh tomatoes throughout the year (Opega *et al*., 2017).

Tomato farmers used pesticides such as Organochlorine for pest and disease control in order to obtain good yield. Organochlorine pesticides are highly persistent and often bioaccumulate when injected. Farmers consider organochlorine pesticides as most effective for pest and disease eradication. They are therefore often used indiscriminately by farmers in Nigeria due to their availability and low cost (Nosakhare *et al.*, 2011).

Farmers and tomato consumers are at immense risk of exposure to these organochlorine pesticides used to control the pests due to the toxic nature of the chemicals. Some of these toxic chemicals are banned or restricted in Nigeria and other countries (Ojo, 2016). Wrong application techniques and time of application of these chemicals to the

vegetables increase the risk of residual deposits (Adeluwa *et al*, 2019). Some can stick to the soil, which the plant can pick up while some can be washing into the soil or volatilization. These processes can lower the initial concentration of pesticides and also introduce their metabolites into plants. Pesticides applied to the shoot of plants can moved down the circular layer through the lipoid and aqueous pathways (Navarro *et al.*, 2017).

Organochlorine pesticides are classified into three subgroups:

i. Dichlorodiphenylethanes such as dicofol, methoxychlor, and perthane
ii. Chlorinated cyclodienes such as aldrin, dieldrin, endrin, chlordane, endosulfan, Dichlorodiphenyltrichloroethane (DDT), and heptachlor.
iii. Hexachlorocyclohexanes (HCH) which include chlordane, lindane, toxaphene, kepone, lindane, benzene hexachloride (BHC) .

These organochlorine pesticides are known for high toxicity, slow degradation and their metabolites can remained in the soil for decade. They can be transported through long distance by wind and water; they can also be imported through the importation of food containing the organochlorine pesticides (Ademola and Gideon, 2012).

In Nigeria, the following organochlorine pesticides are ban by NAFDAC; dichlorodiphenyltrichloroethane (DDT), aldrin, dieldrin, lidane, isodrin, heptachlor, endosulfan and hexachlorobenzene because of concerns on the environment and human health (EPA, 2002). Despite the ban on most of the organochlorine compounds, they are still been used in developing countries like Nigeria for pest control (NAFDAC, 2017). These continue use of organochlorine pesticides has remained a matter of international concern because of their residual persistence in agricultural products (Nosakhare *et al*., 2012).

1.2 Pesticides Misuse and Abuse

There is ample evidence of poor pesticide education leading to wide spread abuse in Nigeria (Buba *et al*., 2017). 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 (Nosakhare *et al*., 2012).

Several research works carried out in African including Nigeria was majorly to assess the level of organochlorine pesticide residues in fresh tomatoes and other vegetable which proved the use of banned organochlorine pesticide and high level of pesticide above the accepted doses or maximum residual limit (Joseph *et al*., 2014, Akinloye *et al*., 2011 & Buba *et al*., 2017). These have become important for monitoring of these persistence pesticides in fruits and vegetables for food safety.

1.3 Organochlorine Pesticide Residues

Residue is any substance or mixture of substances that present in food for man or animals resulting from the use of pesticide and any of its specified derivatives, such as degradation and conversion products, metabolites, reaction products, and impurities that are considered to be of toxicological significance (WHO, 2012).

Each country set up her own maximum residue limits (MRLs) 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), (NAFDAC, 2017).

1.4 Exposures to Organochlorine Pesticide

Exposures to organochlorine pesticide occur through the consumption of the contaminated agricultural products mainly vegetable and fruits. Pesticides are used directly to control pests and diseases, which left some residues in or on the vegetable and fruits even after harvest. As result consumers of these products are exposed to organochlorine pesticides. Exposure to organochlorine pesticides are usually high in vegetable and fruits because they are eaten raw or partially cooked (Oyeyiola *et al*., 2017). There are other ways people can be expose to organochlorine pesticides, these include wind and rainfall which move these chemicals to others places different from where they were used, causing contamination of surface water, air and soil (Fosu-Mensah *et al*., 2016).

1.5 Effect of Organochlorine Pesticide on Human

When exposed to some organochlorine pesticide residues such as lindane, heptachlor, hexachlorocyclohexane, and endosulfan, these residues are stored in adipose tissues because of their lipophilic nature. The acute toxic effects of these compounds accumulated in fat when the dose exceeded the maximum residual limit value MRL (Ojo, 2016). Maximum residual limit (MRL) of Organochlorine pesticide residues are set up by various control organization as maximum amount that is safe for human health and the environment. Amount above this maximum residual limit has serious short term and long term impacts in human body such as damage to reproductive system, immune system and carcinogenic (ATSDR, 2002).

1.6 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 (Das *et al*., 2020). They circulate worldwide via the atmosphere, rivers, oceans and other pathways. Organochlorine pesticides released in one part of the world can reach regions far from their original sources (EPA, 2000).

The organochlorine absorbed by the plant can remain in the plant tissues and be stored in the vacuoles of the plant cells which form conjugates with constituents of the plant or can be subject to a degradation process. The unabsorbed organochlorine pesticide residues on the plant surface can be volatilized or washed off the leaf surface by rain back to the soil (Joseph *et al*., 2014).

The retention and mobility of pesticides in soil is always depending on the strength of sorption reactions and the physiochemical properties of the soil. Sorption interaction of pesticides in the soil environment is usually involved the organic component of the soil and the soil type such as clay, sand and pH of the soils (Fosu-Mensah, *et al*., 2016).

Some of the climate factors which influence organochlorine pesticides persistence are rainfall, temperature air, light intensity, and wind direction. The top soil has been reported to be more contaminated by pesticides residues that can be easily partitioned into the air, which in turn increase the risk of exposures to agricultural products (Ademola & Gideon, 2012, Joseph *et al*., 2014).

1.7 Statement of the Research Problem

Pesticides are one of the major causes of self-poisoning death in low and middle income countries like Nigeria because they are inherently toxic and indiscriminately sprayed to controlled pests and diseases which in turn leave residues in agricultural products like tomatoes and other vegetable crops.

Despite the ban on most toxic organochlorine pesticides, farmers are still using it indiscriminately for agricultural pest control in Nigeria. This continued use of organochlorine pesticides result in contaminating tomatoes and the soil, with serious consequences for humans and the ecosystem in general.

One of the major tasks facing control authorities in most developing countries is the monitoring of organochlorine pesticide residues in process and unprocessed tomatoes from developing countries like Nigeria

1.8 Justifications of the Research Problems

Regular monitoring of organochlorine pesticide residues in food and environment will provide data for health risk assessment to human through direct exposure or food contamination.

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.

Monitoring of pesticides residues level in vegetables would provide a data used to assess the dietary exposures level of pesticides residues found in food and food products and also the results data can be important sources of information portraying the state of environmental contamination.

Due to several health problems causes by pesticides such as immune dysfunction, endocrine disruption, reproductive disorder and cancer. Continuous monitoring will provide information if the residues are above maximum residual limit MRL as recommended by FAO, WHO for vegetable and food commodities.

1.9 Aim and Objectives of the Study

The aim of the research was to assess the levels of organochlorine pesticide residues in fresh, dried tomatoes and soils from selected farmlands in Wank, Gusau, and Zamfara State, Nigeria.

The research was carried out with the following specific objectives;

i. Proximate analysis of fresh and dried tomatoes
ii. Determination and comparison of the organochlorine pesticides residues in the fresh, dried tomatoes and soil samples using GC-MS
iii. Comparison of level of organochlorine pesticide residues in the samples with maximum residues limit (MRL) and calculate the hazard index (HI) of organochlorine pesticides determined

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Food Safety

Food safety is an important issue that concerns every one of us on a daily basis. While consumers are concerned about the safety of their food, farmers may want to protect their crops from pests and diseases. For its part, the government is working to find ways to reduce the risk and safety associated with food. Food assessments with regard to the content of toxic compounds such as pesticide residues are very important for correct information (WHO, 2012).

Global international organisations are concern about the guarantee and control of food safety around the world such organisations are World Health Organization (WHO), the Codex Alimentarius Commission (CAC), Food and Agriculture Organization (FAO), and the Joint Meeting on Pesticide Residues (JMPR) . More also, local and regional bodies are involve in dealing with food safety in Nigeria, such local bodies are National Food and Drug Control Agency (NFDAC) and the Standards Organization of Nigeria (SON) to raise awareness on importance of food safety (WHO, 2012).

The global awareness as prove that food grown in one country can find its way to another country through food export and import. It is therefore important that the global community is aware of food safety issues in other countries. According WHO (2012), foods safety are summarise in; microbiological hazards, chemical hazards and monitoring of food borne diseases. Organochlorine pesticides are among the chemical hazards that top food safety concerns as they are used to control pests in agricultural practice (Garbutt, 2011).

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 (Ojo, 2016).

Most developed countries have put in place regulations and controls on the use of pesticides and banned most organochlorine pesticides such as DDT, methoxychlor, dieldrin, dhclordane, lindane and benzene hexachloride. But most of these organochlorine pesticides are still use in vegetables and fruits in developing countries like Nigeria (Ojo, 2016).

2.2 Maximum Residual Limit

Maximum residue limit can be defined as the highest levels of organochlorine and other pesticide residues that can be expected in food in accordance with good agricultural practice. This Good Agricultural Practices (GAP) can be defined as the good methods that includes time interval of application of pesticides and various trials that give out lowest effective rate for legal requirements in most countries (Garbutt, 2011). The residue data used by the International Regulatory Organization for Maximum Residual Limit (MRL) consider a range of climate conditions, farming practices and different varieties of corps where the pesticide has been applied with a good agricultural program (FAO/ WHO, 2013).

Maximum residual limit (MRL) are established through the use of expert judgment, modeling and statistical methods. In a recent review of estimation methods for the maximum residual limit for pesticides. It was concluded that when setting MRLs, especially in the data selection step, no universally applicable methods and no expert judgment are required (FAO / WHO, 2019). The information from monitored studies is assessed by risk assessment agencies such as EFSA in EU or JMPR for CODEX Alimentarius. The safety limit values are compared with the acceptable daily intake (ADI) for long-term exposure or the acute reference dose (ARfD) for short-term exposure (FAO / WHO, 2019).

2.3 Tomatoes Cultivation in Nigeria

In Africa, Nigeria is ranked the second largest producer of tomatoes and ranked globally the 13th largest producer of tomatoes. It total production annually is estimated to be about 1.701 million tones. The states in Nigeria that engage in commercial production are Gombe, Kastina, Bauchi, Kano, Kaduna and Zamfara State (Arah *et al.,* 2015).

Tomatoes grow well in wet-drained site with a full sun for most of the day and soil pH of 6.2 to 6.8 as well as in loamy soil. It is best cultivated in Nigeria between the months of September to January because it does not required high rainfall. Tomato is generally cultivated by transplanting seeding on ridges and furrows (Arah *et al.,* 2015).

2.4 Tomatoes Processing and Storage

Tomato fruit has a lot of qualities which contributes significantly to human health development when consumed. Tomatoes farmers suffer post-harvest challenges because it is a seasonal crop with high moisture content making it susceptible to microbial deterioration and reducing its shelf-life. Fresh tomatoes deteriorate faster when left on the market for long periods or when left under ambient conditions. Lack of infrastructural facilities for preservation and storage contribute to post-harvest loss of this vegetable fruits (Opega *et al*., 2017).

However tomato fruit can be processed into more convenient and stable shelf life such as tomato paste, tomato juice, tomato concentrated and traditional sun drying. Nigeria lack processing and storage facilities to preserved fresh tomatoes. Therefore, farmers result to traditional way of sun drying, a process where the tomatoes are exposed directly to the sun, the high temperature evaporate the moisture from the tomatoes and reduced the moisture content, which make it safe from micro organisms and increases it shelf life. Sun is the quick tradition method of drying and economically less stressful as compared to other methods such as solar drying and oven drying (Opega *et al*., 2017).

2.5 Chemical Structures and Degradation Products of Organochlorine Pesticides

Due to their chemical similarities, organochlorine compounds have a related chemical structure in which chlorine substitutes for aliphatic or aromatic rings; these compounds share certain physicochemical properties such as persistence, bioaccumulation and toxicity. The basic character fraction of these chemicals across the spectrum is persistence, which defines their half-life for months to years in water and sediment (Osofo and Frempong, (1998).

The degradation and conversion of these persistent chemicals in the environment depends on their physicochemical properties, the environment in which they are located and the threshold level of these chemicals in the environment. Some time degraded products are more toxic which resulting to bioacomolation of the toxicity of the parent compound (Kigozi, 2016).

2.5.1 Endosulfan

Endosulfan is an organochlorine insecticide and accaricide that is being phased out globally. It has two isomers which are only differ in their configuration of the seven members of dioxothiepine oxide rings. The two isomers are alpha endosulfan and beta endosulfan or endosulfan I and endosulfan II. The ratio of alpha-endosulfan and beta-endosulfan is two ratio one (Ademola *et al*., 2012). Endosulfan is a synthetic insecticide that is majorly used to control a range of insects and mites on a wide range of crops. In 2007, it was recommended that endosulfan be included in the banned organochlorine pesticides under the Stockholm Convention on Persistent Organic Pollutants (POPs) due to its persistence and public health concerns (FAO / WHO, 2007).

2.5.2 Dichloro Diphenyl Trichloroethane (DDT)

Dichlorodiphenyltrichloroethane has always use as an insecticide to eradicate insect since 1940. This insecticide always sold in commercial quantity with a technical grade of a mixture of fourteen compounds. The active component is p, p-DDT, which makes up 65 to 80%. The other compounds include o, p-DDT, p, p-DDD, and DDMU. DDT compounds can be broken down to DDD and broken down to DDE under anaerobic conditions; these breakdown products are more persistent than the parent compound (Rathore and Nollet, 2012). Because of the harmful effects on humans, and the environment its uses has been restricted under the Stockholm Convention (PIC, 2010).

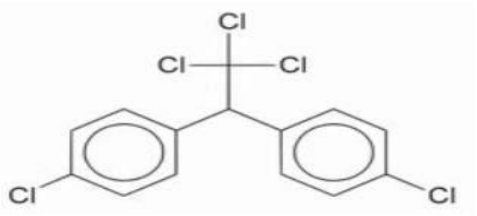

Figure 2.1 Chemical Structure of DDT.

2.5.3 Dieldrin and Aldrin

Dieldrin and Aldrin are related organochlorine pesticides which are extremely persistent in the environment. They are insecticides and both are used in agricultural for vector control, veterinary purpose and termite controlled. Aldrin can be transformed into dieldrin in both plant and animal. Dieldrin breakdown slowly and not easily evaporate into air, but it easily bind to soil organic matter (Rathore and Nollet, 2012), plant take up dieldrin and aldrin residues from the organic matter of the soil. The residues store in the fatty tissue in both human and animal and they metabolise very slowly in the body. Dieldrin and aldrin are not water soluble and it's highly toxic to human causes liver cancer, even with short term exposure. Its production and uses are being eliminated internationally under the Stockholm Convention (PIC, 2010).

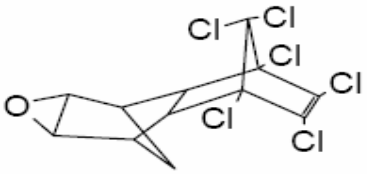

Figure 2.2 Chemical structure of Dieldrin

2.5.4 Hexachlorocyclohexane (HCH)

Hexachlorocyclohexane is a manufacture chemical that has eight isomers and the most common one is gamma HCH which commonly called lindane. It is use as insecticide to control pest in fruits, vegetables and forest crops. It is a solid white powder and the technical grade of lindane contained about 10-15% gamma HCH and other isomers such as alph, beta and deta form of lindane (Osofo and frempong, 1998). The isomer has been identifying as toxic to human when the residues are present in the food chain. Their use was controlled and later banned by the Stockholm Convention (PIC, 2010).

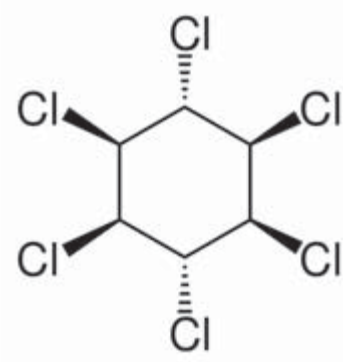

Figure 2.3 Chemical structure of Lindane

2.6 Working Principle of Gas Chromatography Couple with Mass Spectrometer

Various methods have been developed in the last decade for sample preparation determination of organochlorine pesticide residues. The most widely used methods by different researchers is gas chromatograph, because of its high separation power and ability to accommodate selective detectors such as Nitrogen phosphorus detector (NPD), flame ionization detector (FID), electron capture detector (ECD) and Flame photometric detector (FPD).

Gas chromatography coupled with mass spectrometry (GC-MS) is widely used in the analysis of pesticide residues that are highly volatile. Because it's gives fine identification and quantification in various vegetables matrices (William, 2012).

Gas chromatography contains a mobile and stationary phase. The mobile phase is usually helium or nitrogen gas while the stationary phase is packed in the column with layer of liquid or polymer on an inert solid support inside capillary tube. The gaseous sample being analyzed carried by mobile phase call carrier gas, interacts with the stationary phase within the column, this exposes each constituent in the mobile phase to the stationary phase. The retention time of each constituent would depend on affinity of the gaseous sample with stationary phase within the column and elute at different times (William, 2012).

The basic principle of Mass spectrometry for quantitative analysis is that the instrument measured the signal representative of the analyte relative to a known amount of an internal standard. To ensure that the signal is representative of the particular substance to be measured and not a result of some other substances matrix, combination of mass spectrometry with gas chromatographic separation is always use and selective chemical derivatization frequency allows quantification of substances at the ppm and ppb level.

Table 2.1 below shows the techniques, sample treatments, detectors and conditions used by different researchers to determined organochlorine pesticide residues in different sample matrix in the last ten years.

Figure 2.1 below summaries the techniques used by the various researchers, which shows that GC-MS techniques was employed by 39% , follow by 35% researchers who used GC-ECD, while GC-MS/MS, GC-MS/ECD, GC-MS/MSD was 4% each, and GC×GC-ECD, GC-FID, GC-MS/FID, LC-MS were 2% researchers.

Figure 2.2 summaries the sample matrixes analyzed by the researchers in the last ten years, it shows that vegetables and fruits was the most samples matrixes used by different researchers than other food and food products. Tomato 15% was the highest among the vegetables sample matrixes, because tomatoes is one of the most highly consume vegetables in different sources including cooked and uncooked.

Table 2.1 Review of previous Techniques and Samples Matrix used by different Researchers in the last 10 years

MATRIX	SAMPLE TREATMENT	DETECTOR AND CONDITION	ANALYTES	LOD	REFERENCES
Pumpkin and Amaranths	n-Hexane and Dichloromethane	GC-ECD, silica capillary Colum(B-17,30M×0.250M Internal diameter, temperature, 250-290 ^{O}C)	Heptachlor ,Dieldrin,aldrin, Endrin, Endosulfan,and Endosulfan Sulphate	0.014 mg/kg	Adeoluwa *et,al*., 2019
Lettuce, Spinach Onion, Spinach and Soil	Hexane-to-acetone 1:1 V/V, SPE , pesticide cartridge for clean-up	GC-MS (MSD), Colum size HP-5,(30mm × 0.25mm × 0.320µm). oven temperature; 80-280 ^{O}C, flow rate; 10 ^{O}C for 1min, carrier gas; helium 99.9%, 0.5ml per minute	BCH, Chlorothalonil, Heptachlor,Aldrin, Endosulfan,dieldrin, Endrin and DDT.	-	Adebisis *et al*., 2020
Tomatoes	Dichloromethane and Cyclohexane	GC- FID, silica capillary column 60oC, auto-sampler, helium gas (30m×320µm × 0.25µm), with temperature 210 ^{O}C -320 ^{O}C	BCH, Heptachlor, Aldrin, Endosulfan, DDE, Dieldrin, Endrin, Methoxychlor	0.001	Araromi *et al.*, 2020
Lettuce, Spinach, Moringa, Okra, Pepper and Tomatoes	QuEChERS Acetonitrile and clean up with SPE, with PSA	GC-MS with ECD. Nitrogen as carrier gas (Hp-5MS), Column size (30cm × 0.34mm ×0.25µm), 60^{o}C oven temperature, 250^{O}C -300^{O}C	DDT ,Edrin, Endosulfan, Lindane, Methoxyclor	-	Buba *et al*., 2017
Opuntia joconostle	Hexane/dichloromethane 1:1 v/v,	GC-ECD.(Column,HP-5, 30m, 0.25m, 0.25mm,) 200 ^{o}C to 300 ^{o}C, helium gas	HCH, Heptaclor, aldrin, DDE, dieldrin, DDT and DDE		Jose *et al*., 2016
Vegetable (*Telfairia occidentalis and celosia argentea*)	Ethylacetate and Sodium Sulphate	GC-MS, capillary column (HP-5MS-3M, I.D 0.25mm and 0.25µm thickness) pack with 5% phenylmethyl siloxane.	Heptachlor, Aldrin, Endosulfan	-	Njoku *el al*., 2017

MATRIX	SAMPLE TREATMENT	DETECTOR AND CONDITION	ANALYTES	LOD	REFERENCES
Soil and Drinking Water	Acetonitrile and Dichloromethane	GC-ECD, Capillary column (VF-5, 30m -10m internal diameter, 0.25 thicker, 180 ^{O}C -300 ^{O}C temperature)	Lindane, Dieldrin, HCH, DDT	-	Fosu-Mensah *et al.,* 2016
Yellow Pepper	Acetonitrile, magnesium sulphate and sodium chloride	GC-MS with ECD. Nitrogen as carrier gas (Hp-5MS), Column size (30cm × 0.34mm ×0.25µm), 60 ^{O}C oven temperature, injector temperature of 250 ^{O}C -300 ^{O}C	Chlorothalonil, delta Methrin and Chlorpyrifos	-	Raluca *et al.,* 2016
Spinach, Lettuce, Cabbage, Tomatoes, Onion, and Carrots	QuChERS method, clean up with SPE and PSA.	GC-MS, capillary Column (RTX-5, 30m×250µm×0.25µm), helium gas. 190 ^{O}C - 250 ^{O}C temperature	BCH, Lindan, Heptachlor, Aldrin, Endosulfan, Dieldrin	-	Suleiman *el al.,* 2020
Vulgaris	Dichoromethane, Hexane ratio 7:3 volume.	GC-MS, HP-5m column, fused silca (30×0.25×0.25mm). helium gas, auto sampler with temperature of 250-280 ^{O}C.	Endosulfan, lindane, heptachlor, Aldrin and Mitotane	-	Adewole *el al.,* 2021
Tomatoes	Ethylacetate, Sodium suphate	GC-MS, with SGE BPX-5 of 60mm, column (0.25mm×0.25µm). 90 -275 ^{O}C temperature	HCH,HCB, Heptachlor, Aldrin, DDE and DDT	-	Nunifant K.T. 2011
Vegetables (Cabbage, Lettuce and Onion), Soil and Water	Acetone/ Ethylacetate, Sodium sulphte, Hexane/Acetone ration 3:	GC-ECD, VF-5M, capillary column (30m×0.25mm×0.25µm). 250-300 ^{O}C	HCH, Heptachlor, Endosulfan, Dieldrin, Endrin, DDD, DDT and chlordane	-	Vinceat *et al*., 2019

MATRIX	SAMPLE TREATMENT	DETECTOR AND CONDITION	ANALYTES	LOD	REFERENCES
Watermelon, Carrot, Cucumber, Cabbage, Lettuce, Wheat and Millet	N-hexane, Dichloromethane, Ethylacetate, Sodium sulphate, acetonitrite. SPE Cartridges	GC-ECD, HP-5, column (30m×0.25mm×0.25µm). Nitrogen gas was used	Aldrin, BHC,DDT, DDE, DDD, Endosulfan, Lindane, Dieldrin, Heptachlor.	0.1-0.6	Oyeyiola *et al.*, 2017
Tomato and Watermelon	Acetone, Dichloromethane, Cyclohexane 1:1 sodium Suphate was used for clean up.	GC-MS. Column (Rtx-5MS of 30m×0.25mm×0.25µm) temperature program 90 ^{O}C – 260 ^{O}C. Helium gas was used.	HCH, DDD, DDE,Endosulfan, Chlorpyrifos and Cyprmethrin	-	John *et al*., 2017
Sediments	Acetone /hexane 1:1 dichloromethane	GC-MS column (HP-5, 30m×0.32mm×0.25µm) 190-250 ^{O}C. Helium gas used	HCH, DDD, DDE,DDT ,Dieldrin, Endrin, Heptachlor, Endosulfan	-	Kai *et al.*, 2020
Watermelon, Pineapple, Banana	Ethylacetate, Sodium Bicarbonate, Sodium sulphate.SPE use for cleaned up.	GC-ECD, Column (VF-5Ms, 40m×0.25mm×0.25µm) temperature; 270 ^{o}C -300 ^{o}C. Nitrogen gas was used.	HCH, Heptachlor, Aldrin, Chlordane, Endosulfan, Dieldrin endrin, DDT, DDD, Methoxychlor	-	Frederick *el al*., 2018
Water and Sediment	Hexane to acetone (3:1 v/v)	GC-ECD	HCH, DDD, DDE, DDT, Aldrin, Endrin, Dieldrin	-	Nyaundi *et al.*, 2019
Soil	Dichloromethane, SPE extraction cartridge, sodium sulphate	GC-ECD column (30m by 0.25mm i.d by 0.25µm) 280-300^{o}C	HCH, DDE, DDD, DDT	0.094-0.078	Teresial M. & Jun, W. 2019

MATRIX	SAMPLE TREATMENT	DETECTOR AND CONDITION	ANALYTES	LOD	REFERENCES
Soil and sediment	n-hexane,and acetone	GC-ECD.(0.25mm i.d, 0.25µm).250-300 °C, nitrogen	BHC,DDE,DDT,Dieldrin, Endosulfan	-	Navai *et al*., 2018
Bell pepper, egg plant, Cucumber, Cabbage, Carrot, and potato	QuEChERS, Acetonitrile, PSA	GC-MS Column (RTX-5MS, 30M long, 0.25mm internal diameter, and 0.25µm thickness). 250- 300 °C	Chlorpyrifos- methyl, Lmidacloprid, Acetamiprid, Thiophanate-methyl, Metalaxyl, Difenoconazole, Aldrin	-	Mustapha *el al.*, 2017
Kola nuts	N-hexane and Dichloromethane. Cleaned up with activated silica gel	GC-ECD column (30m×0.32mm i.d×0.25µm film thickness).150-200 °C	HCB, Aldrin, Chlordane, Heptachlor, Dieldrin, Endrin, DDT	-	Sosan, M.B. & Oyekunle, A.O. 2017
Tomatoes, Onion and Water.	QuEChERS, and SPE-PSA, cleaned with Magnisum Sulphate and Cartridge.	GC-MS column,(30m length, 250µm internal diameter, 0.25µm film thinknes). 275 °C -310 °C	DDT,DDE, Endosulfan, cyhalothrin, metalaxyl and profenofos	-	Kumelachew *et al*., 2020
Pumpkin, Spinach and Sorrel leaf	Acetonitrile with 1% acetic acid, and clean up with dSPE and PSA	GC-MS with 35% diphenyl, 65% dimethylpolysiloxane column, temperature, 150-290 °C	Endrin, DDT, BHC, Dieldrin, Aldrin and Endosulfan	-	Ibrahim *et al*., 2018
Soil and Sediment	QuEChERS and cleaned with PSA and magnesium Sulphate	GC-MS, column (30m×0.25mm i.d ×0.25µm). temperature (270-290 °C)	DDE, DDT, DDD	-	Mahugija *et al*., 2017
Soil	Hexane/ ethylacetate 9:1 and dichloromethane	GC-ECD, capillary column (HP-5, 30m×320µm i.d× 0.25µm thickness). 250oC to 300oC	Dieldrin, Endosufan, DDT, Aldrin	-	Jumepaeng &Pongpun, 2020
Potato and Carrot	Acetone and n-hexane, cleaned with florisil and sodium sulphate	GC-ECD with VF 1701 (30M×0.25mm ×0.25µm). temperature of 200 to 240 °C	Lindane aldrin ,heptachlor Dieldrin, DDT,	-	Rahmawati *et a*l., 2017

MATRIX	SAMPLE TREATMENT	DETECTOR AND CONDITION	ANALYTES	LOD	REFERENCES
Tomatoes	Acetonitrile, magnesium sulphate and sodium chloride. Clean up with PSA	GC-ECD, Nitrogen was used as carrier gas, and injection temperature was 280 ^{o}C to 300 ^{o}C	HCH, Dieldrin, DDD,DDT, DDE, Endosulfan, Heptachlor.	0.0015	Mohammed &Boateng 2017
Tomato, green chili, Cucumber and country bean	QuChERS with Acetate buffer	GC-MS. Column (30m×0.25mm i.d×) temperature from 160 to 300 ^{o}C	Dimethoate, Melathion and Cloropyriphos	-	Mehedi & Azizur, 2019
Eggplant and Tomatoes	QuChERS , Magnesium Sulphate, and PSA	GC-MS. Column (RTX-5, 3mm×0.25mm i.d,×0.25µm) . temperature 250oc to 270oc.	Endosufan, Malathion, Dimethoate	-	Salah *et,al*., 2020
Tomato, Banana Lettuce, Cucumber Onion.	Dichloromethane, sodium acetate. Clean up with SPE- cartridge	GC-MS. Column (30m×250µm×0.25µm). Carrier gas was Helium. temperature of 110 ^{o}C to 320 ^{o}C	HCH, Heptachlor, Adrin, DDE, DDD, DDT, Dieldrin, Endosulfan, and Methoxychlor	0.13 - 0.06	Cemile O., 2016
Apple, Orange, potato, Tomato, and Cucumber	QuChERS , magnesium sulphate, and PSA	GC-MS/MS , Column (Rtx-5,30m×0.25mm i.d×0.25µm)	HCH, Endosulfan, DDD, DDE, DDT and Heptachlor.	0.01	Ahmed *et, al., 2019*
Tomato	Dichloromethane, sodium sulphate,and silca gel	GC-ECD, capillary column (30m×0.32mm i.d×0.25µm). temperature 200	HCB, HCH, DDE,DDD,DDT and Trans-nonachlor	0.063-0.102	Nsikak & Aruwajoye 2011
Tomato and lettuce	Ethyacetate and hexane 2:1 v/v,	GC-ECD. Column (BPX-5 of 60m capillary with o.25mm i.d×o.25µm). Temperature, 250 ^{o}C -300 ^{o}C. Nitrogen was used as carrier gas	HCH,Aldrin, Dieldrin, Endrin, Heptachlor, DDT, DDE, DDD.	0.001	Kolani *et al*, 2016
Okra,	Hexane/isopropyl 2:1 v/v.	GS-MS. Column (2m packed	Endosulfan, Dimethoate,	-	Sal *et al*., 2018

MATRIX	SAMPLE TREATMENT	DETECTOR AND CONDITION	ANALYTES	LOD	REFERENCES
Cabbage, and Cauliflower	Activated charcoal.	with 3% OV-101, mesh CHW.	and Melathion		
Cabbage , soil and water	Methanol and SPE	GC-ECD, Column (30m×0.32mm i.d×0.25µm) Helium gas flow temperature; 250-300 °C	HCB, lindane, DDE, DDD, DDT, HCH, Endosulfan, and Endo sulfan sulphate.		Owusu and Kafi 2013
cabbage, Tomato, lettuce cucumber and green pepper	Acetonitrile, n-hexane, acetone.(10:90) Cleaned up with SPE	GC-MS column (HP-1, 30m×0.25mm×0.25µm) Temperature; 200 °C to 320 °C. Helium gas was used	Chlorothalonil, Chloropyrifos,	-	Liang *et a*l., 2018
Sweet pepper,	Dichloromethane and clean up SPE - Hexane	GC-MS, FID , capillary column (30m×025mm i.d× 0.25mm thickness) temperature; 230 to 280 °C	Heptachlor, Endosulfan, Dimethoate, Diazion	0.007	Azhari *et al*., 2019
Cucumber and Tomato	Acetonitrile, and cleaned up with C18 cartridge	GC×GC-ECD Column (10m×0.18mm×0,20µm) Helium gas, 250oc to 290oc	HCH. DDT, aldrin, heptachlor, endosulfan		Joseph & Michiga 2010
Fruit and vegetables	QuEChERS	GC-MS. Column (DB35-5, 60m ×0.25mm i.d,0.25µm). Nitrogen gas and temperature 280 °C to 360V.	HCH,DDT,Heptachlor, and Chorodanes		Kapeleka *et al.*, 2020
Green mustard, cucumber, rock melon, Orange,	Dichloromethane, Hexane, acetonitrile, silca gel, and PSA	GC-FPD, column (HP-5, 15m×0.53mm×1.5µm i.d) nitrogen gas, temperature 270-280 °C	Dimethoate, Chloropyrifos, triazophos, Diazinon.	0.01-0.05	Chai, and Nurdzaina, 2011

MATRIX	SAMPLE TREATMENT	DETECTOR AND CONDITION	ANALYTES	LOD	REFERENCES
Watermelon and Soil	Acetonitrile, SPE-Cartridge for cleaned up	GC-ECD, 35% Diphenyl Dimethylpolysiloxane column. At temperature of 200 °C to 290 °C	DDE, DDD, DDT, Aldrin and Dieldrin	-	Joseph C.Akan *et al.*, 2015
Apple, Grapes, Tomato, lettuce, potato, Cabbage	QuEChERS, SPE	GC-MS	Dieldrin, Heptachlor, Endosulfan	-	Balawan & Dipyendu 2017
Grape ,Apple, Orange, Guava	Acetonitrile, and Sodium Sulphate.	LC-MS and GC-MS	DDT, Dichlorvos, Dimethoate, Chlorpyrifos and Endosulfan sulfate	-	Sunaja & Leethyat 2017
Animal Feed and Fat tissue	Acetone and methanol 5:2 v/v, Acetonitrile	GC-MS/MS, Column (30m×0.25 i.d× 0.25µm) Helium gas used, temperature 280 °C to 300 °C	BHC, DDE,DDD,DDT Heptaclor, Aldrin, Endosulfan, Dieldrin, Endrin, and Methoxychlor	-	Paneri *el al*., 2013

KEY: GC = Gas chromatography, MS = mass spectroscopy, ECD = Electron capture Detector, FID = Flame Ionizing Detector.

LOD = limit of detection

Figure 2.4 and 2.5 below shows the various techniques and samples matrix used for determined pesticide residues by different researcher in the last 10 years

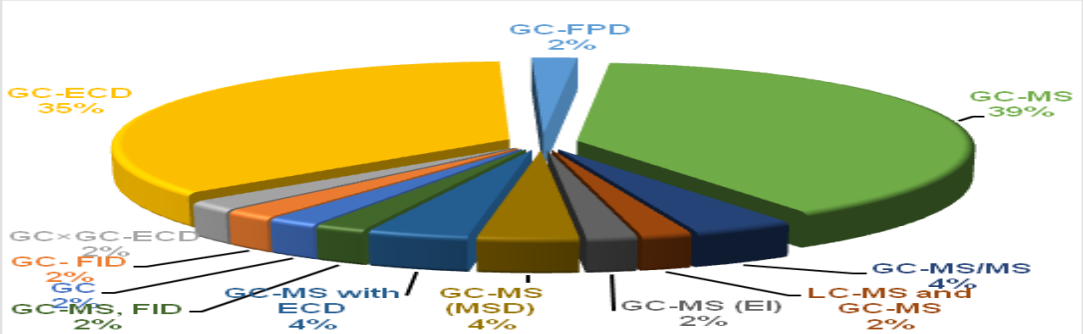

Figure 2.4: Techniques used by different researchers in the last 10 years

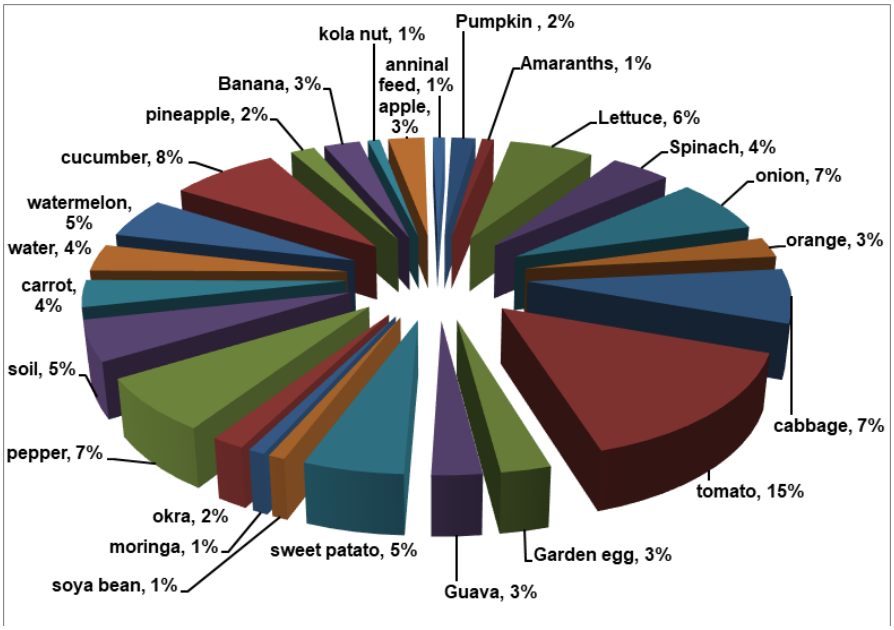

Figure 2.5 Samples matrix analysis by different researcher in the last 10 years

According to the World Health Organization (WHO, 2012), vegetables such as tomatoes are highly consumed worldwide. African accounts for 17% consumptions, and 31% consumptions for European. Tomatoes and other vegetables provide nutrients that are necessary for the body to function properly. A high intake of tomatoes and other vegetables is recommended for more than servings per day to prevent phenomena such as vitamin deficiencies and other serious diseases such as cancer and cardiovascular disease WHO, 2011). These concerns have led an international food safety agency and regulator such as the World Health Organization (WHO) and the Food Agriculture Organization (FAO) to set maximum residue limits (MRLs) for organochlorine pesticide level permitted in tomatoes and other vegetables.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 Chemicals/Reagents

The chemicals and solvents used in the research are as listed below. All the chemicals and solvents were purchased and used without any further purification.

Table 3.1 Chemicals and reagent used in the study

Chemical/solvent	Manufacturer	Purity
Acetonitrile	LobaChemie PVT	99.0%
n-hexane	M&B	90%
Magnesium Sulphate	M&B	99.5%
Sodium Chloride	BDH	99.5%
Sodium hydroxide	Loba chemie	99%
Primary Secondary Amin	Agilent TECH.	99%
Sodium Sulphate	BDH	98%
Sulphuric acid	BDH	98%
Petroleum ether	Naphtha	60%
Methyl red indicator	BDH	99%
Dichloromethane	TNJ Chemical industry	99.5%
Acetic Buffer	Sigma-Aldrich	99%
Ethanol	JHD	99%

Key: M&B = May and Baker, England, JHD = Guangdong Guamghua Sci-Tech Co.,Ltd, China BDH Bristish Drug House, England

3.1.2 Pesticide standard

Sixteen organochlorine pesticides used are deta pentacyclorohexane, alpha lindane, beta lidane, endosulfan I, endosulfan II, heptachlor I, heptachlor II, aldrin, isodrin, dieldrin, mitotane, endrin ketone, methoxychlor, DDMU, DDT and p,p DDE.

3.1.3 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.

3.1.4 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. Each sample was divided into two and one portion was sun dried and the fresh portions were transported to the department of chemistry laboratory, Federal University of Technology Minna, and preserved pending preparation and analysis.

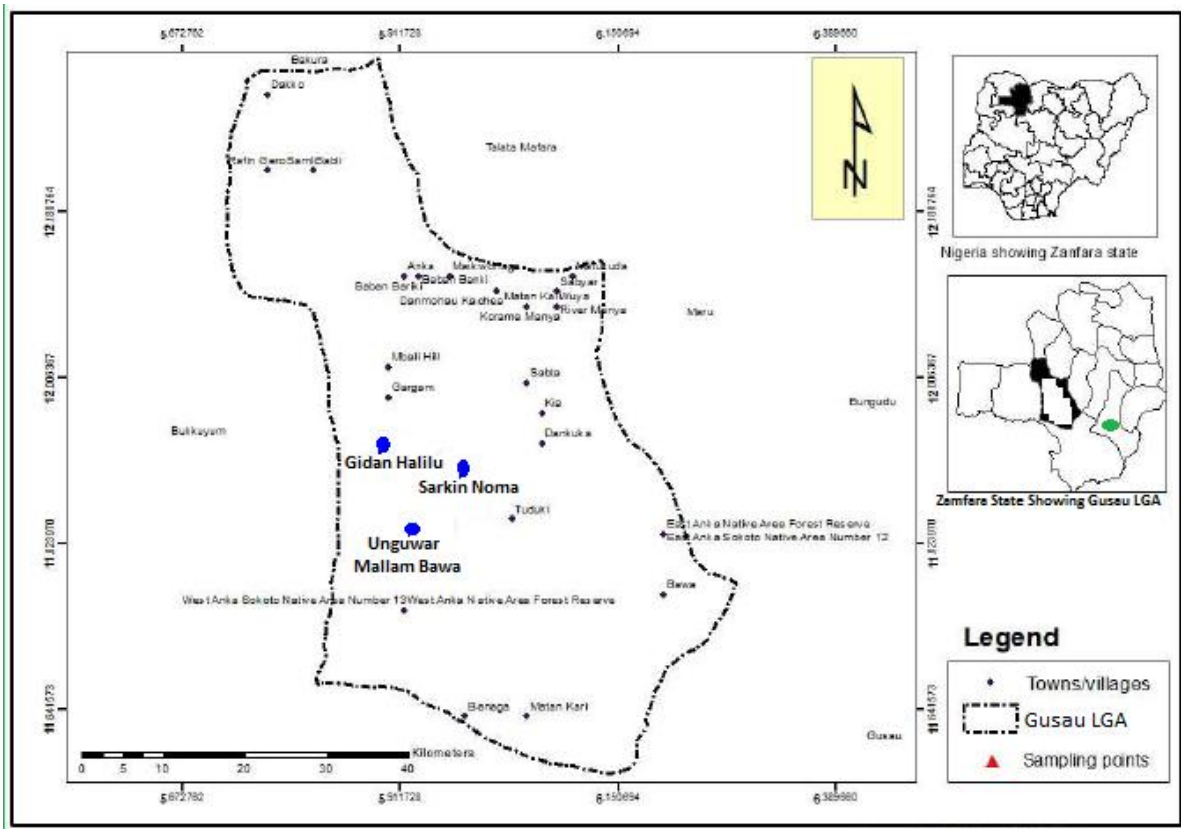

Figure 3.1 Map of samples collection sites

3.1.5 Proximate analysis of fresh and dried tomato

Proximate analysis was carried out to determine the ash, moisture, fibre, lipid, carbohydrate, and protein contents using AOAC Methods (2003, 2000, &2005).

3.1.5.1 Moisture contents

Moisture contents were determined using vacuum oven method as described in AOAC, (2003). Cleaned weighed crucible was placed in an oven at 105^{o}C for 15 minutes, cooled in desiccators and then weighed W_1. Then five grams (5g) of the sample was placed in the crucible, W_2. This was placed in an oven at 105^{o}C for 24 hours, cooled and weighed. This

was repeated until constant weight was obtained, W_3. It was then calculated using equation 3.1.

$$\% \text{ Moisture Content} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad (3.1)$$

Where,

W_1 = weight of the empty crucible

W_2 = weight of empty crucible + samples

W_3 = weight of the crucible + weight sample after heating.

3.1.5.2 Ash content determination

An empty dried Porcelain crucible was weighed (W_1) and five grams (5g) of the sample was placed in the crucible (W_2,) after which the crucible contained the sample was placed in a muffle furnace at 600^{O}C for 24 hours. The crucible with the sample are cooled in a desiccator and are weighed (W_3). The percentage of ash content was then determine using equation 3.2.

$$\% \text{ ash content} = \frac{W_3 - W_1}{W_2 - W_1} \times 100 \quad (3.2)$$

Where: W_1 = weight of empty crucible

W_2 = weight of empty crucible + sample before

W_3 = weight of empty crucible + sample after

3.1.5.3 Determination of fat/lipid content

Soxhlet extraction technique was used to determine the percentage lipid content. five gram (5g) of blended sample was weighed and wrapped carefully with filter paper and placed in

a extractor chamber of the quick fit bottom flask containing 200 cm^3 of petroleum ether. The experiment was allowed to stand for 4 hours. The wrapped filter paper was placed in oven to dry for 3 hours at 105^OC and cooled in desiccators for 30 minutes, then weighed. The percentage of fat/lipid content were determine using equation 3.3

$$\% \text{ Fat content} = \frac{W_2 - W_1}{W_2 - W_1} \times 10 \quad (3.3)$$

Where;

W_1 = weight of empty flask + anti-bumping granules after extraction

W_2 = weight of flask + anti-bumping granules + sample before extraction

3.1.5.4 Determination crude protein

Determination of percentage crude protein content was carried out using semi-micro kjeldal method. Two grams (2g) of sample was weighed with a filter into a kjeldal flask and 25cm^3 of concentrated H_2SO_4 was added using 10cm^3 pipette and heat gently in the digestion unit at 30^OC until it liquid turn brown colour and allowed to cool. The content was diluted with 200cm^3 of distilled water and distillate with distillation apparatus. 50cm^3 of 2% boric acid was measured into a cleaned conical flask with addition of 80cm^3 of 40% sodium hydroxide in presence of seven drops of methyl red indicator and swirl. This was titrated with standard 0.02M HCl until a neutral grey end point was obtained (AOAC, 2005). The percentage content of crude protein were calculated using equation 3.4

$$\% \text{ protein content} = \frac{(ml\ of\ acid) \times (N\ acid) \times (0.014N) \times (100)}{Weight\ of\ sample} \quad (3.4)$$

3.1.5.5 Determination of crude fibre

To determine crude fibre content, ten grams (10g) of the sample were boiled in 10 cm^3 of 1.25% of dilute sulphuric acid, after which the content was washed with water and later boiled with 20 cm^3 of 0.0313 M sodium hydroxide. The remaining residues were dried and weighed the percentage crude fibre was calculated as shown in the equation below

$$\% \text{ Crude Fibre} = \frac{final\ weight \times 100}{original\ weight} \quad (3.5)$$

3.1.5.6 Total carbohydrate content

Total carbohydrate content was obtained by addition of the percentage moisture, fat, protein and ash contents and the sum value was subtracted from 100 as shown in the formula,

% Total carbohydrate = 100 – (% moisture + % fat + %protein + % ash) (3.6) .

3.1.5.7 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 shaked vigorously for 30 minutes. Calibrated glass electrode was dipped into the solution and reading was taken (AOAC, 2005).

3.1.5.8 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 (AOAC, 2005).

3.1.5.9 Determination of soil organic matter

Loss of ignition method as described in AOAC, (2005) 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: LOI % = $\frac{DM}{Ms} \times 100$ (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 (AOAC, 2005).

3.2 Determination of Organochlorine Pesticides

The Quick, Easy, Cheap, Effective, Rugged and Safe (QuEchERS) method was used for sample preparation. This method is valued for its simplicity, low cost, and ability to extract pesticides from various matrices (AOAC, 2017).

The QuEChERS method is 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. The method has been use to determine wide range of pesticide residues in various food matrices. This method was adopted by US Department of Agriculture for pesticide analysis for food and food product (AOAC, 2017).

3.3.1 Extraction procedure

Fresh tomatoes samples were homogenized with 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 shake 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 (AOAC, 2017).

3.3.2 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.

3.3.3 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 carried out 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 (AOAC, 2017).

3.4.1 Measurement and condition of GC-MS

The analyses were carried out at Nigeria Institute of Oceanography and Marine, Lagos. 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 with 99.9% purity and flow rate of 2.17ml/minute while the pressure was 150 kpa. The interface temperature was 300^{o}C.

3.4.2 Sample analysis for organochlorine pesticides residues

Internal standard technique was employed to analyze the fresh, dried and soil extracts. The organochlorine standard used are alpha lindane, delta lindane, Endulfan I&II, heptachlor, aldrin, Isodrin, trans-chloro, P-chlorophenyl ethylene (DDMU), DDT, P,P-DDE, dieldrin, Endrin, mitotane, Endrin keto, melhoxychlor and delta pentachlorocyclohexane with different concentrations ranging from 0.100 to 2.00ppm of the internal standard.

The control and the extracts from sample were analyzed under the same condition as the standard. Residual level in mg/kg was calculated using the formula below;

Residuelevel (mg/kg) =

$$\frac{peak\ area\ of\ the\ sample}{peak\ area\ 0f\ \ the\ standard} \times \frac{\mu L\ of\ standard}{\mu L\ of\ sample\ injected} \times \frac{final\ volume\ of\ standard\ in\ cm^3}{mass\ of\ sample\ in\ g} - - - \quad (3.9)$$

3.5 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 (EPA, 2000) 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 (EPA, 2000).

It was assumed that the quantity of tomato consumed by an average person in day was 0.037 kg/day FAO/WHO, 2015). 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 (FAO/WHO, 2015).

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 (EPA,2011).

$$\text{EADI} = \frac{Residual\ pesticide\ concentration\ mg/kg \times consumption\ rate\ in\ kg/day}{body\ weight\ in\ kg} \qquad (3.10)$$

$$\text{Hazard index (HI)} = \frac{EADI(mg/kg/day)}{Refrences\ dosemg/kg/day} \qquad (3.11)$$

CHAPTER FOUR

4.0 Results and Discussion

4.1 Proximate Analysis of Tomatoes

Table 4.1 Proximate analysis of fresh and dried tomato

Samples	Fresh tomatoes (%)	Dried tomatoes (%)	Difference (%)
Moisture	97.70	10.52	81.18
Ash	0.21	3.93	3.72
Carbohydrate	7.60	76.4	68.80
Protein	2.50	0.12	2.38
Fiber	0.17	6.42	6.25
Lipid	0.20	0.23	0.003

The results of proximate analysis of the fresh and dried tomatoes extract are given in the Table 4.1 above. The results show that the moisture content of fresh tomatoes decreased from 91.70% to 10.52% after sundried. The result was similar to finding of Opadotu *el al.* (2016) on comparison of nutritional value of tomato subjected to different drying methods which gave moisture content in fresh tomatoes as 40.14% and sundried as 9.04% .

Lower moisture content maybe the reason of increase in carbohydrate content of dried tomatoes which was seen to have increased from 7.60% to 76.40% for fresh and sundried respectively. This trend was also reported in the work of Opadotu *et al*. (2016) where fresh and dried tomatoes have carbohydrates content of 8.70% and 30.93% content respectively. Similarly, Mashi *et al.* (2020) observed that fresh and dried tomatoes have 9.94% and

31.77% carbohydrate content respectively. This may be the reason of high calories in the dried sample as reported by Aliyu *et al.* (2018).

A significant increase in the ash content was observed in sundried samples with the fresh and dried tomatoes having 0.21% and 3.93% ash contents respectively. Ash content determines the percentage of mineral elements present in the sample (Opega *et al*. 2017). Increase in percentage of ash content of dried tomatoes indicated that dried tomatoes may provide high percentage of essential mineral elements required by humans.

The fibre content of fresh and dried tomatoes are 0.17% and 6.42 respectively, the percentage fibre content was high in dried samples compare to fresh ones. This is similar to finding of Opadotu *et al.* (2016) who observed an increase in fibre content with decrease in moisture content.

Protein content of fresh and dried tomatoes are 2.5% and 0.23% respectively. Protein is an essential macro nutrient that provides the body amino acids for growth and development (Opega *et al*., 2017). Crude protein content was high in fresh sample compared to dried ones. This shows that decrease in moisture content decrease the crude protein content of the tomatoes. This is similar to the finding of Opadotu *et al.* (2016).

Lipid content was a little high in dried sample compare to fresh sample as shown in the result with obtained value of 0.20% and 0.23% for fresh and dried respectively. This was similar to the finding of Mashi *et al*. (2020) who reported an increase in fat/lipid with decreasing moisture content.

Generally, sundried tomatoes are those that are dehydrated after exposure to sun, they shrink and lose up to 90% of their water content. These are traditional way of preserving postharvest tomatoes. Table 4.1 shows that dried tomatoes can provide high mineral elements because of the high ash content while fresh will provide high protein content.

4.2 Physicochemical Characteristics of Soil

Table 4.2 Physicochemical characteristics of soil farmlands

	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	50.09 ± 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

The results of sand, clay, silt, pH and organic matter of the soils from the farmlands are presented in Table 4.2.

From the Table, the result shows that soil sample B has sand content of 50.09±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 (Fosu-Mensah *et al.*, 2016).

Soil sample B has the highest percentage sand content but low in clay content. It is expected to have low water retention because of its larger particles size (Fosu-Mensah *el a*t., 2016).

Generally the proportion of sand, clay and silt affect the movement of water in soil, sandy soil with large pores and thus high permeability allows rapid flow of water, while clay textures of the soil have low permeability and hence more water retention capacity and tendency to absorb more chemical substances onto it. The behavior of pesticide in the soil environment is greatly influenced by the soil texture. Sandy soil tends to facilitate leaching, clay soils help accumulation through colloid formation. Sandy soil has negative correlation to pesticide because it decreases the retention capacity of the organochlorine pesticide in the soil and in turn reduces the absorption of pesticide by the roots of crops. The clay and silt has positive correlation to the pesticide and have high retention capacity toward the pesticide in the soil and thus increase in absorption of pesticide by the root of crop (Fosu-Mensah *et al,* 2016*).*

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 (Fosu-Mensah *et al*., 2016).

Organic matter of the soil has a positive correlation with organochlorine pesticide because organochlorine pesticides bind strongly with organic matter of the soil (Fosu-Mensah *et al*., 2016*)*.Therefore, soil C with high organic matter is expected to retain more pesticide and it metabolites.

Pesticides are designed to be 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 (Fosu-Mensah *et al*., 2016).

4.1 Organochlorine Pesticides Residues Analysis

Table 4.3 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	0.626	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

The results of OCPs residues in the soil samples are shown in the Table 4.3. From the table, 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 (EPA, 2011).

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 Ademola & Gideon (2012), in the soil of Cocoa plantation in Ondo State of Nigeria. Alpha lindane was also reported in the findings of Fosu-mensah *et al.* (2016) 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 (WHO, 2011). 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 (WHO, 2011).

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 (WHO, 2011).

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. Ademola &Gideon (2012) 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 (Ademola & Gideon, 2012).

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 Fuso-Mensah *et al*. (2016). 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 (WHO, 2012).

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 Fuso-Mesah *et al.* (2016) 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 (WHO, 2012).

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 Idowu *et al.* (2013) 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 (EPA, 2011).

The correlation between the sand, clay, silt, organic matter and pH of farmland as shown in Table 4.2 and the organochlorine pesticide determined in Table 4.3 may be explained thus;

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. Fosu-Mesah *et al.* (2016) reported that negative correlation occur between the soil with low organic matter and pesticide and positive correlation is observed between soil with high organic matter and pesticide.

Table 4.4, OCPs Residues in fresh and dried tomato

OCPs	FT- A (mg/kg)	DT- A (mg/kg)	% Dif.	FT- B (mg/kg)	DT- B (mg/kg)	% Dif.	FT- C(mg/kg)	DT- C (mg/kg)	% Dif.	MRL mg/kg	WHO/ NAFDAC
Deta-pent	ND	ND	NP	0.012	ND	100	ND	ND	NP		Banned
α-lindane	1.668	ND	100	2.775	0.023	99.1	2.160	0.010	99.5	0.2	Banned
β-lindane	ND	ND	NP	0.010	ND	100	0.008	ND	100	0.01	Banned
Endosulfan i	1.183	0.027	97.7	0.171	0.102	40	0.168	0.152	9.5	0.05	Banned
Endosulfan ii	ND	ND		0.005	ND	100	0.007	0.003	57.1	0.05	Banned
Heptachlor I	ND	ND	NP	ND	ND	NP	ND	ND	NP	0.01	NR
Aldrin	ND	ND	NP	ND	ND	NP	ND	ND	NP	0.05	Banned
Isodrin	0.129	0.003	97.7	0.129	0.013	89.9	0.187	0.048	74.3	0.01	NR
Heptachlor II	0.032	ND	100	ND	ND	NP	ND	ND	NP	0.01	NR
Trans-nonane	ND	ND	NP	ND	ND	NP	ND	ND	NP	NP	NR
P,p-DDE	ND	ND	NP	ND	ND	NP	ND	ND	NP	0.05	NR
Dieldrin	O.037	0.025	32.4	0.078	0.013	83.3	ND	ND	NP	0.01	Banned
Endrin ketone	ND	ND	NP	ND	ND	NP	ND	ND	NP	0.01	Banned
Methoxych	ND	ND	NP	ND	ND	NP	ND	ND	NP	0.01	NR
DDMU	0.0067	ND	100	0.007	0.001	85.7	0.031	0.003	90.3	0.01	Banned

Key: ND- not detectable, FT=fresh Tomatoes, DT = dried Tomatoes and OCPs = organochlorine pesticide; Dif = Difference; A,B,C=Farms, NP=no percentage, NR=no record

From Table 4.4 six organochlorine pesticide residues were detected in fresh tomatoes from farmland sample A, including α- Lindan, 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 while endosulfan I, isodrin and dieldrin was detected in dried sample A .

Eight organochlorine pesticides residues were found in fresh tomato sample 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. In dried sample B, the OCPs found are alpha lindane, endosulfan I, isodrin, dieldrin and DDMU with concentration 0.023 mg/kg, 0.0102 mg/kg, 0.013 mg/kg, 0.013 mg/kg and 0.001 mg/kg, respectively.

However, the following were detected in fresh sample 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. While alpha lindane, endosulfan I, endosulfan II, isodrin, and DDMU were detected in dried sample C, with concentration 0.010 mg/kg, 0.152 mg/kg, 0.003 mg/kg, 0.048 mg/kg, and 0.003 mg/kg, respectively

Alpha lindane found in fresh sample A, (1.668 mg/kg) indicating a 100% reduction in concentration after sun drying. The concentration of alpha lindane (2.775 mg/kg), found in fresh sample B was reduced to 0.023 mg/kg after sun drying which indicates a 99.1% reduction in concentration. Similarly, alpha lindane found in fresh sample C with concentration of 2.160 mg/kg reduced to 0.01 mg/kg at 99.5% in the sun dried sample.

The reduction in the amounts of some OCPs after sun drying may indicate that the process degrades such OCPs.

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 (EPA, 2011).

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 Buba *et a*l. (2017) which determined alpha lindane (0.001 mg/kg) for tomatoes samples from Mubi Adamawa in Nigeria. Alpha lindane was also detected in finding of Aderonke *et al*. (2018) on fresh tomatoes with mean value concentration less than 0.2 mg/kg. Kolani *et al*. (2016) 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 linadne was detected in fresh sample B and C with concentration of 0.0 1 mg/kg and 0.008 mg/kg, respectively but non in the sun dried samples. The reduction in concentration of beta lindane after sundried can be attributed to the volatility of the compound and possible degradation on exposure to the sun (Agata, 2009). 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 Kolani *et al*. (2016) 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 (WHO, 2011).

Endosulfan I was detected in fresh tomato sample A with concentration 1.183 mg/kg but after sun drying, reduced to 0.0027 mg/kg. Similarly, the concentration of endosulfan I in fresh tomato sample B, 0.71 mg/kg reduced to 0.102 mg/kg after sun drying indicating a 40% reduction. However, endosulfan I in tomato sample C was 0.168 mg/kg which reduced to 0.152 mg/kg after sun drying an amounting to 9.5% reduction.

The percentage of reduction of endosulfan after sundried was very low compared to alpha lindane and beta lindane organochlorine pesticide, this can be attributed to the stability of endosulfan I as reported by Ademola & Gideon (2012).

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 (Aderonke *et al*., 2018).

Concentration of endosulfan I detected in fresh tomato sample was similar to the findings of Aderonke *et al*. (2018) who detected endosulfan I in tomato sample with concentration of 0.16 mg/kg. Mohemmed & Boteng (2016) 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 Suleiman *et al*. (2020) in fruit and vegetable with mean concentration of 0.048 mg/kg. The results was higher than finding of Buba *et al*. (2017) 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 and not in the sun dried samples while endosulfan II detected in fresh tomato sample C with concentration 0.007 mg/kg reduced to 0.003 mg/kg in the sundried sample. Reduction in concentration of

endosulfan II was higher than that of endosulfan I, which can be attributed to the stability of endosulfan I compared to endosulfan II. It has been reported that endosulfan II can converted to endosulfan I during the thermal degradation in the soil which may be absorbed through the roots of the crop (Adeoluwa *et al.*, 2019).

Endosulfan I detected in three fresh tomato samples was higher than MRL set by the WHO/NAFDAC, (0.05 mg/kg) but below the maximum residual limit MRL after sun drying. Endosulfan was recommended to be included among the banned organochlorine pesticide under the Stockholm Convention on Persistent Organic Pollutants (POP) (FAO/WHO, 2013).

In fresh tomato sample A, Isodrin was found with at a concentration 0.0129 mg/kg. This was reduced to 0.003 mg/kg after sun drying representing a 97.7% reduction. In fresh sample B an 89.9% reduction in concentration before and after sun drying whose concentration were 0.129 mg/kg and 0.013 mg/kg respectively. However, for sample C, isodrin detected was 0.187 mg/kg in fresh which reduced to 0.048 mg/kg after sun drying, representing 74.3% reduction.

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 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. After sun drying, the concentration of isodrin was less than MRL in dried sample A and within MRL in dried sample B, but high than MRL in dried sample C.

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 (WHO, 2011).

Heptachlor II was present only in fresh tomato sample A at a concentration of 0.032 mg/kg. This may indicate degradation or instability when exposed to the sun. Heptachlor has been banned by the WHO/FAO because the insecticide causes liver disease in animal and is also suspected to be carcinogenic in human FAO/WHO (2013). 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, 0.0524 mg/kg was detected through the findings of Suleiman, *et a*l. (2020) in fruits and vegetable obtained along River Galama, Zaria. Heptachlor was detected in tomato sample by Aderonke *et al*. (2018) with mean concentration of 0.003 which was lower than result obtained in this research. Araromi *et al*. (2020), also 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 (EPA, 2000).

Deildrin (0.037 mg/kg), was detected in fresh tomato sample A and reduced to 0.025 mg/kg after sun drying, but in fresh tomato sample B with concentration 0.078 mg/kg and 0.013 mg/kg in the sun dried sample The concentration of dieldrin was high in fresh tomato samples B compared to sample A. The decreased in concentration after sun drying maybe attributed to volatilization or degradation of the compound on exposure to the sun.

The result obtained was similar to the concentration of dieldrin, (0.024 mg/kg) from the findings of Nsikak & Aruwajoye (2011) in *solamium lycopersium* but lower than dieldrin detected in finding of Araroma *et al*. (2020) with concentration of 0.007mg/kg in tomato obtained from Ado-Ekiti.

Dieldrin 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 (EPA, 2011).

2,2-bis(chlorophenyl)-1-chloroethane DDMU was detected in fresh tomato sample A with concentration 0.007 mg/kg but none in the dried sample., 0.007 mg/kg was found in fresh sample B which reduced to 0.001 mg/kg after sun drying, while 0.031 mg/kg was found in fresh sample C which reduced to 0.003 mg/kg after drying.

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 has been banned worldwide for agricultural application because of its health hazard and unfavorable environmental effect (WHO, 2011).

Concentration of DDT detected in fresh samples was similar to the findings of Nsika &Aruwajoye, (2011) with mean value of 0.006 mg/kg in fresh tomato. It was also found by Buba *et al*. (2017) 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. Generally, the results showed that sun drying significantly reduced the

concentration of DDMU. This can be attributed to volatilization, because DDT is a volatile organic compound that has high vapor pressure and low water solubility (Agata, 2012).

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 WHO, (2011).

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.

Generally, there was significant reduction in the concentration of organochlorine pesticide residues after sun drying the samples. This reduction in concentration of the OCPs may be attributed to factors including, but not limited to, volatilization and degradation on exposure to the sun, (Fuso-Mensah *et al*., 2016).

All the OCPs determined in the samples have been banned in Nigeria by the National Food and Drugs Control (NAFADC 2017), 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 (Ademola *et al.*, 2012, Njuku *et al*., 2017, Josoph *et al*., 2014, Buba *et al*., 2017). 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 Ademola *et al*. (2012)

4.4 Organochlorine Pesticide Residue in Soil, Fresh and Dried Tomatoes from Farmland A

Table 4.5, OCPS Residue in fresh, dried sample and soil A (mg/kg)

	Organochlorine pesticides							
Samples	**αlindane**	**Endosulfan**	**isodrin**	**heptochor**	**DMMU**	**Dieldrine**	**Endosulfan**	**Lindane**
Fresh A	1.668	1.183	0.013	0.032	0.168	0.037	0.00	0.00
Dried A	0.00	0.027	0.00	0.00	0.00	0.025	0.00	0.00
Soil A	0.626	0.069	0.148	0.00	0.004	0.031	0.011	0.016

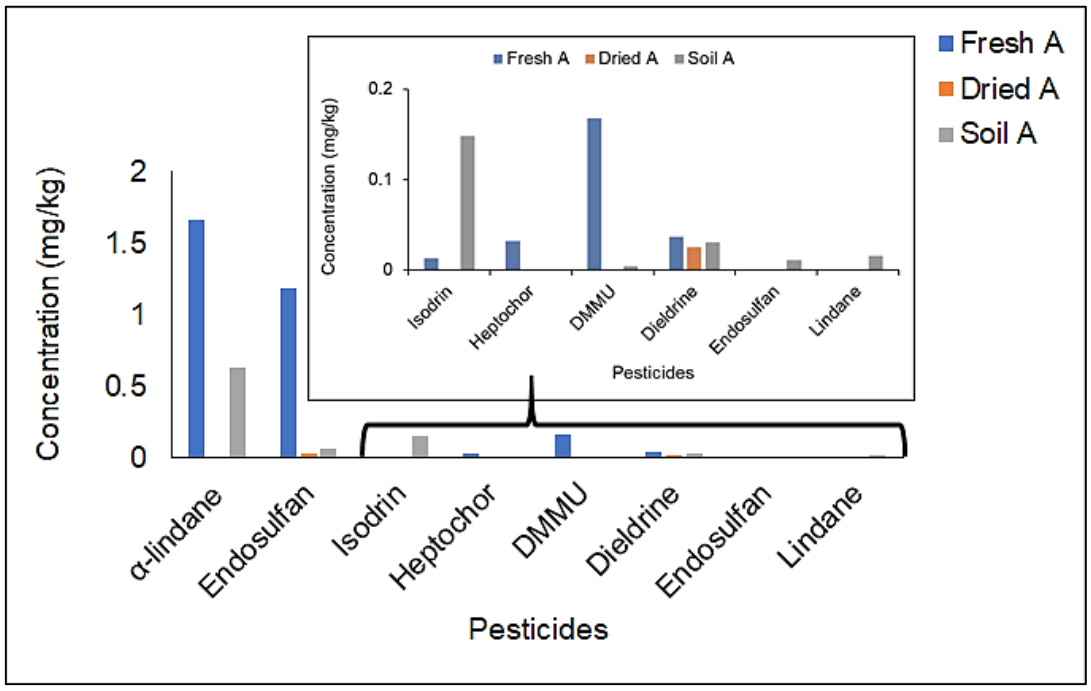

Figure 4.1 Comparison of OCPs residues in fresh, dried tomatoes and soil sample A

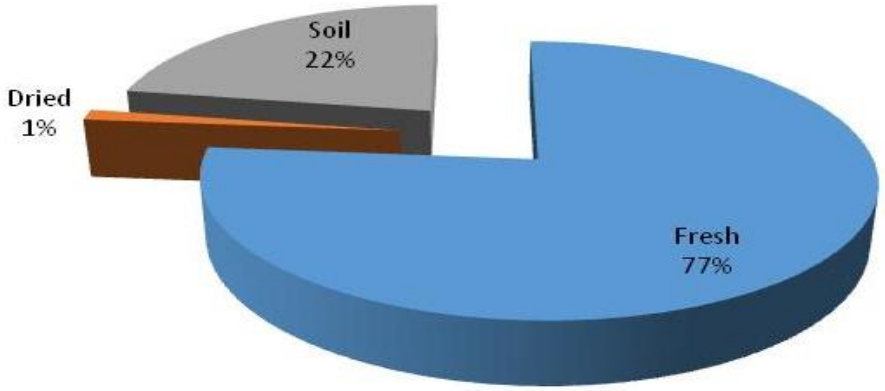

Figure 4.2 Total of OCPs Residues in fresh, dried tomatoes and soil sample A

From Table 4.5 and figure 4.1, shows the comparison of concentration of OCPs residues in fresh, dried tomatoes and soil sample A while figure 4.2 shows the percentage total of OCPs present in fresh, dried tomatoes and soil samples from farmland A

Figure 4.2 shows that the total concentration of OCPs in fresh samples reduced from 77% to 1% after dried, and the total concentration of OCPs in the soil sample A is 22%.

Out of six organochlorine pesticide residues detected in fresh sample A as shown in table 4.5 and figure 4.1 namely; alpha lindane, isodrin, heptachlor, endosulfan I, dieldrin and DMMU their concentration are reduced significantly after sundried. This shows that as fresh tomatoes samples are exposed to the sun, they lose moisture contents with the organochlorine pesticide residue and its metabolites present in the fresh sample A.

Alpha lindane, Endosulfan, isodrin, heptachlor, DMMU, Dieldrin are detected in fresh tomatoe samples 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 fresh 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 (Joseph *et al*., 2014).

4.5 Organochlorine Pesticide Residue in Soil, Fresh and Dried Tomatoes from Farmland B

Table 4.6 OCPS residue in fresh, dried and soil samples B (mg/kg)

	Organochlorine pesticide residue							
OCPs	**Deta-Pent**	**αlindane**	**βlindane**	**Endosulfan i**	**Isodrine**	**DMMU**	**deidren**	**Endosulfan ii**
Fresh B	0.012	2.775	0.010	0.171	0.029	0.007	0.078	0.005
Dried B	0.00	0.023	0.00	0.102	0.013	0.001	0.013	0.00
Soil B	0.00	0.00	0.00	0.124	0.00	0.00	0.031	0.00

The table above shows, the concentration of OCPs residues in fresh, dried tomatoes OCPs residues present in the soil samples B

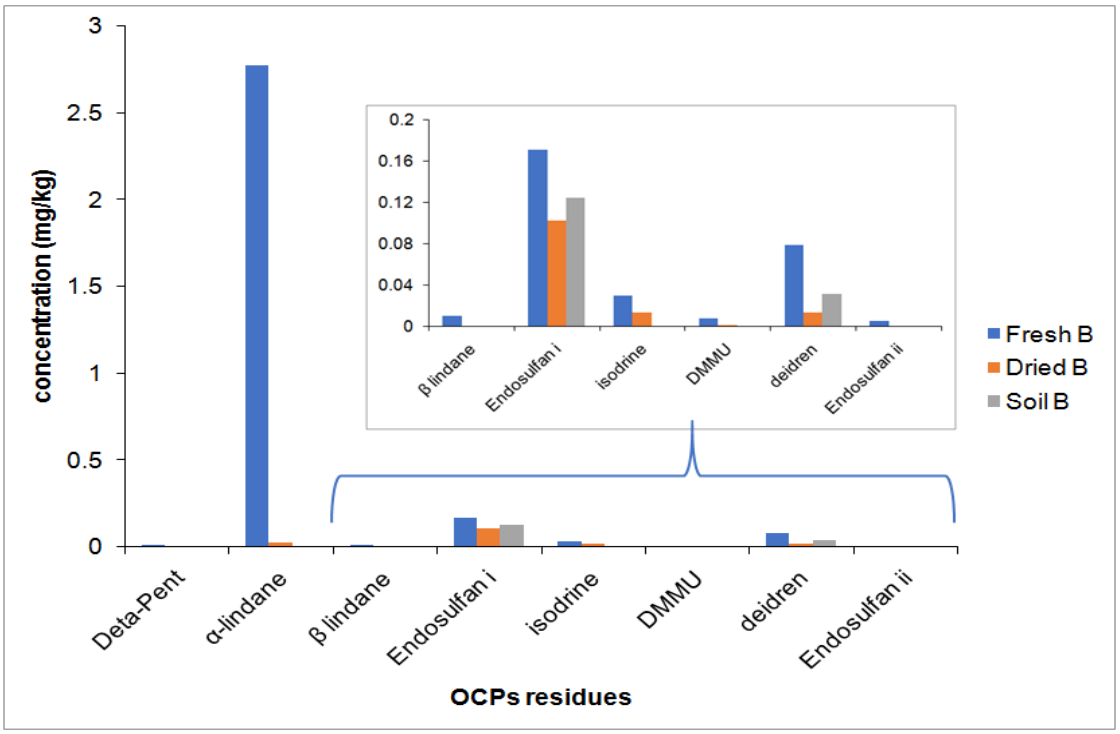

Figure 4.3 Comparison of OCPs present in fresh, dried tomato and soil sample B

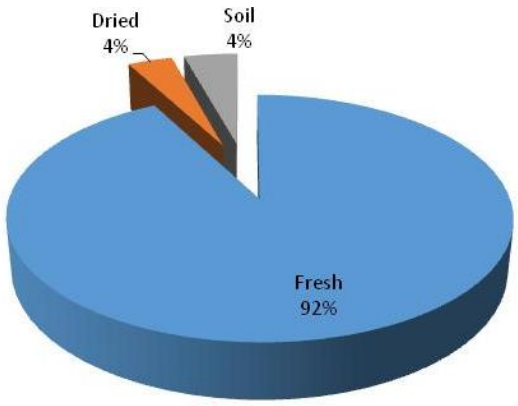

Figure 4.4: Total OCPs Residues in fresh, dried tomatoes and soil sample B

Table 4.6 and Figure 4.3 shows the comparison of organochlorine pesticide residues in fresh, dried tomatoes and the soil sample in farmland B. while figure 4.4 shows the total OCPs present in fresh dried and soil sample.

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 4.2. 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 (Fuso-Mensah *et al*., 2016).

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.

4.6 Organochlorine Pesticide Residue in Soil, Fresh and Dried Tomatoes from Farmland C

Table 4.7, OCPS Residue in fresh, dried and soil samples C (mg/kg)

	Organochlorine pesticide residue							
OCPS	**α-lindane**	**β-lindane**	**Endosulfan I**	**Isodrine**	**DMMU**	**Endosulfan II**	**Dieldren**	**Heptachlor**
Fresh C	2.160	0.008	0.168	0.187	0.031	0.057	0.00	0.00
Dried C	0.010	0.00	0.156	0.048	0.003	0.003	0.00	0.00
Soil C	0.050	0.00	0.054	0.028	0.003	0.014	0.006	0.006

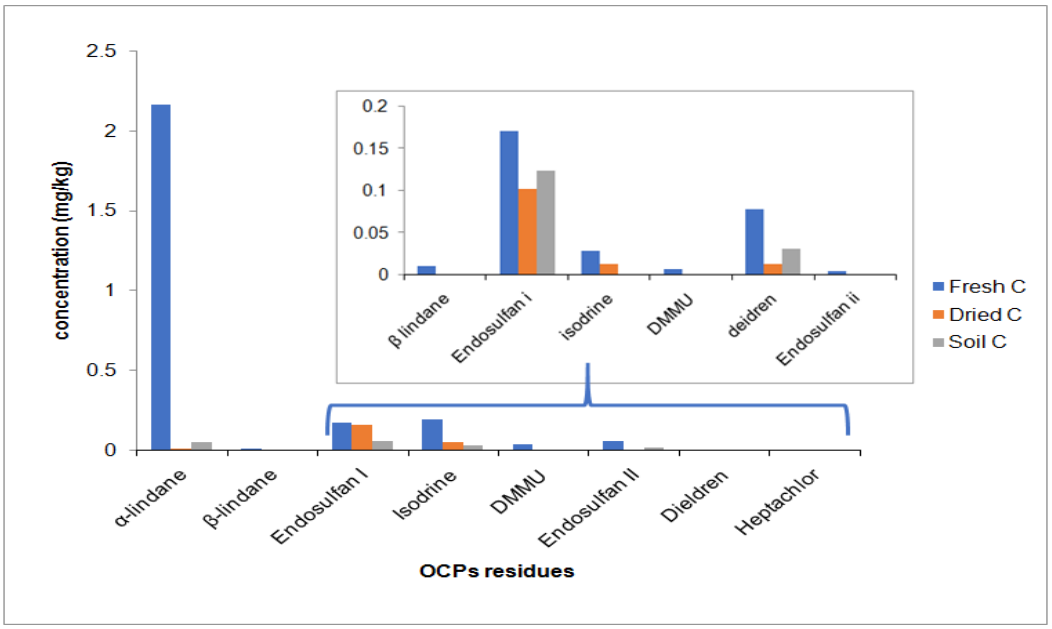

Figure 4.5 Comparison of OCPs Present in fresh, dried tomatoes and soil sample C

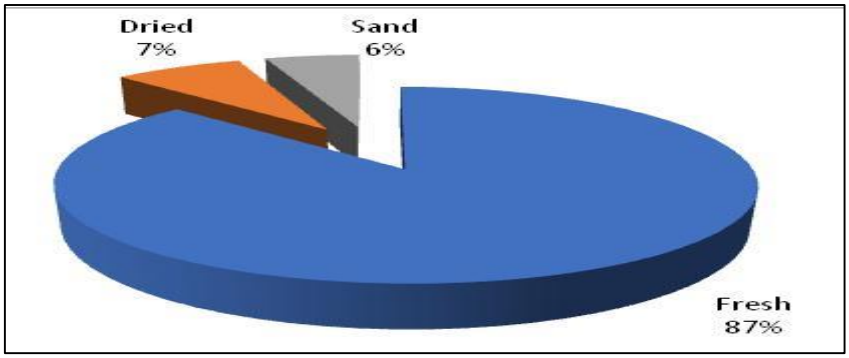

Figure 4.6 Total OCP Residues in fresh, dried tomatoes and soil sample C

Table 4.7 and figure 4.5 shows the comparison of the concentration of organochlorine pesticide residues present in fresh, dried tomatoes and soil samples from farmland C while figure 4.6 shows the total organochlorine pesticide residues present in fresh, dried tomatoes and farmland soil 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), dieldrin (0.006 mg/kg), heptachlor (0.006 mg/kg) was detected in soil farmland sample C. But dieldrin, and heptachlor was not detected in the fresh tomato samples C. The percentage of organochlorine pesticide residues in fresh tomato are higher than the percentage of organochlorine pesticide detected in the soil sample these may be attributed to fact that plant absorbed pesticide from soil through the root and through the leaves after application of pesticide (Joseph *et al*., 2014).

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 4.2 and therefore, has ability to hold water capacity and pesticide (Fosu-Mensah *et al*., 2016).

The quantity of pesticide absorbed depends on the nature of pesticide and how it was formulated, and its mode of application (Navarro *et al*, 2017).

4.7 Health Risk Estimation of Organochlorine Pesticides Residues

Table 4.8: 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}	$1.37x10^{-4}$	AD-0.399	N0
				CHD-2.737	YES*
βHCH	0.005	5.286×10^{-6}	$3.70\ x10^{-6}$	AD-7.6 $x10^{-8}$	NO
				CHD-7.4×10^{-4}	NO
Endosulfan I	0.05	9.059×10^{15}	$6.341\ x10^{-6}$	AD-2 $x10^{-3}$	NO
				CHD-1.3×10^{-5}	NO
Isodrin	0.01	6.824×10^{-5}	$4.777\ x10^{-6}$	AD-6.8 $x10^{-4}$	NO
				CHD-4.7 $\times10^{-4}$	NO
DDMU	0.01	3.541×10^{16}	$2.449\ x10^{-5}$	AD-3.5 $x10^{-5}$	NO
				CHD-2.4×10^{-6}	NO
Dieldrin	0.001	4.838×10^{-5}	$2.826\ x10^{-6}$	AD-4.0 $x10^{-4}$	NO
				CHD-2.8×10^{-4}	NO
Endosulfan II	0.05	2.854×10^{-6}	$1.778\ x10^{-6}$	AD-5.7 $x10^{-5}$	NO
				CHD-3.9×10^{-4}	NO
Heptachlor II	0.001	1.445×10^{-6}	$1.012\ x10^{-5}$	AD-0.144	NO
				CHD-1.012	YES*

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

The table above 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 WHO (2012), if hazard index is equal or greater than one such compound pose health risk and need further monitoring. The result was similar to Adeoluwa *et al*. (2019) 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 Aderonke, *et al*. (2018) 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 (FAO/WHO, 2013).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The results obtained from the present research shows that a number of organochlorine pesticide residues are present in the fresh and dried tomato selected from the studied farmlands in Zamfara State. They include α HCH, β HCH, Endosulfan I, isodrin, DDM, dieldrin, and Endosulfan II in fresh 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. But the concentration reduced after sundried to 0.027 mg/kg for endosulfan, 0.129 mg/kg for isodrin, and 0.025 mg/kg for dieldrin, while lindane and heptachlor were not detected after sundried. α- HCH, endosulfan and isodrin detected in fresh samples are higher than maximum residual limits (MRLs) set up by FAO/WHO. The concentration of organochlorine pesticide residues in dried tomato samples are below the maximum residual limits, while some are not detected. This indicates that traditional drying of tomatoes can significantly reduce the concentration of organochlorine pesticide residues present.

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. The present study also provides data on organochlorine pesticide residues in dried tomato sample. There is a significant reduction in concentration of the residues present in fresh sample.

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. It was observed that banned

organochlorine pesticides are still being used by farmers. Farmers should be educated on when and how to apply and method of application.

5.2 Recommendations

The following are recommended from the current studies of organochlorine pesticide residues from fresh and dried tomatoes sample.

- Continuous monitoring of all banned organochlorine pesticide residues in other vegetables fruit and food substances grown in Zamfara state and other part of Nigeria should be encouraged.
- Drying of tomato should be encouraged whenever high level of pesticides are suspected and educating formers on methods of application of the pesticide, when and how to apply.
- Strict monitoring of all banned and continuous assessment of levels of organochlorine pesticides residues in fruit vegetable from different parts of the country should be encourage and the data should be used for proper regulation.
- Further research should be carrying out for alternative greener pesticides to avoid the risk of using the banned pesticides.

REFERENCES

Adebisis, S. A., Olatunji, A. O. & Awojide, S. H. (2020). Evaluation of pesticide residues in some fruits and vegetables in Osogbo, south western, Nigeria. *International Journal of Scientific and Engineering Research,* 11(2), 357 - 365 retrieved from https://www.ijer.org

Ademola, F. A., & Gideon A. I. (2012). Organochlorine pesticides Residues in cocoa farm in Ondo state central district, Nigeria. *Journal of Environment and Natural Resources Research,* 2(2), 10 -19

Adeoluwa, O. A., Mosudi, B. S., & John, A.O. (2019). Dietary exposures assessment of organochlorine pesticides in two commonly grown leafy vegetable in south western Nigeria. *Elesiver Publisher*, https://doi.org/j.heligon.2019.eo1895

Aderonke, O. O., Oluwatoyin, T. F., Latifat, M. A., Demilola, E. F., & Muyideen, O. M. (2018). Human health risk of organochlorine pesticides in foods grown in Nigeria. *Journal of Health and Pollution,* 7(15), 63 - 70

Adewole, E., Ojo, A., Oludoro, O., Ogunmodede, T. O., & Awonyemi, O.T. (2021). Risk assessment of organochlorine pesticide residues in *phaseolus vulgaris purechased* in Igbara- oke, Ondo state, Nigeria. *Pakistan Journal of Biological Science*, 24(3), 357-365

Agata, W. (2009). Effects of heat treatment on organochlorine pesticide residue in selected fish species. *Journal of Food and Nutritional Science* 59(3), 213-235

Ahemed, N.B., Mohammed, M. A., May, M. A., Thang, V. N. & Ahmed, S.M. (2019). Pesticides evaluation in Egyptian fruits and Vegetables: A safety assessments study. *Journal of Environment Science and Technology*, 12(2), 81 – 91

Akinloye, O.A., Adamson, I., Ademuyiwa, O. & Arowolo, T. A. (2011). Occurrence of paraquat Residues in some Nigeria crops, vegetables and fruits. *Journal of Environmental Chemistry and Ecotoxicology*, 3(7), 195-198

Aliyu L., Usman A., & Mani U. (2018). Evaluation of nutritional composition of healthy and Infected dried Tomato chips sold in Sokoto metropolis. *A Journal of Innovation Food*.6 (2), 1-4

AOAC, (2000). *Official method of Analysis of Association of Analytical Chemists* International. 17th Edition, Horowitz, Maryland, 2000.

AOAC, (2003). *Official Methods of Analysis, Association of Official Analytical Chemist*, Wahington, D.C, 2003

AOAC, (2017), *Official methods of analysis "Quechers*" international, 19th edition, (USA), 2017.

AOAC,(2005). *Official methods of analysis of the AOAC* International. (18thed.). Gaithersburg (USA): AOAC International; 2005.

Arah, I. K., Kumah, E. K., Anku, E. K., & Amaglo, H. (2015). An overview of post-harvest losses in tomato production in Africa: causes and possible prevention strategies. *Journal of Biology, Agriculture, and Healthcare*, 5(16), 78-8

Araromi, A. A., Ayodele, O., Azeez, M. A., & Olanipekun, E. O.(2020). Assessment of trace organic in tomatoes from selected market in Ado- Ekiti state, Nigeria. *Journal of Materials and Environmental Science*, 11(12), 2084 – 2094, Retrieved from https://www. jmataenvirosci.com

ATSDR (2002). A agency for toxic substances and disease registry. Toxicological profile for DDT,DDE, DDM, DDMU. *U.S Department of Health and Human Service.*

Azhari, A., Nawadar, H., Ahemed, M.& AbdulElaziz, S. (2019). Pesticide residues in samples of sweet pepper (*Capsicium annum*) from Khartoum state, Sudan. *Journal of EC Pharmacology and Toxicology* 7(7), 568 -576

Balawan, J. M. & Dipyendu, P. (2017). Analysis of banned organochlorine pesticide residues in fruit and vegetable sample from a market in shilling. Meghalaga, Using Gas chromatography mass spectrometer. *Research Journal of Recent science*, 6(12), 9-11

Buba, M., Maitera,O. N., Dass, P.M. & Abraham, E.A. (2017). Determination of organochlorine Pesticides residues level in some selected vegetable cultivated in Mubi-North Mubi- south LGA, Adamawa State, Nigeria. *Journal Applied Science*, 2(1), 25- 40

Cemile, O. (2016). Determination of organochlorine pesticides in some selected vegetable samples using GC-MS. *Journal of environmental. Studies*. 25(3), 1141- 1147

Chai, K. & Nurdzaina, Z. (2011). Analysis of pesticide residues in fruits and vegetables using modified quencher's methods. *Malaysia Journal of chemistry*. 13(1), 026 - 30

Das, S., Aria, A., Cheng, J.O., Souissi, S., Hwang, J.S., & Kof, C. (2020). Occurrence and distribution of anthropogenic persistent organic pollutants in costal sediments and mud shrimps from the wetland of central Taiwan. *Plos 12 (1). 10: 1371/Journal.Pone.*

EPA, (2000). Supplementary Guidance for conducting health risk assessment of the chemical Mixtures. Washington DC, EPA.

EPA, (2002). Guidance on cumulative risk assessment of pesticide chemicals that have a Common Mechanism of toxicity.

EPA, (2011). Health Canada and EPA adopt OECD calculator for establishing legal limits for Pesticide residues. www.epa.gov/oppfead1/ international/work *Sharing/oecd-Factsheet.html*. Accessed 7th October 2011.

FAO &WHO (2013). Pesticide residues in food and feed codex alimentarium commission. Joint FAO and WHO food standard program. *Roma Italy*

FAO/WHO (2007). The WHO recommended classification of pesticides by Hazard and Guideline to classification.

FAO/WHO (2015). Pesticide residues in food and feed, Glossary of terms, retrieved: 2015

FAO/WHO (2019). Pesticide residues in food 1999. Joint FAO/WHO Meeting on PesticideResidues, FAO, Rome, 153.

Fosu-Mensah. B.U., Elvis, D. O., Godfred., D., & Christopher, G. (2016). Assessment of organochlorine pesticide residues in soil and drinking water sources from cocoa farm in Ghana. *Spring Plus*, (5): 869.

Frederick, F, Nathanel, O. B., Lawrence, S.B. & Samuel, A. (2018). Risk of human dietary exposure to organochlorine pesticide residues in fruit from Ghana. *Scientific reports*. Retrieved from www.nature.com/scientific reports

Garbutt, N. (2011). The global World of Good Agricultural practice introduction. Global gap Tour 2011 Conference, warsaw, 15th September, 2011.

Ibrahim E. G., Yakubu N., Nnamonu J., & Yakubu M. (2018). Determination of organochlorinePesticide Residues in pumpkin, Spinach, and Sorrel leave Grown in Akwanga, Nassarawa State, Nigeria. *Journal of environmental protection 9*(2), 508-515

Idowu, G.A., Aiyesanmi, A.F. & Owolabi, B. J. (2013). Organochlorine pesticide residues levels in river water and sediment from cocoa- producing area of Ondo state central senatorial district, Nigeria. *Journal of environment chemistry and ecotoxicology*, 5(9), 242 -249

John, A, M., Farhat, A, K.& Ester, H.J.(2017). Assessment of pesticide residues in tomatoes and watermelons (Fruits) from markets in Dares Salaam, Tanzania. *Journal of Apply Science Environment*. 21 (3), 497-501

Jose, J.P., Rutilio, O., Maria, L. R., Javier, O., Daniel, R. & David, M. (2016). Presence of organochlorine pesticides in Xiconostle (*Opuntta Joconostle*) in the central region of mexico. *International journal of food contamination*, 3(21), 22-29

Joseph, C. A., Muas, M.M., Maimuna, W.& Zakari, M.(2015). Residues of organochlorine pesticide in watermelon (*citrulu lanatus*) and soil samples from Gashua, Bade local government area Yobe state, Nigeria. *Advance in analytical chemistry*, 5(3), 61-68

Joseph, S. & Michigan, U. (2010). GC×GC-ECD of organochlorine pesticides in cucumber and tomatoe. *Journal of life science and chemical analysis* retrieved from www.leio.com

Joseph,C.A., Lami , J., Zaynab, M.C., Zakari, M. & Fanna, I.A.(2014). Determination of some organochlorine pesticide residues in vegetable and soil sample from Alau Dam and Gongulong agricultural sites, Borno State, North Eastern Nigeria. *Journal of world Academy of Science, Engineering and Technology*.8 (4), 56-63

Jumepaeng, T. & Nirand, P. (2020). Development of sample method for organochlorine pesticides analysis in soil samples. *Journal of environmental science* 7(5), 380 - 386

Kai, M. C., Yun Wang, B. C., Xiaomeng, L. C., Shuying, H. J., Xiaoyan, L. B. & Hongwei, K. (2020). Organochlorine pesticides in sediment of Zhang river Estuary mangrove national natural reserve: implication of its source charge in Chinas mangroves. *Journal of Sustainability*, 12 (3016)

Kapeleka, J. A., Sauli, E., Sadik, O. Ndakidemi, P. A. (2020). Co exposure risk of pesticide residues and bacterial contamination in fresh fruits and vegetable under small holder horticultural production system in Tanzania. *Plos.* One 15(7).

Kigozi, M. (2016). Hazard identification of organochlorine pesticide residues, case study of tomatoes and carrots from selected market in the central Uganda. *Internationa*l *journal of advance research*, 4(8), 56-62

Kolani, L., Gbenonchi, M. & Komla, S. (2016). Assessment of organochlorine pesticide residues in vegetables samples from source, agricultural area in Togo. *America journal of analytical chemistry* 7(332-341), retrieved online https//www.scirp.org/journal/ajac

Kumelachew, M. L., Marja, L., and Jocob, B. (2020). Pesticide residue levels in vegetable and surface waters at the central Rift Vally (CRV) OF Ethiopia. *Journal of environmental monitoring*. 12(5), 546 - 554

Liang, F., Shengzhong, D., Shiyang, L. & Fangxu, X. (2018). Muiti-residues determination of pesticides in vegetables on Dacian market by gas-chromatography. *Journal of food, nutrition and population Health,* 2(1), 1-7

Mahugija, A. M., Lutamyo, N., & Mmochi, J. (2017). Level and distribution of pesticide residues in soil and sediments in eastern Lake, Tanganyika environs. *International journal of Biochemistry science*, 11(5), 2537 – 2547

Mashi, J. A., Idris, R.I., & Markus, F. D. (2020). Proximate mineral and vitamine content of fresh, blenched and dried tomatoes (*lycopersicum esculentum*). *Asian food science journal*, 18(4), 11 – 18

Mehedi, H. & Azizur, O. (2019). Pesticides residues in selected vegetable collected from wet markets of Banglash. *Advance journal in social science research*, 6(5), 15-23

Mohammed, M. & Boateng, K. K. (2017). Evaluation of pesticide residues in tomato (*lycopersicum esculentum*) and the potential health risk to consumers in urban areas of Ghana. *Journal on pollution* 3(1), 69-80

Mustapha, F. A., Dawood, G. A., Mohammed, S. A., Vimala, Y. D. & Nisar, A. (2017). Monitoring of pesticide residues in commonly used fruits and vegetables, in kuwart. *International Journal of Environment Research and Public Health*. Doi: 10.3390/ijerph/14080833

NAFDAC (National Agency for Food and Drug Administration and Control) (2017). Pesticides regulation and guide line for usage. As approved by governing council, Nigeria.

Navai, A. I., Famil, Y.H, & Murad, S. (2018). Determination of organochlorine pesticide in the soils and sediments taken from the kura- araks river system using G/ECD. *Biological and Chemical Research*,9(5), 283 – 294

Navarro, S., Vela, N. & Navarro, N. (2017). Review: An Overview on the environment behavior of pesticides residues in soils. Spanish *Journal of Agricultural Research*, 5(3), 357-375

Njoku K., Ezeh, C., Obidi, F.O., & Akinola, M.O.,(2017). Assessment of pesticide residues levelIn vegetables sold in some market in Lagos State, Nigeria. *Journal of Biotechnology*, 10(32), 63-60.

Nosakhare,O., Dirisu, A.,& Olomukoro, J.O.(2012). Implications of pesticide usage in Nigeria. *Journal of Tropical freshwater Biology*, 21 (1) 15-25

Nsikak, U. B. & Aruwajoye, I. O. (2011). Assessment of contamination by organochlorine pesticide in *Solanum lycopersicum L. and capsicum annum L.*: A market survey in Nigeria. *Africa Journal of Environmental Science and Technology* 5 (6), 437- 442

Nunifant, K. T. (2011). Levels of organochlorine pesticide residues in fresh tomatoes from selected farming communities in Navarongo, Ghana. Master of sciences Thesis submitted to Nkirumal Univerisity of science and technology Ghana.

Nyaundi, J., Getabu, A., Onchieku, J., Kinaro, Z., Bassa, S., Nyamweya, C., Hilda, N., & Getenga, Z. (2019). Occurance and distribution of organochlorine pesticide Residues in water and sediments of earthern fish pond in south western Kenya. *Uganda journal of Agricultural science* 19(2), 47-60

Ojo, J. (2016). Pesticide and its Health in Nigeria. *Ife Journal of Science*, 18(4), 90-97

Opadotu, O. O., Adekeye, S. A, Ojukwu, E. O, & Adewumi, A. A. (2016). Comparative analysis of nutritional value of tomatoes subjected to different drying conditions. *International journal of basic and applied science*, 5(1), 6-9.

Opega, J. L., Yusuf .P. A., Kadiri A.O., & Ishaka N.A. (2017). Effect of drying methods and Storage conditions on nutritional value and sensory properties of dehydrated Tomato power (*lycopersico esculentum*). *International Journal of Biochemistry Research and review*. 10:9734//IJBCRR/2017/33103PIC Chemicals

Osofo, S. & Frempong, E. (1998). Lindane and endosulfan residues in water and fish in the Ashanti region of Ghana. *Journal of science*, 1(1), 135 - 140

Owusu, G. B. & Korshiwor, A. (2013). Level of organochlorine pesticides residual in cabbage cultivated in farm along river oyansia, Accra-Ghana. *America Journal of Scientific and Industrial Research.* 4(5), 489 - 498

Oyeyiola, O., Oluwatoyin, T., Latifat, M., Demilola, E., & Muyideen, O. (2017). Human health risk of organochlorine pesticides in foods grown in Nigeria. *Journal of Health Pollution.*7 (15), 63 - 70

Paneri, S., Biondi, D., Vigo, R.C. & chiesa, L. M. (2013). Occurrence of organochlorine pesticides residues in Animal feed and fatty tissue. https://dx.doi.org/ 10.5772/ 54182

PIC (2010). "An introduction to the chemicals listed in the rotardam convention" that are subjected to the international legally-binding prior informed consent procedure, www.pic.in

Rahmawati, S., Listya, C.K., Minoru, Y. & Katharina, O. (2017). Risk analysis on organochlorine pesticides residues in pototo and carrot from conventional and organic farm in citarum watershed Area, west java, province, Indonesia. *Journal Sain Dan Teknolog*. 9(1), 1-15

Raluca, M. H., Manuela, O.P., Brindusa, M. R. & Maria, G. (2016). Human health risk assessment of possible residues in field grown yellow peppers. *International Proceeding of Chemical, Biological, and Environmental Engineering*. 94(5), 29 -36

Rathore, H.S. & Nollet, L.M.L. (2012). Pesticides: evaluation of environmental pollution taylor and francie group, LLC. USA. 544-545

Sah, S. B., Gupta, R. N., Kumar, M., Mandal, S. K., Saha, T. & Singh, S. P. (2018).pesticide residues from Gate vegetable samples in Bihar. *International Journal of Current Microbiology and Applied Sciences*, (7), 4090 - 4096

Salah, E., A., Mohammed, E. A. & Sala, E. M. (2020). Determination of pesticide residues in eggplant and tomatoes from central market in Khartoum state, using Quechers method and gas liquid chromatography- mass spectrometer. *Biomedical Journal of Scientific and Technical Research*. Doi. 10.26717/Bjstr.2020.24.004035

Samuel, A. & Devid, T. (2013). Level of organochlorine pesticide residues in selected consumable vegetables commonly sold in Benin City market. *Journal of Apply. Science and Environment*. 22(10), 1624 -1630

Sosan, M.B. & Oyekunle, J.A. (2017). Organochlorine pesticide residues levels and potential human health risk in kola nuts from selected market in Osun State, southwester Nigeria. *Asia Journal of Chemical Science*, 2(4), 1-11

Suleiman, F., Nuhu, A A., Omoniyi, K.I. & Yashim, Z. I. (2020). Determination of organochlorine pesticides residues in some vegetables and fruit by Quechers techniques and gas chromatography Mass Spectrometer. *FUDMA Journal of Science*, 4(2), 365-370

Sunaja, K.D. & Leethyat, M. (2014). Monitoring of pesticides residues in commonly used Fruits and vegetable in Bengahuru. Mapana *Journal of Sciences*, 16(2), 29 - 40

Teresial, O. D., Immanuel, O. E., & Modupe, O. A. (2020). Residual organochloeine pesticide in the salad vegetables cultivated in Lagos, Nigeria and their human health risk. *Journal of Advance Environmental Health Research*, 8(2), 131- 139

Ugonna, U., Jolaoso. M. A., & Onwualu, A.P. (2015). Tomato value chain in Nigeria issues, Challenges and strategies. *Journal of Scientific Research and Report*s 7(7), 501-515

Vinceat, O. A., Mosudi, B. S. & John, A, O. (2018). Human risk assessment of organochlorine pesticides residues in vegetable from Kumasi, Ghana. *Hindaw Journal of Chemistry,* 18(5), 11- 22

WHO (2012). Gen/food regional per capital consumption of raw and semi processed agricultural conditions, Geneva.

WHO (2011). Global strategy for food safety: food for better life, Gevneva,

William, G. (2012). The application of GC/MS to the analysis of pesticides in food stuffs. PerkinElmer, Inc. Shelton, CT USA.

APPENDIX A

Data File Name: C:\msdchem\1\methods\OldMethods\PESTICIDE 6217.M\STD 3 PESTICIDE.

Acquired Date: 26 Jun 2019 11:34 Method Name: C:\msdchem\1\methods\OldMethods\new

Table 1.**Retention Time and Area of the for Pesticide standard**

Compound Name	RT (min)	Area
.delta.-Pentachlorocyclohexene	10.159	100359
.alpha.-Lindane	12.923	839323
.delta.-Lindane	14.279	285072
Endosulfan ether	14.474	117269
Heptachlor	15.155	854440
Aldrin	15.967	682374
Heptachlor epoxide	17.043	855120
trans-Chlordane	17.689	1316219
.alpha.-Endosulfan	18.038	347299
Chlordane	18.13	1021528
Dieldrin	18.742	696366
p,p'-DDE	18.908	1277524
Endrin	19.349	257557
Endosulfan	19.732	297686
Mitotane	20.178	1254666
Endosulfan sulfate	21.037	216606
Endrin ketone	22.416	302161

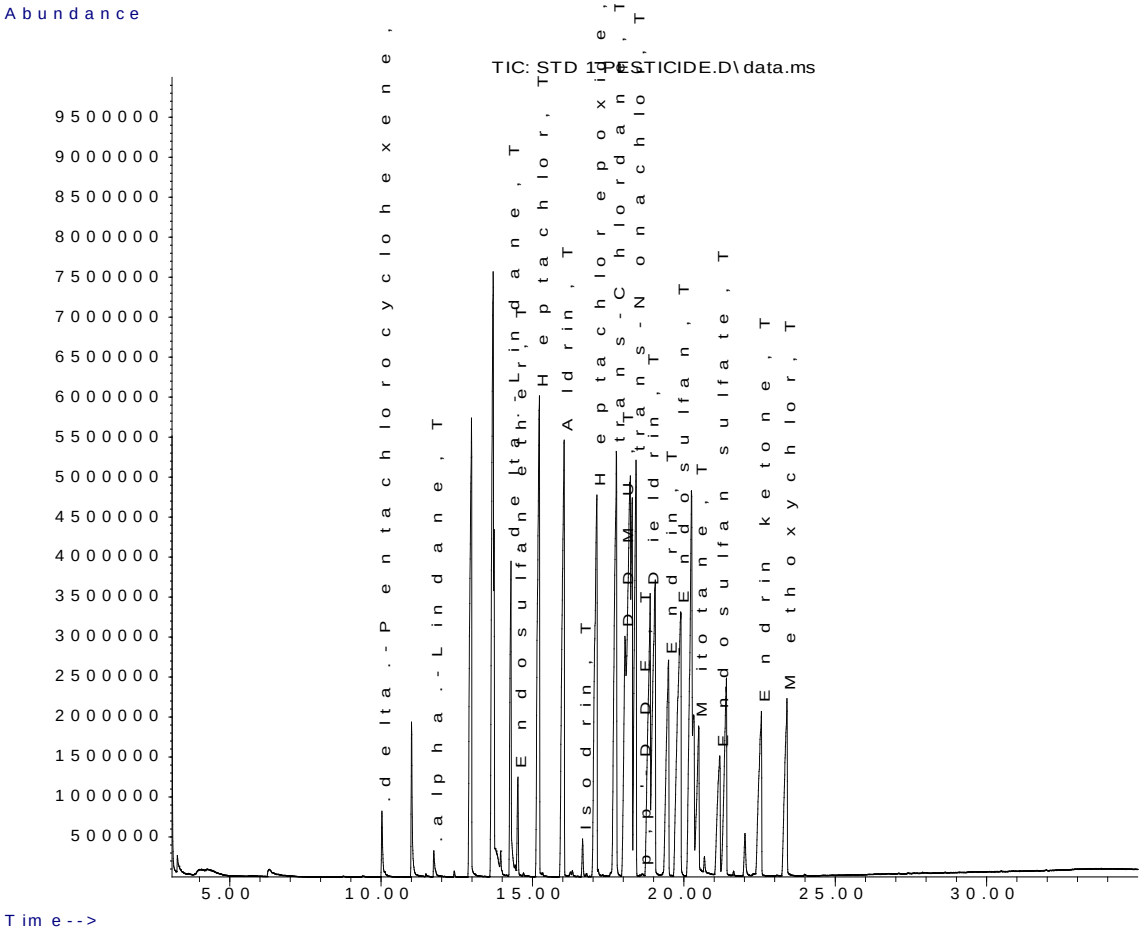

Figure 1: Chromatogram of pesticide standard

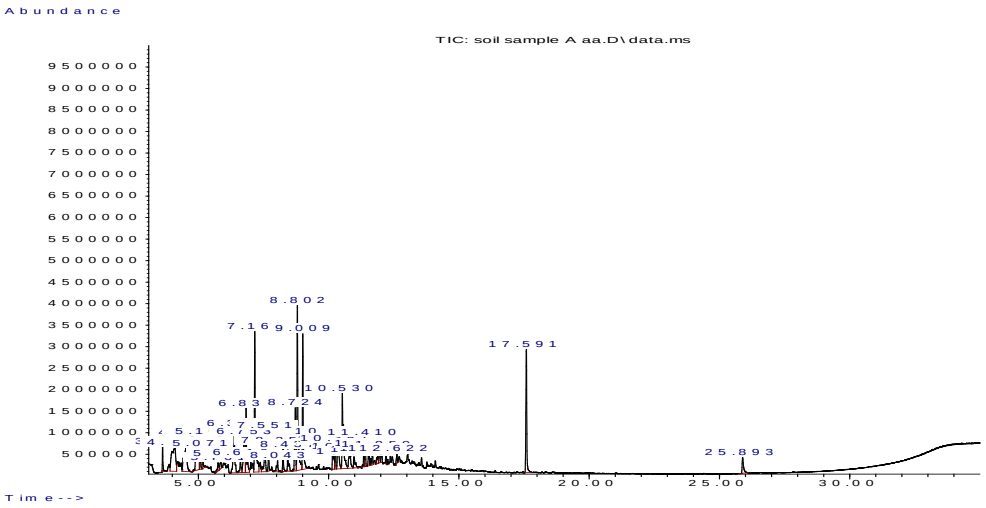

Figure 2: soil sample chromatogram

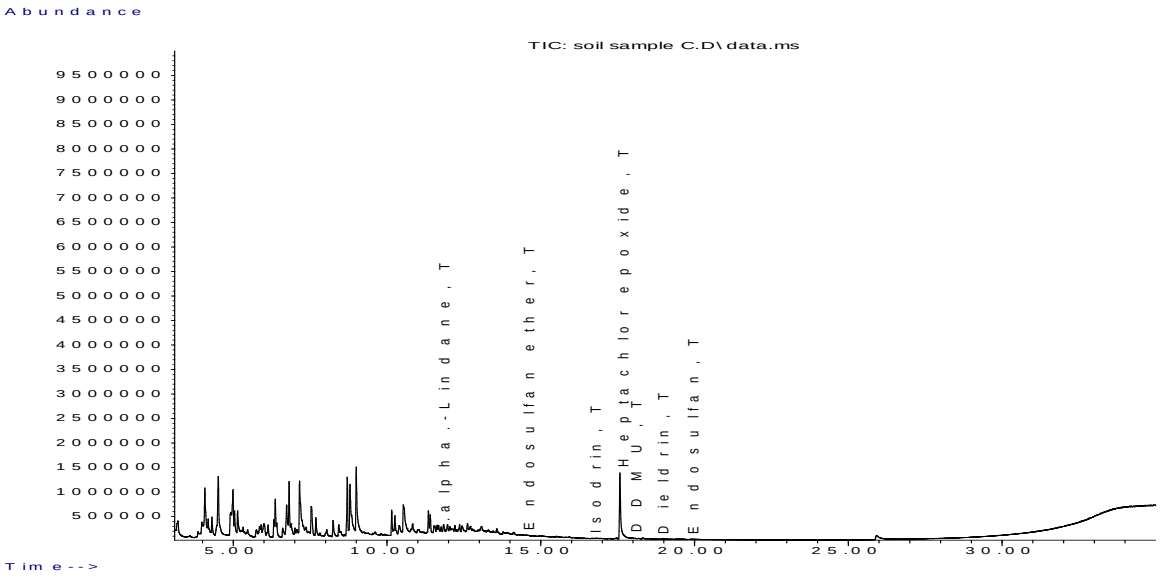

Figure 3: Tomatoes samples chromatogram