

**ASSESSMENT OF ORGANOCHLORINE INSECTICIDE
RESIDUES IN COWPEA GRAINS AND DRIED YAM CHIPS IN
SELECTED MARKETS IN ILE-IFE, OSUN STATE**

OLUFADE, YUSUF AYODEJI

B. Agric. (Agricultural Economics) Ife

(AGPO9/10/H/2254)

**A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTERS OF
SCIENCE TO THE DEPARTMENT OF CROP PRODUCTION AND
PROTECTION, FACULTY OF AGRICULTURE, OBAFEMI AWOLOWO
UNIVERSITY, ILE IFE, NIGERIA**

2012

CERTIFICATION

We certify that this work was carried out by OLUFADE Yusuf Ayodeji of the Department of Crop Production and Protection, Obafemi Awolowo University, Ile Ife.

Supervisor

Dr. M.B. Sosan

Co-supervisor

Dr. J.A.O. Oyekunle

(Department of Chemistry)

Head of Department

Dr. (Mrs.) A.O. Salami

DEDICATION

This thesis is dedicated to my parents whom Allah has used to bring me this far.

OBAFEMI AWOLowo UNIVERSITY

ACKNOWLEDGEMENT

I am grateful to my supervisor, Dr. M.B. Sosan who worked closely with me throughout the period of the study. His constructive criticisms, comments and advice helped to shape this thesis. He also provided encouragement and supported me during the study. He surely deserves my sincere thanks. I also offer my sincere thanks to my Co-supervisor, Dr. J.A.O. Oyekunle who never left me alone, especially during the challenging periods in the Laboratory.

Worthy of being mentioned are: the Head of Department-Dr. (Mrs.) A.O. Salami, Drs O.K. Adekunle, O.J. Soyelu, J.T. Opabode, (Mrs) A. Oluwaranti, R. Akinwale, Mr. N. Osude, Mr. R. Ajibade, Mr. Oyerinde (a.k.a Baba Oye), Prof. T. Alimi (Agricultural Economics), Dr. Oseni (Animal Sciences) Dr. S.A. Muda (Soil Science and Land Management), Dr. W.O. Oladepo (aka Engineer), Mr. Oyeyemi (Soil Science and Land Management), Mr. Oguntoye (TEEAL officer) and Mrs. Oluyemi Idowu.

I am grateful to my parents, Alh. R.A. Olufade and Hajia F.A. Olufade, my brother and sisters (Idrees, Sherifah, Hawau, and Zainab), my cousins (especially Rafi'a, Hajarrah, Halimah, Abdul Gafar, Sekeenah and Rasheedah) for their prayers, encouragement and moral support. These cherished people deserve my sincere thanks. I also acknowledge the consistent care, concern and love from Alh. Mikail Olufade, Mrs. Seilah Oguntade, Mrs. Azeezah Ayanwale, Mr. Abdullah Anifowoshe, Ustaz Musliudeen Kazeem and Bro. Musliudeen Abolore Osho; without which this study would not have been possible.

All my efforts would probably have been a pariah like the DDT (Dichlorodiphenyltrichloroethane), without the 'systematic support' bestowed on me by my only friend-in-Jehovah, Mr. Femi Ajayi (a.k.a. Ajayijesha). He was a strong source of motivation, and provided me a PC which was used to complete the study. I am also indebted to a number of

friends: Tafawa (in Gwoza), Tanimu (in Kaduna), Abdullahi (Chadian), Misbaudeen Disu, Lekan Faniran, Salmah *nee* Mustapha, Toyiybah Alabi, Zainab Umar Sharubutu and Aisha Oluwabunmi Olatunde.

Finally, I give Glory to Almighty Allah (SWT) who saw me through the entire M.Sc. programme. I owe Him my entire life and “surely, my prayers, my sacrifices, my living and my death are for Allah, the Lord of the entire universe”.

OBAFEMI AWOLOWO UNIVERSITY

TABLE OF CONTENT

Title page	I
Certification	II
Dedication	III
Acknowledgment	IV
Table of Content	VI
List of Tables	IX
List of Figures	XI
List of Abbreviations	XII
Abstract	XIV
CHAPTER ONE: INTRODUCTION	1
1.1 Background to the Study	1
1.2 Statement of Problem	8
1.3 Justification	8
1.4 Aims and Objectives	10
CHAPTER TWO: LITERATURE REVIEW	11
2.1 Review of Some Previous Studies on OCs in Foodstuffs	11
2.2 Pesticide Use and Importation	14
2.3 Exposure Routes and Food Contamination	15
2.4 Bioaccumulation of OCs in Food Chain and their Persistence in the Environment	17
2.5 Health Effects of OCs in Humans	18

2.6 Classes and Analysis of OCs in Foodstuffs	20
2.7 State of Insecticides Monitoring Efforts in Nigeria	22
2.8 Safety Indices	24
2.8.1 The Acceptable Daily Intake (ADI)	24
2.8.2 Acute Reference Dose (ARfD)	25
2.8.3 MRL (Maximum Residue Limit)	26
CHAPTER THREE: MATERIALS AND METHODS	29
3.1 Study Area	29
3.2 Sample Collection and Preparation	29
3.3 Laboratory Analysis	29
3.3.1 Extraction Process	29
3.3.2 Clean-up Process	31
3.3.3 Gas Chromatographic Analysis	31
3.4 Statistical Analysis	34
3.5 Quality Control Measures Adopted	34
3.5.1 Percent Recovery (%R) Determination	34
3.5.2 Determination of Detection Limit	35
CHAPTER FOUR: RESULTS	36
4.1 Recovery and Limit of Detection of some Organochlorine Compounds in Foodstuffs	36
4.2 Levels of OCs in Cowpea Grains and Dried Yam chips from Odo Ogbe and Better Life Markets	36
4.2. 1 Levels of OCs in Cowpea Grains from Odo Ogbe and Better Life Markets	36

4.2.2 Levels of OCs in Dried Yam Chips from Odo Ogbe and Better Life Markets	44
4.3 EU-MRLs and Percent Concentrations of OC Residues in Cowpea Grains and Dried Yam Chips	54
4.3.1 EU-MRLs and Percent Concentrations of OC Residues in Cowpea Grains	54
4.3.2 EU-MRLs and Percent Concentrations of OC Residues in Dried Yam Chips	58
4.4 Correlation Coefficients of OCs in Cowpea Grains and Dried Yam Chips from the Two Markets	62
4.5 Principal Component Analysis of OCs in Cowpea Grains & Dried Yam Chips from the Two Markets	69
CHAPTER FIVE: DISCUSSION	85
5.1 Levels of OCs in Cowpea Grains from Odo Ogbe and Better Life Markets	85
5.2 Levels of OCs in Dried Yam Chips from Odo Ogbe and Better Life Markets	88
5.3 Percent Concentration of OCs and MRL Comparison	90
5.4 Variation of OCs in Cowpea Grains and Dried Yam Chips Samples from the Two Markets	92
CHAPTER SIX: CONCLUSION AND RECOMMENDATIONS	94
6.1 Conclusion	94
6.2 Recommendations	94
REFERENCES	96
APPENDIX	108

LIST OF TABLES

Table No.	Title	Page
1	Structural classification of organochlorine insecticides	21
2	Operating conditions of the gas chromatograph	33
3	Levels of chlorinated benzenes (mg/kg) in cowpea grains from Odo Ogbe and Better Life markets	38
4	Levels of dichlorodiphenylethanes (mg/kg) in cowpea grains from Odo-Ogbe and Better Life markets	40
5	Levels of cyclodienes (mg/kg) in cowpea grains from Odo Ogbe and Better Life markets	42
6	Levels of chlorinated benzenes (mg/kg) in dried yam chips from Odo- Ogbe and Better Life markets	45
7	Levels of dichlorodiphenylethanes (mg/kg) in dried yam chips from Odo-Ogbe and Better Life markets	47
8	Levels of cyclodienes (mg/kg) in dried yam chips from Odo Ogbe and Better Life markets	49
9	EU-MRLs and Percent concentration of OCs residues in cowpea grains from Odo Ogbe and Better Life markets	55
10	EU-MRLs and Percent concentration of OCs residues in dried yam chips from Odo Ogbe and Better Life markets	59
11	Correlation Coefficients of OCs Detected in Cowpea Grains from Odo-Ogbe Market	63
12	Correlation Coefficients of OCs Detected in Cowpea Grains from Better Life Market	65
13	Correlation Coefficients of OCs Detected in Dried Yam Chips from Odo-Ogbe Market	66
14	Correlation Coefficients of OCs Detected in Dried Yam Chips from Better Life Market	68

15	Total Variance Explained of OCs in Cowpea Grains from Odo Ogbe market and the Principal Components	70
16	Component Matrix ^a of OCs in Cowpea Grains from Odo Ogbe market	71
17	Total Variance Explained of OCs in Cowpea Grains from Better Life market and the Principal Components	72
18	Component Matrix ^a of OCs in Cowpea Grains from Better Life market	73
19	Total Variance Explained of OCs in Dried Yam Chips from Odo Ogbe market and the Principal Components	78
20	Component Matrix ^a of OCPs in Dried Yam Chips from Odo Ogbe market	79
21	Total Variance Explained of OCs in Dried Yam Chips from Better Life market and the Principal Components	81
22	Component Matrix ^a of OCs in Dried Yam Chips from Better Life market	82



LIST OF FIGURES

Figure No.	Title	Page
1	Map of Ile-Ife town showing Odo Ogbe (Ife Central LGA) And Better Life (Ife East LGA) markets	30
2	Comparative level of OCs in cowpea grains from Odo Ogbe and Better Life markets	43
3	Comparative levels of OCs in dried yam chips from Odo Ogbe and Better Life markets	50
4	Comparative levels of OCs in cowpea grains and	
5	dried yam chips from Odo Ogbe market	52
6	Comparative levels of OCs in cowpea grains and	
7	dried yam chips from Better Life market	53
8	Percent concentration (by grouping) of cyclodienes amongst other classes in OC residues detected in cowpea grains from Odo Ogbe market	56
9	Percent concentration (by grouping) of cyclodienes amongst other classes in OC residues detected in cowpea grains from Better Life market	57
10	Percent concentration (by grouping) of cyclodienes amongst other classes in OC residues detected in dried yam chips from Odo Ogbe market	60
11	Percent concentration (by grouping) of cyclodienes amongst other classes in OC residues detected in dried yam chips from Better Life market	61
12	Scree Plot of OCs in Cowpea Grains from Odo Ogbe market Showing Extracted Components	75
13	Scree Plot of OCs in Cowpea Grains from Better Life market Showing Extracted Components	76

14	Scree Plot of OCs in Dried Yam Chips from Odo Ogbe market Showing Extracted Components	83
15	Scree Plot of OCs in Dried Yam Chips from Better Life market Showing Extracted Components	84

LIST OF ABBREVIATIONS

ADI- Acceptable Daily Intake

ARfD- Acute Reference Dose

ATSDR- Agency for Toxic Substances and Disease Registry

BHC- Benzene Hexachloride

CAC- Codex Alimentarius Commission

DCM- Dichloromethane

DDD- Dichlorodiphenyldichloroethane

DDE- Dichlorodiphenylethylene

DDT- Dichlorodiphenyltrichloroethane

ETDIs- Estimated Total Dietary Intakes

EU- European Union

EU-MRLs- European Union Recommended Maximum Residue Limits

FAO- Food and Agriculture Organization

FDA- Food and Drug Administration

FEPA- Federal Environmental Protection Agency

FMI- Food Marketing Institute

GAP- Good Agricultural Practice

GC-ECD: Gas Chromatography with Electron Capture Detector

HCH- Hexachlorocyclohexane

IARC- International Agency for Research on Cancer

JMPR- Joint Meeting on Pesticide Residue

MPIs- Maximum Permissible Intakes

MRLs- Maximum Residue Limits

NAFDAC- National Agency for Food and Drug Administration and Control

NOEAL- No Observed Effect Adverse Level

NOEL- No Observed Effect Level

OCs- Organochlorines

PAN- Pesticide Action Network
PCs- Principal Components
PCA- Principal Component Analysis
PICS- Purdue Improved Cowpea Storage
POPs- Persistent Organic Pollutants
UNDP- United Nation Development Programme
UNEP- United Nation Environmental Programme
WHO- World Health Organization

OBAFEMI AWOLOWO UNIVERSITY

ABSTRACT

The study established the presence and determined levels of organochlorine insecticides residues in samples of cowpea grains and dried yam chips sold in wholesale markets in Ile-Ife and ascertained whether the residue levels were above their respective permissible levels; with a view to assess the likely dietary intake of organochlorine insecticide (OC) residues in these food items which are widely consumed by the people of Ile-Ife and its environs, and be able to ascertain the safety of the food items for human consumption.

Five (5) samples each of cowpea grains and dried yam chips were collected from randomly selected traders in each of the wholesale markets, making a total of ten samples per food product. All samples were analyzed for residues of organochlorine insecticides to determine the presence and levels of residues in the sampled cowpea grains and dried yam chips using Gas Chromatography with Electron Capture Detector (GC-ECD) after the extraction and cleanup of all samples. Data were analyzed using descriptive statistics, correlation and Principal Component analysis (PCA).

The results showed that all the cowpea grains and dried yam chips samples from the two markets contained various sub-group of OCs which included chlorinated benzenes, cyclodienes and dichlorodiphenylethanes. The predominant chlorinated benzene, cyclodiene and dichlorodiphenylethane compounds in cowpea grains from the two markets were γ -BHC (lindane), heptachlor and DDD (a DDT metabolite). Eighty five percent and 90% of OCs detected in cowpea grains sampled from Odo Ogbe and Better Life markets respectively had their mean concentration (mg/kg) greater than the EU-MRLs. While, in the dried yam chips sampled from the two markets, δ -BHC (an isomer of γ -BHC) was predominant. The

predominance of two cyclodiene compounds, heptachlor (0.264 ± 0.038 mg/kg) and aldrin (1.050 ± 0.908 mg/kg), were observed in the dried yam chip samples from Odo Ogbe and Better Life markets respectively. Methoxychlor (0.039 ± 0.006 mg/kg) and DDD (0.141 ± 0.038 mg/kg) were the predominant dichlorodiphenylethane compounds in the dried yam chip samples from Odo Ogbe and Better Life markets respectively. Seventy five percent and 95% of OCs detected in dried yam chip samples from Odo Ogbe and Better Life markets respectively had their mean concentrations (mg/kg) above the EU-MRLs. The results also revealed that a strong correlation existed among a number of OC insecticide residues suggesting a common origin. Principal Component Analysis (PCA) results of cowpea grain samples from Odo Ogbe and Better Life markets accounted for 10 and 8 OCs respectively, causing variation in the 20 OCs detected; while the results of the dried yam chips from Odo Ogbe and Better Life markets accounted for 9 and 6 OCs respectively, responsible for the variations in the 20 OCs detected.

The study concluded that Better Life market in general, recorded higher OC residues in the foodstuff samples than in those from Odo Ogbe market; and that levels of OC insecticide residues in cowpea grains and dried yam chips sampled from the two markets were generally above the EU-MRLs, suggesting that the foodstuffs were not safe for human consumption.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Cowpea (*Vigna unguiculata* L. Walp) is an important major staple food crop in sub-Saharan Africa. West Africa produces about 75% of the world cowpea which is produced primarily in Nigeria. In Nigeria, the greatest production of cowpea comes from the northern region. The north produces about 1.7 million tonnes from 4 million hectares. This represents over 60% of total production. The seeds form a major source of plant proteins, vitamins to man, and feed for animals. The young leaves and immature pods are eaten as vegetables (Adetiloye *et al.*, 2006).

The most commonly occurring insect pests of cowpea in tropical Africa are the cowpea aphids, *Aphis craccivora* Koch (Aphididae:Homoptera); the legume bud thrips, *Megalurothrips sjostedti* Tryb. (Thripidae:Thysanoptera); the legume pod borer, *Maruca vitrata* Fab. (Pyralidae:Lepidoptera); a species complex of pod sucking bugs with two coreids-*Clavigralla tomentosicollis* Stal. (Coreidae:Hemiptera) and *Anoplocnemis curvipes* Fab. (Coreidae:Hemiptera). The bruchid, *Callosobruchus maculatus* Fab. (Bruchidae:Coleoptera) is the major storage pest of cowpea grains in tropical Africa (Singh *et al.*, 1990). Insect pests are major constraints to cowpea production in West Africa. The crop is severely attacked at every stage of its growth by a myriad of insects that make the use of tolerant varieties and insecticide sprays imperative (Dugje *et al.*, 2009). Just as with other crops, the market prices for cowpea are usually at their lowest at the time of harvest. However, storing cowpea grains to sell when prices

go up brings another problem-weevil (*Callosobruchus maculatus*). These insects can eat their way through the stored crop in a matter of weeks, leaving just powder (Kuagi *et al.*, 2010).

Yam is well distributed in the humid tropics of the Southern part of West Africa, which includes Nigeria, where they are valued as important source of carbohydrate. The existing species are: *Dioscorea rotundata*, *D. alata*, *D. cayenensis*, *D. dumentorum*, *D. bulbifera*, *D. esculenta*, *D. trifida*, *D. compositae*, *D. japonica* and *D. hispida*. (Adetiloye *et al.*, 2006). There are also species of wild yam growing in Nigeria whose tubers are collected for eating in times of food shortage (Adelusi and Lawanson, 1987). Nigeria produces about 30 million tonnes of yam making it the world's largest producer of yam (FAO, 2004).

In Nigeria and other West African countries, yam is sold either as fresh tuber or as dried chips. In both forms, yam can be stored with varying successes and benefits. The farmer's primary objectives in processing yams into chips are: reduction of post-harvest losses, removal of inedible and unmarketable parts, reduction of transportation costs, earn higher income, convert the fresh tuber into more convenient form, to produce a form that can store longer than fresh tubers, and to provide raw materials for agro- industries (Eze, 1998). To overcome the problems of loss and seasonal supply of yams, a transformation into chips was initiated by farmers. This is a craft transformation of matter into a fresh dehydrated form by solar drying (Babajide *et al.*, 2007). To facilitate a convenient processing of yam tubers into yam flour, yam chips and pellets (Ayemibo, 2010). However, during storage, the chips are often infested by boring insects (Adisa, 1985) which cause considerable damage in a few months. The most common among these are *Sitophilus zeamais* Motshulsky (Coleoptera: Curculionidae), *Dinoderus oblonguntatus* Lesne, *D. porcellus* Lesne, and *D. minutus* Fabricius (Coleoptera:

Bostrichidae); as well as *Palorus subdepressus* Wollaston -Coleoptera: Bostrichidae (Oni, 1995; Dumont and Vernier, 1997).

Vernier (1998) noted that weevil infestation in storage increased losses in terms of dry matter and visual quality of dried yam chips. Yam chips are commonly stored in jute sacks with the application of some insecticides such as actellic, phostoxin or a mixture of lindane and/or kerosene with water (Orkwor *et al.*, 1997). Such preservation treatments have met the farmer's goal of reducing post-harvest losses and earning higher income, but pose health and environmental pollution risks (Eze *et al.*, 2006).

Pesticide can be defined as any chemical substance or mixture of substances intended for preventing, destroying, repelling, or mitigating the effect of any pest of plants and animals. They include insecticides, herbicides, rodenticides, nematocides, avicides, acaricides, fungicides, molluscides, repellents and attractants used in agriculture, public health, horticulture, food storage or a chemical substance used for a similar purpose [National Agency for Food and Drug Administration and Control, (NAFDAC, 1996; Hamilton and Crossley, 2004)].

Pesticides are transformed in soil, water, air and food particles into metabolites and other degradation products. The transformations may be microbiological (metabolism), hydrolysis (reaction with water) or photolysis (broken down by sunlight). Transformation usually proceeds through small changes to the parent pesticide molecule to complete mineralization to carbon dioxide, water, chloride, phosphate and so on. For some pesticides, the initial transformation products may also be residues of concern in food or drinking water and should be included in the risk assessment process. Some transformation products are more persistent than the parent pesticide, e.g. dichlorodipenylethylene (DDE) is more persistent than Dichlorodiphenyltrichloroethane -DDT (Hamilton and Crossley, 2004).

Pesticides are used widely in agriculture since significant economic damage can occur when insects, nematodes, fungi and other micro- and macro-organisms affect food and commodity crops. The quantity and types of pesticides required to ensure high crop yield and

For more information, please contact ir-help@oauife.edu.ng

OBAFEMI AWOLOWO UNIVERSITY