

CHRISTINE ABEY ASHAOLU

***STRATEGIES FOR EFFECTIVE REGULATION AND
CONTROL OF PESTICIDES TOWARDS IMPROVED
ENVIRONMENTAL SAFETY AND SUSTAINABILITY IN
NIGERIA***



UNIVERSIDADE DO ALGARVE

Faculty of Science and Technology

2019

CHRISTINE ABEY ASHAOLU

***STRATEGIES FOR EFFECTIVE REGULATION AND
CONTROL OF PESTICIDES TOWARDS IMPROVED
ENVIRONMENTAL SAFETY AND SUSTAINABILITY IN
NIGERIA***

**ERASMUS MUNDUS MASTER IN CHEMICAL INNOVATION AND REGULATION
(MESTRADO ERASMUS MUNDUS EM INOVAÇÃO QUÍMICA E REGULAMENTAÇÃO)**

SUPERVISED BY:

DRA. ISABEL CAVACO

DR. DANIEL SAINZ

Declaration of Authorship

I declare that I am the author of this work, which is original. The work cites other authors and works, which are adequately referred in the text and are listed in the bibliography.

CHRISTINE ABEY ASHAOLU

Copyright: Christine Abey Ashaolu, The University of Algarve (Univeridade do Algarve) and University of Barcelona (Universitat de Barcelona) has the right to keep and publicise this work through printed copies in paper or digital form, or any other means of reproduction, to disseminate it in scientific repositories and to allow its copy and distribution with educational and/or research objectives, as long as they are non-commercial and give credit to the author and editor.

Acknowledgement

I would humbly like to acknowledge everyone who played a role in my academic accomplishments. First, my parents, especially my late father (Mathew Sinoke Aluko) who laid the academic foundation and excellence in me, without my parents i could never have attained this current level of success. Secondly my ever-loving Husband, Children, Brothers and Sisters for each of whom has supported me throughout the research process.

My sincere appreciation to the National Agency for Food and Drug administration and Control (NAFDAC) Nigeria, for their support at the experimental stage of this research.

Many thanks to my supervisors Professor Isabel Cavaco and Professor Daniel Sainz for their guidance, support and enabling environment provided to successfully complete this research.

My profound gratitude to the European Commission for the scholarship award to earn a Master of Science Degree in Chemical Innovation and Regulation from two top European Universities.

I appreciate you all for your unwavering support

Dedication

This Research Project is Dedicated to my Late father Elder Mathew Sinoke Aluko

ABSTRACT

Ever since plant was first cultivated for food, there has been the need to protect it against diseases and pests and the intervention of chemicals after the world War II to combat pests and disease-causing organisms have greatly increased the global use of pesticides. Pesticides are beneficial to man and his environment but can also pose adverse effects if not effectively regulated and controlled, hence, regulations are developed to ensure safety of pesticides throughout its life cycle.

It is however evident that, irrational and indiscriminate distribution and use of Plant Protection Products in Nigeria has resulted into high residue levels in food leading to contamination and pollution of the environmental matrices. The EU ban in 2015 on the importation of beans from Nigeria due to the detection of high levels of pesticide residues and use of unauthorized pesticides are also reflections of the indiscriminate use and ineffective control and regulations of Plant Protection Products in Nigeria.

From the Pesticide residue analysis conducted in this study, the concentration of the organochlorines ranged from ND-0.88mg/kg, organophosphates ND-5.25mg/kg and pyrethroids ND-4.55mg/kg. Over 50% of the total samples analyzed showed residue levels above the EU Maximum Residue Limit (MRL). The National Pesticide Trade data revealed larger quantities of herbicide imports compared to other classes of imported pesticides. The current Nigeria pesticide regulations was found not to include some safety indicators as compared to those of EU and USA regulations on placing Plant Protection Products on the market.

Recommendations for safety control and regulation systems for placing plant production products on the market in Nigeria have been articulated.

Keywords: Safety, Regulations, Pesticides, Maximum Residue Limit, Nigeria

Resumo

Desde os primórdios da agricultura que a humanidade sente a necessidade de proteger as plantas de doenças e pragas. O desenvolvimento de produtos químicos que se seguiu à 2ª Guerra Mundial permitiu combater eficazmente pragas e organismos patogénicos, aumentando muito o uso global de pesticidas. Os pesticidas podem ser benéficos para o Homem e o meio ambiente, mas podem também causar efeitos adversos se não forem efetivamente regulados e controlados. É por isso essencial desenvolver e implementar regulamentação que garanta a segurança durante todo o ciclo de vida dos pesticidas.

No caso da Nigéria, é flagrante que a distribuição indiscriminada e o uso irracional de fitofármacos resultou em elevados níveis de contaminação e poluição das matrizes ambientais e mesmo em resíduos de pesticidas nos alimentos. Em 2015 a União Europeia proibiu a importação de feijão da Nigéria devido à deteção de elevados níveis de resíduos de pesticidas, e à utilização de pesticidas não autorizados.

Neste trabalho realizou-se a análise de resíduos de pesticidas em amostras de feijão recolhidas localmente em mercados na Nigéria, tendo-se obtido concentrações de organoclorados até 0,88 mg/kg, organofosforados até 5,25 mg/kg e piretróides até 4,55 mg/kg. Mais de 50% do total de amostras analisadas apresentaram níveis de resíduos acima do limite máximo residual (Maximum Residual Limit) definido pela UE. Os dados obtidos através dos registos de comércio internacional de pesticidas revelaram quantidades de herbicidas importados muito superiores à importação de pesticidas. Verificou-se que a atual regulamentação de pesticidas na Nigéria não inclui alguns indicadores de segurança, quando comparados com a regulamentação da UE e dos EUA sobre a colocação de produtos fitofarmacêuticos no mercado. Conclui-se com a articulação de um conjunto de recomendações para sistemas de controle de segurança e regulamentação para colocação de produtos fitofarmacêuticos na Nigéria.

Table of Contents

Declaration of Authorship.....	i
Acknowledgement	ii
Dedication	iii
ABSTRACT.....	iv
List of Tables	viii
List of Figures	ix
Abbreviations.....	x
1 INTRODUCTION	1
1.1 Evolution of Pesticides.....	1
1.2 Classification of Pesticides	2
1.3 Regulation of Pesticides.....	3
1.3.1 Overview of EU Framework on the Regulation of PPPs	4
1.3.2 Overview of U.S.A. Framework on the Regulation of PPPs	6
1.3.3 Overview of the Nigeria Framework on the Regulation of PPPs.	7
1.4 International Agreements and Organisations that Addresses Pesticide Use.....	9
1.5 Environmental Fate of Pesticides.....	11
1.6 Pesticide Use and Contamination	12
1.7 Human and Environmental Health Effects of Pesticides	15
1.7.1 Health effects	15
1.7.2 Environmental Effects:	16
1.8 Statement of the Problem.....	16
1.9 Aim	18
1.10 Objectives of The Study.....	18
2 METHODOLOGY.....	19
2.1 Information Gathering.....	19
2.2 Experimental	20
2.2.1 Sampling Sites:	20
2.2.2 Chemicals and Materials	22
2.2.3 Standard	22
2.3 Analytical Technique	23
3 RESULTS AND DISCUSSION.....	28
3.1 Plant Protection Products Regulations	28
3.2 Nigeria Pesticide Trade Data	30

3.3	Analytical Results of Pesticide Residues	37
4	CONCLUSION	45
5	BIBLIOGRAPHY	47

List of Tables

Table 1.1 Summary of PPPs related regulations in the in EU	5
Table 1.2 Summary of PPPs related Regulations in the USA.....	7
Table 1.3 Summary of PPPs related Regulations in Nigeria.	8
Table 1.4 Selected publications on Pesticide Residues in Food crops.....	13
Table 1.5 Results of some Pesticide monitoring program by the EU in 2017	15
Table 1.6 Notification/Alert notices on Boarder rejections of Beans imported from Nigeria (2015-2016).....	17
Table 2.1 Names of sampling sites	21
Table 2.2 GC Operating Conditions	22
Table 2.3 validation Table	23
Table 2.4 Recovery results for Organophosphates	24
Table 2.5 Physicochemical properties of analytes	25
Table 3.1 Comparative Assessments of Plant Protection Products Regulations.....	28
Table 3.2 Assessments of PPPs Authorisation Indicators.....	29
Table 3.3 Quantities (Tons) of Imported Pesticides.....	31
Table 3.4 Top 15 Pesticides Exporting countries to Nigeria 2013-18	33
Table 3.5 Imported pesticides (€) from other African Countries from 2013-2017.....	35
Table 3.6 Manufacturing Sectors in Nigeria.....	35
Table 3.7 Organochlorine concentrations (mg/kg) in Beans samples from all Locations	37
Table 3.8 Organophosphates concentrations (mg/kg) in Beans samples from all Locations	39
Table 3.9 Pyrethroids Concentrations (mg/kg) in Beans Samples from all Locations	41
Table 3.10 Overall concentration (mg/kg) range of pesticide residues and EU-MRLs.....	42

List of Figures

Figure 1.1 Chemical and Biological Classification of Pesticides.	3
Figure 1.2 Summary of Approval Scheme of PPPs in the EU.....	4
Figure 1.3. Summary of Approval Scheme of PPPs in the United States.....	6
Figure 1.4 Summary of Approval Scheme of PPPs in Nigeria.....	8
Figure 1.5 Environmental Fate of Pesticides.	12
Figure 2.1 White Beans Samples	20
Figure 2.2 Brown Beans samples.....	20
Figure 2.3 Location of the Federal Capital Territory (FCT), Nigeria.....	21
Figure 2.4 Map of FCT showing sampling sites.....	21
Figure 2.5 Recovery Chart for organophosphate.....	24
Figure 3.1 Quantities (kg) of Pesticides imported from 2013-2018	31
Figure 3.2 Percentatge of Imported pesticides from 2013-2018.....	32
Figure 3.3 Tonnes of Active Substances (AS) used globally.....	32
Figure 3.4 Pesticide import value 2013-2018	34
Figure 3.5 Pesticide Export Value 2013-2018.....	34
Figure 3.6 Manufacturing Industries in Nigeria January. 2019	36
Figure 3.7 Organochlorine Concentrations (mg/kg) in White Beans Samples.....	37
Figure 3.8 Organochlorine Concentrations (mg/kg) Brown Beans Samples.....	38
Figure 3.9 Organophosphates Concentrations (mg/kg) in white Beans samples.....	39
Figure 3.10 Organophosphates Concentrations (mg/kg) in Brown Beans samples.....	40
Figure 3.11 Pyrethroids Concentrations (mg/kg) in white beans samples.....	41
Figure 3.12 Pyrethroids Concentrations (mg/kg) in Brown Beans samples.....	42
Figure 3.13 Percentage of Pesticides below and above MRL.....	43

Abbreviations

AI	Active Ingredients
AS	Active Substance
CAS	Chemical Abstract Service number
DDT	Dichloro-Diphenyl Trichloroethane
EC	European Commission
EFSA	European Food Safety Authority
EU	European Union
FCT	Federal Capital Territory
FMITI	Federal Ministry of Industry, Trade and Investment
FRN	Federal Republic of Nigeria
GC	Gas Chromatography
GUP	General Use Pesticides
HHPs	Highly Hazardous Pesticides
IPM	Integrated Pest management
IVM	Integrated Vector Management
LOD	Limit of Detection
LOQ	Limit of quantification
MAN	Manufacturers Association of Nigeria
MOE	Ministry of Environment
MRL	Maximum Residue Limit
NAFDAC	National Agency for Food and Drug Administration and Control
NBS	National Bureau of Statistics
NCS	Nigeria Custom Service
ND	Not Detected
OCPs	Organochlorine Pesticides
OPs	Organophosphate Pesticides
PPPs	Plant Protection Products
PFPD	Pulsed Flame Photometric Detector
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe
RMS	Rapporteur Member State
RUP	Restricted Use Pesticides
SUP	Sustainable Use pesticides
USA	United States of America
USEPA	United States Environmental Protection Agency

1 INTRODUCTION

1.1 Evolution of Pesticides

Ever since plant was first cultivated for food, there has been the need to protect it against diseases and pests and the sophistication level of protection has increased with time. losses of farm produce due to pests and diseases ranges between 10-90% with average value of 35-40% for all potential fibre and food crops¹ The intervention of chemicals after the World War II to combat these agricultural pests and disease-causing organisms has greatly increased the global use of certain category of agrochemicals known as Pesticides^{2,3}. The first use of pesticides was recorded about 4500 years ago by Sumerians who used Sulfur compounds to control insects and mites, whilst Chinese used mercury and arsenical compounds about 3200 years ago to control body lice⁴. Pyrethrum derived from dried flowers of *chrysanthemum cinerariaefolium* was also used as insecticide over 200 years ago. Smokes (burning of chaffs, straws, dung, animal horn etc) were used against mildews, blights and insects⁴. Any substance used then had to be of either plant or animal origin as there were no chemical industries at that time, although, weeds were mainly controlled using salt/sea water or by weeding⁵. Many inorganic chemicals have been used as pesticides since the ancient time and indeed, copper sulphate and lime-based mixtures are still currently in use to control fungi.

The growth of synthetic pesticides (organochlorines) accelerated in the 1940s with Dichloro-Diphenyl-Trichloroethane (DDT) being the most popular due to its broad-spectrum activity and low mammalian toxicities. In 1962, Rachel Carson launched public environmental conscience through her book titled “Silent Spring” which inspired widespread concern of adverse effects of synthetic pesticides on human health and the environment⁶. This alongside other public concerns over the harmful effects of pesticides on non-target species led to the phasing out of organochlorines in most industrialized countries in 1970s⁷. The organophosphate (OPs) and carbamate pesticides later replaced the organochlorines. Though, the United States Environmental Protection Agency (USEPA) later considered a ban on some of the OPs when they began to contaminate groundwater and having high toxic effects on mammals. This led to the phasing out of residential uses of diazinon, and chlorpyrifos in early 2000⁷. This gradual phasing out of OPs has led to a more dynamic shift to green pesticides with more pressure to balance the need to increase food production and ensure safety of people⁸. Today, the pest management toolbox has expanded to include crops designed to produce their own insect resistance and herbicide tolerance known as Genetically Engineered Crops¹⁰.

According to the European Union Definition⁹

“A Pesticide is something that prevents, destroys, or control a harmful organism (‘Pest’) or disease, or protects plants or plant products during production, storage and transport”

Pesticide is a broad term which include both Plant Protection Products (PPPs) for agricultural applications and Biocides for non-agricultural purposes. PPPs are to plants the equivalent of medicines for humans. They are treatments used to keep crops healthy by protecting them from pests and diseases and are used in both conventional and organic agriculture. PPPs can be synthetic or natural chemicals and minerals. They contain one or more active ingredients with other substances like: adjuvants, safeners, synergists, co-formulants and usually available as solid or liquid formulations. Examples of Liquid formulations are: Emulsifiable Concentrate (EC), Solutions (S), Suspensable Concentrate (SC), Wettable Powders (WP), Granules and Aerosols. Solid formulations include: Dry Powder (DP), Water Soluble powder (SP), Water Dispersable Granules (WG), and Baits. Pesticides are used in agriculture (Crop protection, Ectoparasites), Public Health (Vector control, General hygiene, Disinfectants) and Industry (Protection of materials, water treatment, post-harvest storage). Pesticides are known to have adverse effects on man and the environment if not adequately **controlled** and/or **regulated**

1.2 Classification of Pesticides

Pesticides can be either organic or inorganic, natural or synthetic and can be grouped in several different ways. They are most commonly classified as either Chemical or Biopesticides (Figure 1.1) and/ or according to the following categories:

- Chemical class (Chemical structure),
- Target Organism (The pest they control)
- Mode of Action (How they control the pest)
- Activity Spectrum (Broad spectrum or Selective)
- Toxicity (LD₅₀)

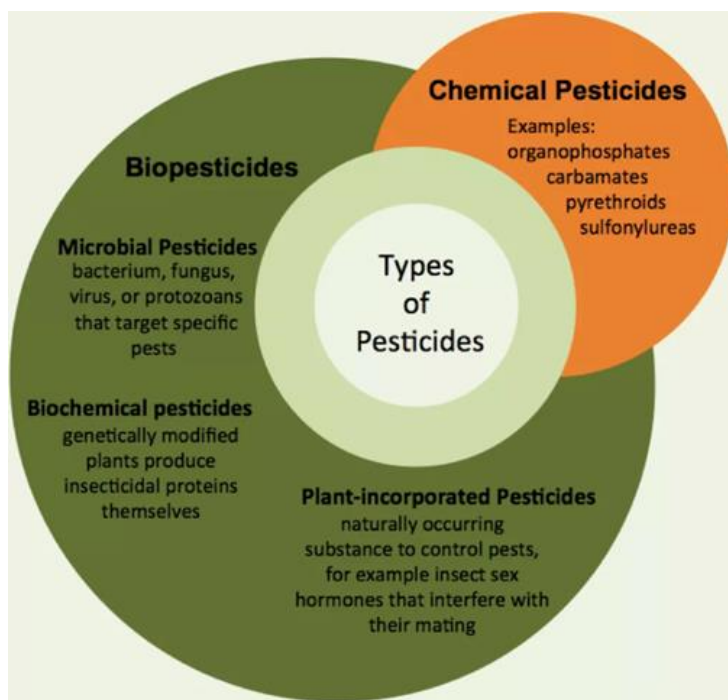


Figure 1.1 Chemical and Biological Classification of Pesticides¹⁰.

The Chemical pesticides studied in this research are: organochlorines (DDT, Aldrin, Lindane), organophosphates (Dichlorvos, Dimethoate, Diazinon, Chlorpyrifos) and the pyrethroids (Permethrin and Cypermethrin)

1.3 Regulation of Pesticides

In view of pesticides' intrinsic properties to cause harm to both target and non-target organisms, regulations are developed to minimize these risks. The primary aim of pesticides regulations is to protect human health and the environment. It prevents barriers to trade and sets out safety criteria to be followed throughout its life cycle. It requires expertise, skills and considerable amount of time of regulatory authorities, resources and commitment of manufacturers. Registration of pesticides is a legal administrative process whereby the responsible national government authority approves the sale and use of pesticides following the evaluation of comprehensive scientific data which demonstrate the effectiveness for its intended purpose and that it does not pose an unacceptable risk to human or animal health and the environment¹¹.

1.3.1 Overview of EU Framework on the Regulation of PPPs

The EU classified pesticides into two main groups: Plant Protection Products (PPPs) and Biocides. Authorisation of PPPs is accomplished by **Regulation (EC) No. 1107/2009** concerning placement of PPPs on the market¹². The approval of PPPs involves three main steps namely: Approval of Active substances, Authorisation and Monitoring of Pesticides. The authorization process involves three partners namely: European Food Safety Authority (EFSA), European Commission (EC) and Member States (MS) (Figure 1.2). Over a hundred specific tests are carried out before the approval of a PPP in the EU. Tests carried out included but not limited to: Physicochemical properties, Toxicity and Metabolic studies, Residues, Environmental/Ecological studies and efficacy. Mutual recognition of authorisation is possible. Chapter II and III of Regulation (EU) 1107/2009 explained the requirements, contents and procedures (criteria) for the approval of Active Substances, Adjuvants, synergists, co-formulants and authorization of PPPs. Annex II of the regulation specified the criteria for pesticides to be considered as **candidate for substitution** in order to gradually phase out or replace with safer alternatives. Criteria for low risks active substance is also specified in point 5 of Annex II. Persistent Organic Pollutants (POPs), Bio-accumulative and Toxic Substances (PBTs) are not considered for approvals under the regulation as stated in Annex II. The EU PPPs related Regulations are summarised in Table 1.1 below

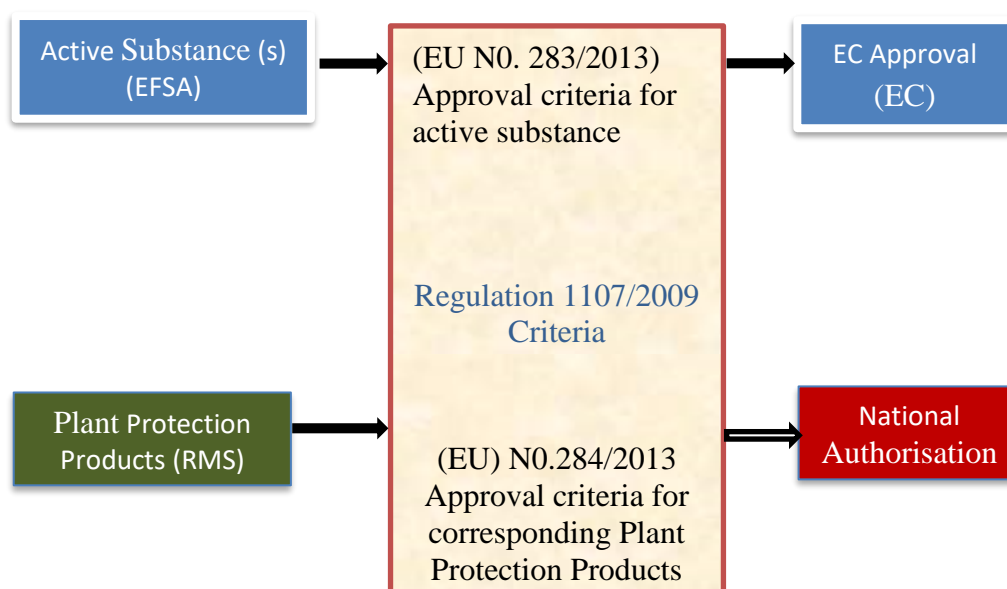


Figure 1.2 Summary of Approval Scheme of PPPs in the EU

Table 1.1 Summary of PPPs related regulations in the in EU

Pesticides Regulations	Title/Actions
Regulation (EC) N0. 1107/2009	Concerning placement of Plant Protection Products (PPP) on the Market.
Commission Regulation (EU) N0. 283/2013	Setting data requirements for active substances in accordance with Regulation (EC) No. 1107/2009
Regulation (EC) No. 1272/2008	Classification Labelling and Packaging (CLP) regulation for dangerous preparations including pesticides
Commission Regulation (EU) N0. 284/2013	Setting data requirements for PPPs in accordance with Regulation (EC) No. 1107/2009
Commission Regulation (EU) 547/2011	Labelling requirements for PPPs
Regulation (EC) N0. 396/2005	Maximum Residue levels of pesticides in or on food and feed of plant and animal origin
Directive 2009/128/EC	Sustainable use of Pesticide
Directive 2009/127/EC	Introduces requirements for the inspection and maintenance of machinery for pesticide application
Commission Regulation (EC) N0. 889/2008	Laid down rules for the implementation of council regulation (EC) 834/2007 on organic production, labelling and control. Allows only the use of pesticide in organic agriculture only when other methods of pests and disease control are ineffective. Only PPPs listed in Annex II of the regulation is allowed and must document the need to use it
Regulation (EC) N0. 1185/2009:	Concerning statistics on pesticides. Ensures comprehensive statistical data on sale and use of pesticides in the EU. Contained rules for collecting information in each member state (Eurostat)
Directive 2000/60/EC	Establishing a framework for community action in the field of water policy. Sets limits for chemicals in aquatic environment and includes provisions for monitoring pesticides
Council Directive 98/83/EC	Concerned with quality of water intended for human consumption (Drinking Water Directive) -fixes the maximum pesticide concentration in drinking water
Directive 2008/105/EC	Directives on Environmental Quality Standards (EQS) in the field of water policy. Specifies limits on concentrations of some pesticides and other substances in surface waters.
Directive 2006/118/EC	Ground Water Directive (GWD). Protection of underground water against pollution and deterioration. Active Ingredients (AIs) in pesticides including their metabolites, degradation and reaction products)
Directive 2004/35/CE	Environmental liability Concerned with environmental damage (protected species, natural habitats, etc) caused by occupational activities such as placement of PPPs on the market amongst other activities.
Directive 2008/98/EC.	Record keeping, Monitor and Control obligation from cradle to grave. From waste production to final disposal or recovery.
Regulation (EU) N0. 528/2012	Placing on the market and use of biocidal products (BPR)

1.3.2 Overview of U.S.A. Framework on the Regulation of PPPs

The Framework of the United States of America is very similar to that of the EU excepts that approval at all stages is carried out by the United States Environmental Protection Agency (Figure 1.3). The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and Federal Food Drug and Cosmetic Act (FFDCA) are the Primary Federal statutes that gives USEPA the authority to regulate all pesticides in the United States.

Pesticides are divided into three main groups namely: Conventional, Antimicrobial and Bio-Pesticides and authorization processes are in three stages like that of the EU. Regulations of pesticides in the United States is accomplished based on the **U.S. 40 Code of the Federal Regulations (40 CFR). Parts 150-189**¹³. The EPA work harmoniously with other federal and state agencies to enforce pesticide regulations as many states requires registration before pesticide can be distributed or sold in its boarders. The United States related PPPs Regulations are summarised in Table 1.2

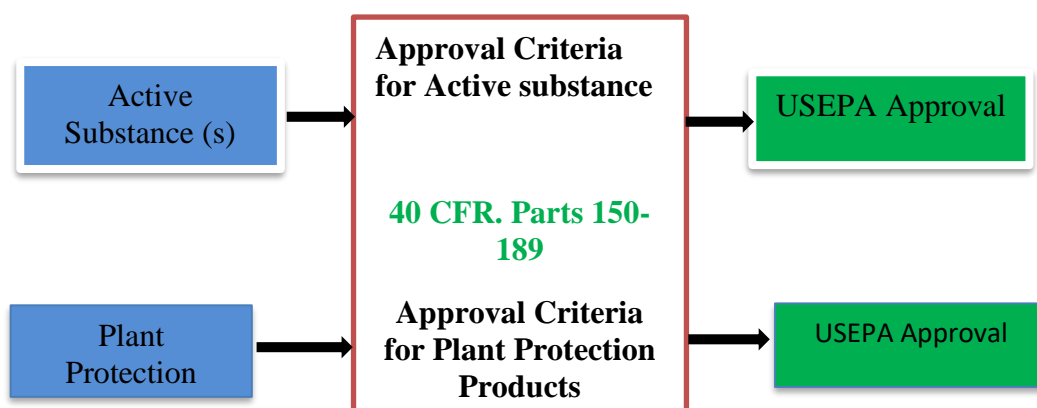


Figure 1.3. Summary of Approval Scheme of PPPs in the United States.

Table 1.2 Summary of PPPs related Regulations in the USA

Pesticide Regulations	Title
U.S. 40 Code of the Federal Regulations (40 CFR). Parts 150-189	Pesticide Programs: Authorization of Pesticides
Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA act)	Authorized EPA to regulate the sale, use, and distribution of pesticides.
Federal Food Drug and Cosmetic Act (FFDCA):	Authorized EPA to set limits on the amount of Pesticide residues allowed in food or animal feed.
Food Quality Protection Act of 1996 (FQPA)	This act amended FIFRA and FFDCA by increasing the safety standards for new pesticides used on foods. FQPA also requires older pesticides and previously established tolerances to be periodically re-assessed using the new tougher standards.
Pesticide Registration Improvement act (PRIA)	Establishes the fees and timelines associated with pesticide registration
Endangered Species Act (ESA)	Requires EPA to assess the risk of pesticides to threatened or endangered species and their habits.
40-CFR Part 171 Certification of Pesticides Applicators	Certification of Applicators (Commercial and Private) for restricted use pesticides and equipment maintenance
Restricted Use Classification: 40CFR 152.60 - 152.175	Restricts a product or its use to a certified applicator or someone under direct supervision of certified applicator
Safe Drinking Water Act (SDWA). 1974.2004	Regulates the nation's public drinking water supply- (Maximum Concentration of Pesticides and other chemicals)
Clean Water Act. (CWA) 1972	Regulates quality of surface waters-specifies limits of some pesticides and pollutants discharged into surface water.
Resource Conservation and Recovery (RCRA) Act 1971. (40CFR part 239-282)	Gives USEPA authority to control hazardous wastes from cradle to grave (Disposal of pesticides)

1.3.3 Overview of the Nigeria Framework on the Regulation of PPPs.

The Federal Republic of Nigeria (FRN) operates two major classifications namely:

Chemical and Biopesticide. The approval of PPPs involves Efficacy assessments, Authorization of PPPs and Monitoring. Similar to the U.S., approval at all stages is carried out by the National Agency for Food and Drugs Administration and Control (NAFDAC) as mandated by the **NAFDAC ACT CAP N1 LFN, 2004**. Authorization of PPPs are in line with the **Pesticide Registration Regulation 2018**¹⁴ and Biopesticide Registration Regulation 2014¹⁵ (Figure 1.4) Efficacy, Field trial (in case of biopesticides) assessments with Good Manufacturing Practices are ensured before final authorization of PPPs. Comprehensive certificate of analysis, certificate of manufacture and free sale are mandatory documents for approval of imported PPPs. Although, some claims may be re-evaluated if deemed necessary. The Nigeria related PPPs regulations are summarised in Table 1.3 below:

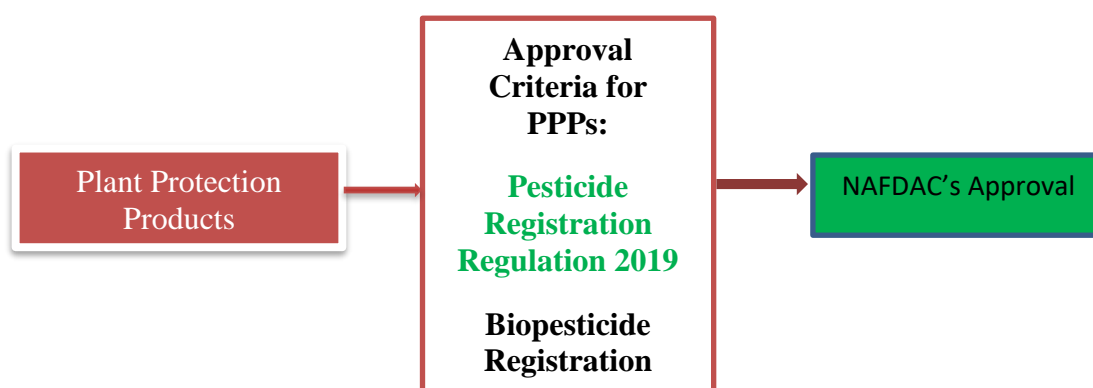


Figure 1.4 Summary of Approval Scheme of PPPs in Nigeria

Table 1.3 Summary of PPPs related Regulations in Nigeria.

Pesticide Regulations	Title
NAFDAC Act CAP N1 Law of Federal Republic of Nigeria	Mandated NAFDAC to control and regulate pesticides with all other regulated products
Pesticide Registration Regulation 2019	Sets requirements for the registration of all pesticides that are manufactured, imported, exported, advertised, sold, distributed or used in Nigeria.
Biopesticide Registration Regulation 2014 (Draft)	Prescribes minimum requirements for the importation, exportation manufacture, distribution, advertisement, sale & use of bio-pesticides
Water Resources Act 101 of 1993. "6 and Drinking Water Quality-NIS 554:2015	Sets limits for pesticides and other pollutants in water
National Environmental (Surface and Groundwater quality control) Regulations 2011	Preserve the physical, chemical and biological integrity of surface and ground water.
National Environmental Standards and Regulations Enforcement Agency (Establishment Act), 2007	Enforce compliance with handling and disposal of pesticides and other hazardous wastes
Doc. Ref, No: R&R-GDL-oo16-oo	Set guidelines for the registration of pesticides made in Nigeria.
Doc. Ref. No: R&R-GDL-oo9-oo	Set guidelines for the registration of imported pesticides
Doc. Ref. No.:CER-GDL-007-00	Set guidelines for issuance of permit to import restricted chemicals and agrochemicals.
Doc. Ref. No: VMAP-GDL-016-05	Guidelines for listing as pesticides, agrochemicals, fertilizers, Biopesticides and Bio-fertilizers marketers
Doc. Ref. No: VMAP-GDL-016-06.	Guidelines for issuance of permit to import field trial samples
Doc. Ref. No: VMAP-GDL-016-07	Guidelines for issuance of permit to import bulk pesticides, agrochemicals, and fertilizers

1.4 International Agreements and Organisations that Addresses Pesticide Use.

Pesticide related International Agreements/Treaties are:

- **Chemical Weapon Convention (CWC)** is the convention on the prohibition of the Development, Production, Stockpiling, and Use of chemical weapons and on their destruction. The convention was signed on 13th January 1993 and entered into force on 29th April 1997. Prohibits use of organophosphorus compounds (that can also be formulated as pesticides) as a neurotoxic chemical warfare agent
- **Stockholm Convention** on Persistent Organic Pollutants (POPs) adopted on 27th May 2001 and entered into force on 17th May 2004. It aims to eliminate or restrict the production and use of POPs¹⁶ like the organochlorine pesticides
- **Rotterdam Convention** on the Prior Informed Consent Procedure for certain Hazardous Chemicals and Pesticides in international trade is a multilateral treaty adopted on 10th September 1998 and entered into force 24th February 2004. It promotes shared responsibilities and cooperative efforts among parties in the international trade of certain hazardous chemicals. It contributes to the environmentally sound use of hazardous chemicals by facilitating information exchange about their characteristics and calls on exporters of hazardous chemicals to use proper labelling and inform purchasers of any known restrictions or bans¹⁶
- **Basel Convention** on the control of transboundary movements of hazardous wastes and their disposal was adopted on the 22nd March 1989 in response to a public outcry, following the discovery in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes from abroad. The convention entered into force on May 1992 and was designed to reduce the movements of hazardous wastes between nations and specifically to prevent transfer of wastes from Developed Countries to Less Developing Countries (LDCs). It also intended to minimise the amount and toxicity of wastes to ensure environmentally sound management of hazardous and other wastes generated¹⁶.
- **Montreal Protocol** on substances that depletes the ozone layer (a protocol to the Vienna convention for the Protection of the Ozone Layer) was designed to protect the ozone layer by phasing out the production of numerous substances that are responsible for ozone depletion¹⁶. It was agreed on September 16, 1987 and entered into force 1st January 1989.
- **International Plant Protection Convention (IPPC)** is a 1951 multilateral treaty aimed to secure coordinated and effective actions to prevent and control the introduction and spread of pests and plant products¹⁷.

- **Globally Harmonised System of Classification and labelling of Chemicals (GHS)** is an internationally agreed standard managed by the United Nations. A worldwide initiative to promote standard criteria for classification and labelling of chemicals according to their Health, Physical and Environmental Hazards. It uses Hazard Communication Elements such as: pictograms, hazard & precautionary statements, signal words and Safety Data Sheets (SDS) in a logical and comprehensive manner.
- **Strategic Approach to International Chemicals Management (SAICM)** is a policy framework to promote chemical safety around the world, adopted on the 6th February 2006. SAICM's has the overall objective of achieving Sound Management of Chemicals (SMC) throughout their life cycle, such that, chemicals are produced and used in ways that minimise significant adverse impacts on human health and the environment. Unlike other conventions, SAICM does not restrict or ban specific types of hazardous chemicals. It is a platform for national authorities to exchange information on chemicals management and policies, for the purpose of achieving SMC throughout their lifecycle in the world.
- **International Code of Conduct on Pesticide Management** provides a framework that guides government regulators and other stakeholders on best practices in the management of pesticides throughout its life cycle.

International Organisations that addresses the issue of pesticide use are as follows:

- **Organisation for Economic Co-operation and Development (OECD) Pesticide Programme** is aimed at increasing the efficiency and effectiveness of pesticide regulation by OECD governments, geared towards reducing the risks of agricultural pesticides¹⁸.
- **Food and Agricultural Organisation (FAO)** issued an international code of conduct on the distribution and use of pesticides and promote the exchange of information and best practices.
- **World Health Organisation International Programme on Chemical Safety (IPCS)** deals with pesticide safety and administers pesticides evaluation schemes¹⁹.
- **Joint FAO/WHO Meeting on Pesticide Residues (JMPR)** Is an international expert scientific group on review of residues and analytical aspects of pesticides²⁰.
- **Pesticides Action Network (PAN)** Is an international coalition of around 600 Non-Governmental Organisations (NGOs) which advocates for more ecologically sound alternatives to hazardous pesticides²¹.

- **National Pesticide Information Center (NPIC)** is a cooperative agreement between Oregon State University and USEPA to provide objective science-based information about pesticides for informed decision making. It publishes annual reports to summarize pesticide incidents and inquiries as they are reported²².

1.5 Environmental Fate of Pesticides

Pesticides are introduced into the environment either through production, direct application (utilization), accidental loss or disposal. About 98% of sprayed insecticides and 95% herbicides reached a destination other than their target species²³. The way pesticides move, transformed and get degraded in the environment depends on a whole lot of factors ranging from their molecular structures, physicochemical properties, reactivity, prevailing environmental conditions (temperature, Sunlight etc) and behaviours in the various environmental compartments (Air, Water, Soil, Biota) (Figure 1.5)

The various transformations are greatly influenced by the tendency of the pesticides to be able to partition in the various environmental compartments and this partition tendency depends on the Octanol Water Partition constant (K_{ow}), Air Water Partition constant (Henry's Constant (KH)), Partition coefficient of water-solid exchange (K_{oc}), Solubility in water and the vapor pressure (V_p) of the pesticide compound. Some of the transformations changes the structure of the pesticides (sinks) resulting into other metabolites or residues. All these factors in part or in combination of one another jointly affect the transformation and fate of pesticides in the environment.

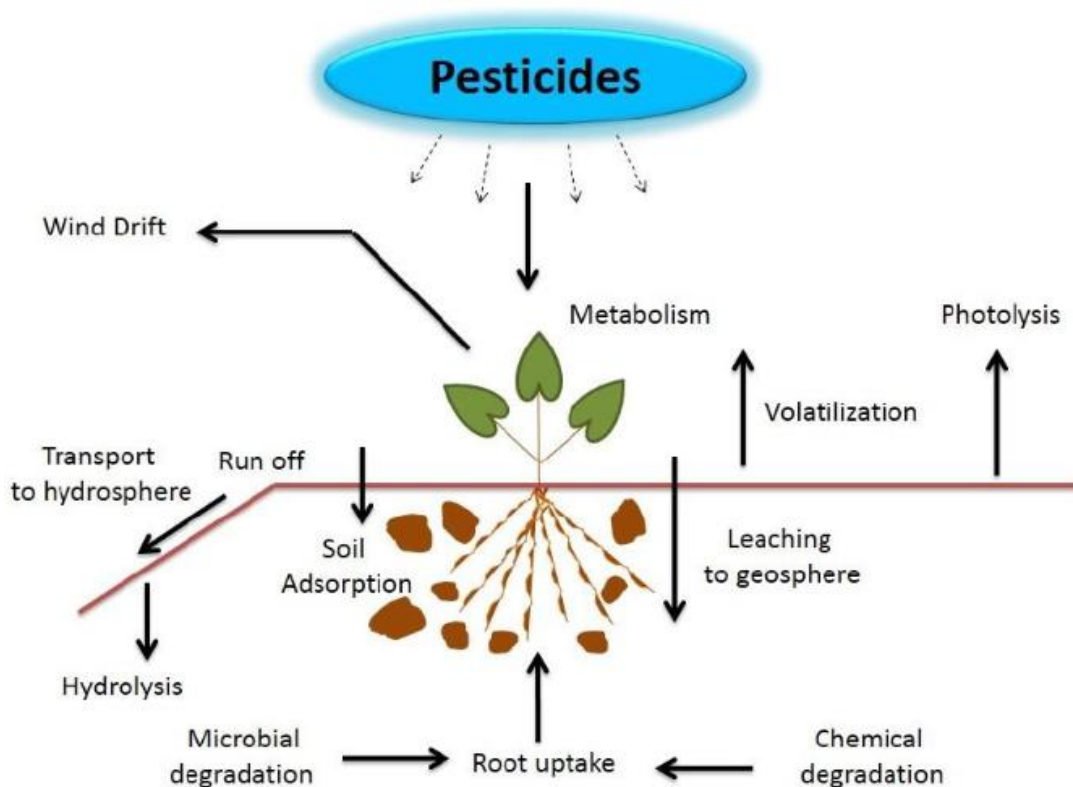


Figure 1.5 Environmental Fate of Pesticides²⁴.

1.6 Pesticide Use and Contamination

When pesticides are sprayed, only 15% gets to the target species (Pests and Pathogens) while the remaining 85% are distributed in soils and air²⁵. Over 95% pesticide poisoning were reported to have occurred in Low- and Middle-Income Countries (LMIC)¹¹.

Pesticide misuse may be attributed to factors such as:

- Less stringent and ineffective pesticide regulations
- Non-Enforcement of Maximum Residue limits on food crops
- Perception of pesticide risks by both agrochemical marketers and users
- Unwillingness of farmers to accept the risk of crop loss
- Poor storage, handling and disposal methods^{26, 27}
- Illiteracy and lack of understanding of pesticide hazards and risks^{28, 29}.
- Inadequate information dissemination on pesticide's risks
- Uncertified applicator and inadequate Personal Protection Equipment

The possible high levels of pesticide residues in crops and other environmental matrices have led to researchers' keen interests on Pesticide residue analysis. Table 1.4 below summarises some researchers results on pesticide residues in food crops.

Table 1.4 Selected publications on Pesticide Residues in Food crops

Pesticides Concentration			Samples	Country	Instrumentation	Reference
Organochlorines	Organophosphates	Pyrethroids				
Aldrin 15.5 ug/kg DDT 78.5 ug/kg	-		Beans (Cowpeas)	Nigeria (Lagos)	GC-MS	³⁰
DDT: 2.33-165.52(ng/g) Aldrin: 0.95-5.28 (ng/g) Lindane:0.30-1.30 (ng/g) (Ondo)	-		Cocoa Beans	Nigeria (Ondo & Ile Ife)	GC-ECD	³¹
DDT:0.38-24.29(ng/g) Aldrin: 0.13-10.24 (ng/g) Lindane:0.08-1.11(ng/g) (Ile-Ife)	-					
	Dichlorvos (0.024-0.381) mg/Kg	Cypermethrin: (0.003 – 0.146) mg/Kg	Beans (Cowpeas)	Nigeria	GC-ECD	³²
	Dimethoate: (0.073-0.083) mg/kg					
	Chlorpyrifos: (0.003-0.06) mg/kg					
	Diazinon (0.029 -0.08) mg/kg					
(ND-5.15) ug/g (DDT-Heptachlor epoxide)	-	-	Beans (Cowpeas)	Nigeria	GC-ECD	³³
(1.13-2.46) ug/g DDT: (PRE-storage) 1.47 ± 1.08ug/g (Post storage)- (1.13 ± 0.83 µg/g). Endrin (Pre- storage) 2.46 ± 1.85 µg/g (Post storage) 2.15 ± 1.65 µg/g	Dichlorvos: (0.008-0.262) ug/g 0.008 ± 0.002 µg/g (Pre-Storage) 0.262 ± 0.109 µg/g) (Post storage)		Beans	Nigeria (Borno)	GC-MS	³⁴
(0.01-1.25) mg/kg (Dichloran-Lindane)	-		Maize, Guinea	Nigeria (Nassarawa)	GC-ECD	³⁵

			Corn and Millet			
-	Dichlorvos ($\mu\text{g}/\text{kg}$) Wet- Season: 10.8 ± 1.34 Dry Season: 2.45 ± 1.34		Cocoa Beans	Nigeria (Ekiti)	GC-FPD	³⁶
-	Diazinon: $\mu\text{g}/\text{kg}$ Wet: ND Dry: 5.96 ± 1.38					
-	Chlorpyrifos: $\mu\text{g}/\text{kg}$ Wet: 0.822 ± 0.215 Dry: ND					
0.043-0.509 (mg/kg) Aldrin 0.098-0.760mg/kg Dieldrin-Heptachlor	-	-	Cowpeas	Nigeria (Ile ife)	GC-ECD	³⁷
Aldrin: 0.067-4.682 (mg/kg)	-	-	Dried Yam			
-	Dichlorvos: (0.06-0.212) ppm Chlorpyrifos: (0.12-0.22) ppm Diazinon 0.67ppm		Beans	Nigeria (Ondo)	GC-MS	³⁸
Endosulfan: 0.006-0.123 mg/kg DDT: 0.002-0.003 mg/kg Aldrin: 0.001-0.004 mg/kg Lindane: 0.001-0.002 mg/kg	Chlorpyrifos- 0.009-0.021(mg/kg) Diazinon ND Dimethoate: 0.004-0.11	Permethrin 0.001-0.003 (mg/kg) Cypermethrin 0.002-0.011 (mg/kg)	Cowpeas	Ghana (Ejura)	GC-PFPD for Organophosphates GC-ECD for organochlorines	³⁹
Endosulfan 0.028-0.274 mg/Kg	Chlorpyrifos (mg/kg): 0.008–.019	Permethrin (mg/kg)-0.002-0.007 Cypermethrin 0.004-0.006 (mg/kg)	Maize			
-	(0.02-5.4)- Peripheral Zone (0.02-4.62) Urban area (OPS)		Cowpeas	Cameroon (Ngaoundere)	GC-NPD	⁴⁰

Endosulfan 0.4026mg/kg	Chlorpyrifos (2.6505mg/kg) Chlorpyrifos2.650 mg/kg		Beans	India	HPLC	⁴¹
---------------------------	---	--	-------	-------	------	---------------

In the EU, reports are regularly prepared on pesticide monitoring programs of food products. Table 1.5 below showed some reports⁴² published by Expert Committee on Pesticide Residues in Food (PRIF) in 2017.

Table 1.5 Results of some Pesticide monitoring program by the EU in 2017

Pesticides (mg/kg)	Sample	Country
Dithiocarbamates 5.3 (MRL=0.1) Dithiocarbamate=7.9mg/kg Malathion-0.03 (MRL 0.02)	Mung Beans	China
Dimethoate: 0.3 (MRL 0.02)	Beans with Pod	Mexico
Dithiocarbamate:2.8	Beans with Pod	India
Carbendazim 0.02 MRL (0.01)	Rice	UK
Deltamethrin:0.1 MRL 0.01	Spring greens and kale	Spain
Profenofos 0.05 (MRL 0.01)	Okra	Egypt

1.7 Human and Environmental Health Effects of Pesticides

Insecticides are generally the most acutely toxic while herbicides are associated with chronic effects³. About 2.2million people from developing countries have been reported to be at increased risk of exposure to pesticides⁴³. Human routes of exposure to pesticides are via inhalation, ingestion and dermal contact with majority via intake of food contaminated with pesticides⁴³

1.7.1 Health effects

Acute effects of pesticide poisoning may include nausea, vomiting, dizziness, diarrhoea, abdominal pain, blurred vision, blindness, headache, stinging of the eyes and skin, throat and nose irritations, rash, blisters and itching⁴³. Acute poisoning rarely leads to death, but chronic effects are often lethal because they damage the vital organs. Chronic effects may include neurological effects: loss of coordination and memory, reduced motor signalling and reduced visual ability^{44, 23}. It could be carcinogenic, mutagenic and toxic to reproduction-Still birth/birth defects⁴⁵

1.7.2 Environmental Effects:

Pesticides are not only toxic to humans but also to the environment and wildlife. The toxic effects of pesticides and their metabolites are now being recognized as prevalent and alternative ways to balance the need to feed the world without disastrous effects on the environment are still being sought for. One of the principal stressors thought to have been affecting stream of macro invertebrates are the insecticides⁴⁶. Other environmental effects include the disruption of ecological balance (Biodiversity loss/collapse), contamination of various environmental matrices with burden on bilateral trade and consequent economy melt down⁴⁷.

1.8 Statement of the Problem.

Beans is one of the major indigenous grain crops in Nigeria that is often contaminated with pesticide residues, they are grain legumes rich in water soluble vitamins and valuable source of protein and dietary fibre⁴⁸. The existence of weak pesticide regulations and the need to meet up with quality agricultural produce (food crops) of the overwhelming Nigeria population (over 200million people) is one of the factors responsible for the overuse and misuse of PPPs in Nigeria. A situation which has consequently led to food contamination (food poisoning), environmental (Soil, water, air) pollution, destruction of wildlife, public health issues and consequent environmental damage^{3,23,45}.

There has also been series of public outcry and concerns by professional institutes and societies⁴⁹ on the indiscriminate use of pesticides (Dichlorvos) for post-harvest storage of dried beans products. At the international scene, The EU officially banned the importation of beans from Nigeria (since June 2015) due to high levels of pesticide residues and use of unauthorised pesticides⁵⁰. Table 1.6 below summarises the notification lists from the European Union on Rapid Alert System for Food and Feed (RASFF)⁵¹ on dried Beans imported from Nigeria between 2015-2016.

Table 1.6 Notification/Alert notices on Boarder rejections of Beans imported from Nigeria (2015-2016)

Notification Date	Reference	Distribution/Classification	Pesticides	RASFF Results (mg/kg)	EU (MRL) mg/kg
08/01/16	2016.0017	UK/Information for attention (HB)	Chlorpyrifos Dimethoate Dichlorvos (UAS)	0.069 0.12 0.027	0.01* 0.01* 0.01*
26/10/2015	2015.BRC	Italy-IT/border rejection (WB)	Trichlorfon (UAS)	3.9	0.01*
08/09/2015	2015.BKV	Ireland (IE)/Border rejection (BB)	Cypermethrin Dimethoate Dichlorvos UAS Trichlorfon UAS	0.024 0.02 0.11 0.35	0.05 0.01* 0.01* 0.01*
22/07/2015	2015.BFC	Ireland (IE) Border rejection (BB)	Chlorpyrifos Cypermethrin Dimethoate Dichlorvos UAS Trichlorphon	0.03 0.023 0.037 0.1 0.34	0.01* 0.05 0.01* 0.01* 0.01*
22/07/2015	2015.BFB	IE/Border rejection (BB)	Cypermethrin Dimethoate Dichlovos (UAS) Trichlorfon (UAS)	0.86 0.038 0.17 0.66	0.05 0.01* 0.01* 0.01*
22/07/2015	2015.BEZ	IE/Border rejection (BB)	Dimethoate Dichlorvos (UAS) Trichlorfon UAS	0.013 6.3 8.4	0.01* 0.01* 0.01*
01/07/2015	2015.BCB	UK/border rejection (DB)	Chlorpyrifos UAS Dichlorvos	0.12 0.32	0.01* 0.01*
30/06/2015	2015.BBW	UK/border rejection (DB)	Dichlorvos UAS. Cyhalothrin	0.03 0.37	0.01* 0.05
17/06/2015	2015.BAD	UK/Border Rejection (DB)	Dichlorvos UAS	0.18	0.01*
10/06/2015	2015.AZJ	UK/Border rejection (DB)	Chlorpyrifos Dimethoate Profenofos UAS Dichlorvos UAS	0.41 1.9 0.08 4.6	0.01* 0.01* 0.01* 0.01*

04/05/2015	2015.AUG	UK/Border Rejection (B)	Dichlorvos UAS	0.39	0.01*
29/04/2015	2015.ATY	UK/Border rejection (DB)	Dichlorvos UAS	10.8	0.01*
15/04/2015	2015.AQV	UK/Border rejection (DB)	Dichlorvos UAS Trichlorfon UAS	0.26 0.097	0.01* 0.0
08/04/2015	2015.APT	UK/Border rejection (DB)	Dimethoate Dichlorvos UAS Omethoate UAS Trichlorfon UAS	0.059 0.26	0.01* 0.01* 0.01* 0.01*
06/03/2015	2015.AKD	UK/Border rejection (DB)	Dichlorvos UAS	0.03	0.01*
19/01/2015	2015.ACL	UK/Border rejection (DB)	Dichlorvos UAS	0.04	0.01*
“	2015.ACK	UK/Border Rejection	Trichlorfon UAS Dichlorvos UAS	0.13 0.20	0.01* 0.01*
05/01/2015	2015.AAH	DB	Dichlorvos UAS Cyhalothrin	0.07 0.06	0.01* 0.05
05/01/2015	2015.AAE	UK/Border Rejection (DB)	Dichlorvos UAS	0.03	0.01*

Ref: RASFF PORTAL: <https://webgate.ec.europa.eu/rasff-window/portal/?event=notificationsList&StartRow=44201>⁵¹

Key: *Limit of Detection, RASFF-Rapid Alert System for food and Feed, (HB)-Honey Beans, (UAS)-Unauthorised Substance, (DB)-Dried Beans (BB)-Brown Beans, (WB)-White Beans, (B)-Beans

1.9 Aim

The aim of this research therefore, is to develop strategies for improved regulation and control of pesticides towards promoting environmental safety and sustainability of Plant Protection Products (PPPs) in Nigeria.

1.10 Objectives of The Study

1. Evaluate the sustainability of existing PPPs regulations in Nigeria.
2. Conduct PPPs residue analysis on dried beans from Nigeria.
3. Generate recommendations and develop regulatory control strategies towards improved safety of Plant Protection Products in Nigeria.

2 METHODOLOGY

This chapter embraced two major distinctive strategies in realising the objectives of the research, viz, information gathering and experimental (residue analysis) strategies. The research was executed in three countries namely: Spain (September 2018-February 2019), Nigeria (March 2019) and Portugal (April-September 2019)

A comparative assessment of the Regulations concerned with the placement of PPPs on the market of the EU, USA with the FRN was carried out. The PPPs regulations of the EU and USA were compared with that of the FRN in order to identify gaps and conducts needs assessments towards a sustainable PPPs regulation in Nigeria.

Pesticide residue analysis was also conducted on dried beans (Cowpeas) crops to ascertain residue levels and evaluate the effectiveness of the current PPPs regulations. The residue results obtained were then compared with the EU Maximum Residue Limit (MRLs). All these approaches were undertaken in order to generate recommendations towards improved environmental safety and sustainable PPPs regulations in Nigeria.

2.1 Information Gathering

- I. **Website Data Source:** Regulations on the placement of Plant Protection Products on the market were sourced from the official websites of the EU, USA, and FRN namely: https://ec.europa.eu/food/plant/pesticides_en, <https://www.epa.gov/pesticide> and <https://www.nafdac.gov.ng/chemicals/>.
- II. **Nigeria Pesticide Trade Data:** Trade data from 2013-2018 was obtained from the Federal Government Agencies in Nigeria namely: Nigeria Customs Service (NCS), Federal Ministry of Industry Trade and Investment (FMITI)⁵², National Bureau of Statistics (NBS)⁵³, Manufacturers Association of Nigeria (MAN) and the National Agency for Food and Drug Administration and Control (NAFDAC).

Categories of data obtained were:

- List of manufacturing chemical industries in Nigeria (January 2019)
- Quantities of imported pesticides (2013-2018)
- Categories of imported Pesticides (2013-2018)
- Pesticide Import Value (2010-2018)
- Pesticide Export Value (2010-2018)

These data were collated, reviewed and analysed

2.2 Experimental

This focused on the sampling of Cowpeas (*Vigna unguiculate*) commonly referred to as **beans** and conducting pesticide residue analysis.

- The two main beans varieties (White and Brown) shown in Figure 2.1 and Figure 2.2 below were sampled from the six main markets located in the six different zones known as Area Ccouncils (Figure 2.3) of the Federal Capital Territory (FCT), Nigeria
- Samples were analysed for nine (9) pesticide residues: DDT, Aldrin, Lindane, Dichlorvos, Dimethoate, Diazinon, Chlorpyrifos, Permethrin and Cypermethrin
- Chemical analysis was performed in NAFDAC Central Laboratory Complex, Oshodi, Lagos, Nigeria
- Results obtained were compared with the EU-Maximum Residue Limits (MRLs)

2.2.1 Sampling Sites:

The Beans samples were taken from the six major markets located in the six main Area Councils (Zones) that made up the Federal Capital Territory as illustrated in Table 2.1 and Figure 2.4



Figure 2.1 White Beans Samples



Figure 2.2 Brown Beans samples

The names of the markets and their respective locations are as shown in Table 2.1

Table 2.1 Names of sampling sites

Markets	Location	
Wuse & Garki Modern Market Markets	Abuja (AMAC)	L1
Bwari Market	Bwari (BWR)	L2
Kuje Market	Kuje (KUJ)	L3
Gwagwalada Market	Gwagwalada (GWA)	L4
Kwali Market	Yangoji-Kwali (KWL)	L5
Abaji Market	Abaji (ABJ)	L6



*Figure 2.3 Location of the Federal Capital Territory (FCT), Nigeria⁵⁴
(Coordinates: 8°50'N 7°10'E)*

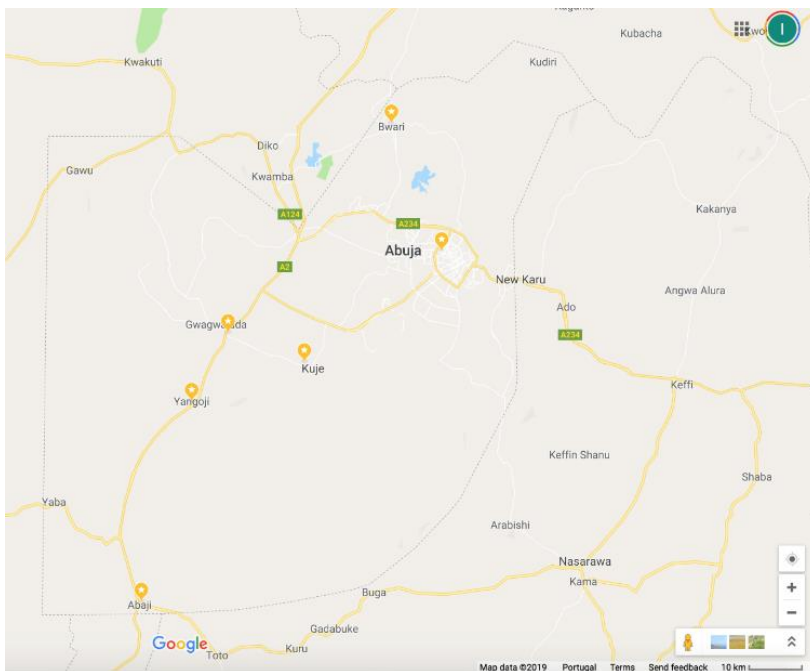


Figure 2.4 Map of FCT showing sampling sites

Location of markets where samples were collected are marked as stars (obtained from maps.google.com, July 2019)⁵⁵

2.2.2 Chemicals and Materials

The chemicals used for the analysis were as follows:

Acetonitrile (CH₃CN), Formic Acid (CH₂O₂), Acetone (C₃H₆O), n-Hexane (C₆H₁₄).

Extraction salts: (Magnesium Sulphate-MgSO₄, Sodium Chloride-NaCl, Sodium Citrate Tribasic Dihydrate- Na₃C₆H₅O₇.2H₂O and Sodium Citrate dibasic sesquihydrate C₆H₆Na₂O₇.1.5H₂O).

Clean up Salts: Primary Secondary Amine (PSA), Octadecyl-(C-18), PolychlorinatedBiphenyls-PCB153 (C₁₂H₄Cl₆) & MgSO₄. These chemicals were Emsure® grade by Sigma-Aldrich, Germany.

Other materials used included: Centrifuge, (EPPENDORF, Germany), Rotary Evaporator (HEIDOLPH, Germany), Wash bottles (Alcon-UK) and Industrial Blender (WARING USA).

Gas Chromatography (GC) Agilent 7890A with Nitrogen carrier gas (99.999% purity).

The GC operating conditions are tabulated in Table 2.2 below.

Table 2.2 GC Operating Conditions

Detectors	T ⁰ (°c) Program	Oven T ⁰ (°c)	P ⁰ (psi)	Column	H2 Flow	Airflow
ECD	Initial Temp. 100°C, hold 1min Rate 10°C/min, to 200°C, hold 2min Rate 10°C/min to 300°C, hold 5min	250	15.595	VF-5 Pesticides 30m x 0.25mm x 0.25µm Column flow: 1.2mL/min		
FPD	Initial Temp. 60°C, hold 1min Rate 10°C/min, to 200°C, hold 1min Rate 20°C/min to 270°C, hold 1min	250	15.595	HP-5, 5% Phenyl Methyl Siloxan 30m x 320µm x 0.25µm Column flow: 1.2mL/min	75ml/min	100ml/min

2.2.3 Standard

Working standards were prepared by dilution from the stock solutions, stored in glass vials and kept in the refrigerator at 4°C when not in use.

- **Organochlorines (OCPs) and Pyrethroids**

Stock solution: Lindane-500ppm, Aldrin-1004ppm, DDT-991.76ppm, Permethrin 995ppm and Cypermethrin 1000ppm

Intermediate Solution: 10ppm each of the organochlorines and Pyrethroids were prepared.

Working solutions (ppm) of the following concentrations were prepared for both OCPS and Pyrethroids: 0.02, 0.05, 0.1, 0.2, 0.5

- **Organophosphates (OPS)**

Stock Solution (ppm): Chlorpyrifos-990.91, Dimethoate 1022.43, Diazinon 1077.12, Dichlorvos-1043, Chlorpyrifos -990.91.

Intermediate: 10ppm each of the OPS were prepared

Working solution (ppm):0.05, 0.1, 0.2, 0.5,1

- **Internal Standard (PCB 153):** Stock Solution-20ppm, Working Standard-0.1ppm

Calibration curves were based on the working standard solution.

2.3 Analytical Technique

The European Standard EN 15662:2008 of QuEChERS multiresidue method⁵⁶ for pesticide residue analysis was employed.

500g of the Dried Beans samples was homogenised with blender and 5g weighed into 50ml centrifuge tube, 10ml each of Acetonitrile and water was added and vortexed for 1min. 6.5g of already prepared extraction salts (4g coarse MgSO₄, 1gNacl, 1g Na₃C₆H₅O₇.2H₂O and 0.5g C₆H₆Na₂O₇.1.5H₂O) was added and vortexed again for 1min followed by centrifuging at 3000rpm for 5mins. 6ml of the clear organic phase was then transferred via micro pipette to a 15ml tube and 1.2g of already prepared clean-up salt (150mg PSA, 150mg C-18 and 900mg MgSO₄,) was added and vortexed for 1min. 5ml of the supernatant was decanted into 15ml test tube and 50µL of 5% Formic Acid was added. 2ml of extract was pipetted into 50ml round bottom flask and evaporated to dryness using rotary evaporator. The dried extract was then reconstituted to 2ml using mixture of Hexane: Acetone (4:1) with 100µL of 0.1ppm PCB153. The 2ml reconstituted sample was then transferred into GC vials for analysis. Electron Capture Detector (ECD) was used for the quantification of Organochlorines and Pyrethroids while Flame Photometric Detector (FPD) was used for the organophosphates.

Method validation: The Limit of Detection (LOD) and Limit of Quantification (LOQ) for the organochlorines and Organophosphates are tabulated in Table 2.3 below:

Table 2.3 validation Table

Compounds	LOD (ppm)	LOQ (ppm)
DDT	0.009	0.030
Lindane	0.006	0.020
Aldrin	0.005	0.017
Chlorpyrifos	0.009	0.029
Dimethoate	0.008	0.027
Dichlorvos	0.011	0.038
Diazinon	0.005	0.018

Recovery studies for the organophosphates was conducted (Table 2.4) and this was done by spiking the beans samples with 0.05ppm each of the organophosphate's pesticides followed by GC-FPD instrumentation. Percentage recovery was calculated using the formula below:

$$\% \text{ Recovery} = \frac{\text{Concentration from GC analysis}}{\text{Original Conc. (0.05ppm)}} \times 100$$

Table 2.4 Recovery results for Organophosphates

Pesticides	Conc. From GC (ppm)	% Recovery
Dichlorvos	0.471	94.2
Dimethoate	0.51	102
Diazinon	0.51	102
Chlorpyrifos	0.41	82

The recovery chart for organophosphates is illustrated in Figure 2.5 below

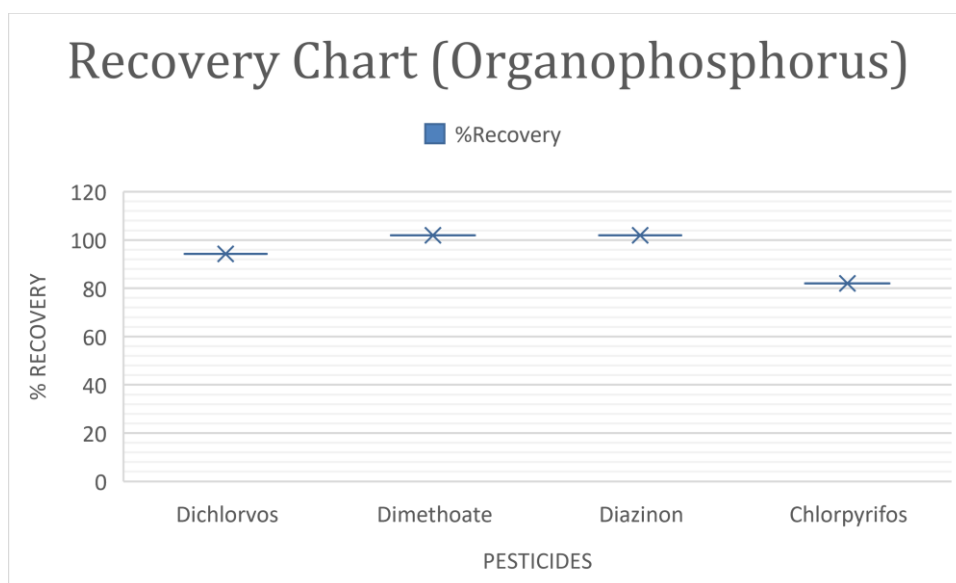
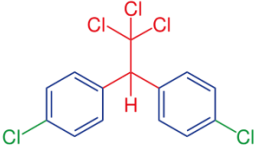
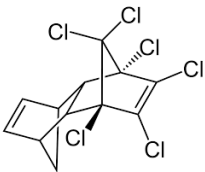
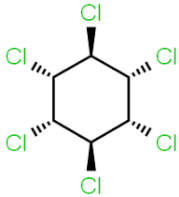
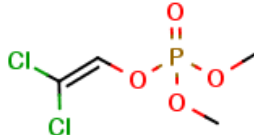
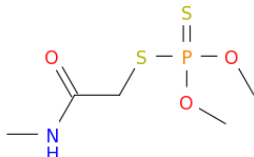
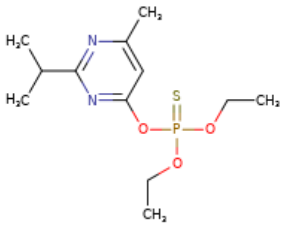


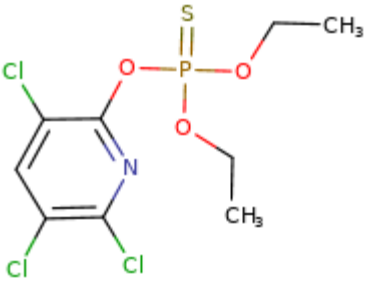
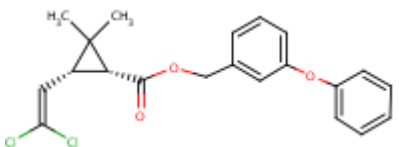
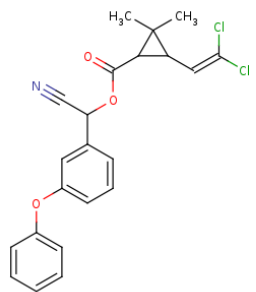
Figure 2.5 Recovery Chart for organophosphate

The Physicochemical parameters of the analytes of interests are tabulated in Table 2.5 below.

Table 2.5 Physicochemical properties of analytes

Pesticides	Chemical Structure	Physicochemical properties*
Dichloro-Diphenyl-Trichloroethane		Colourless crystal or off-white powder with a slight aromatic odour Molecular Formula: C ₁₄ H ₉ Cl ₅ CAS: 50-29-3 Mol. Weight: 354.48 g/mol Melting Point: 108.5 ⁰ c Boiling Point: 367.95 ⁰ c Octanol/Water (K _{ow}): Log (K _{ow}) 6.911 Water Solubility: 0.0055mg/L@25 ⁰ c Soil Adsorption Coefficient (K _{oc}): 2.20x10 ⁵ (LogK _{oc})=5.343 Vapour Pressure (VP): 1.60X10 ⁻⁷ mmHg @25 ⁰ c Henry's Constant (HK): 4.768x10 ⁻⁴ atm. m ³ /mol
Aldrin		Colorless to dark brown crystalline solid with a mild chemical colour. Molecular Formula: C ₁₂ H ₈ Cl ₆ CAS: 309-00-2 Mol. Weight: 364.90g/mol Melting Point: 120.88 ⁰ C Boiling Point: 329.86 ⁰ C Octanol/Water: Log (K _{ow}) 6.75 Water Solubility: 0.01415mg/L@25 ⁰ c Soil Adsorption Coefficient (K _{oc}): 1.056x10 ⁵ (LogK _{oc})=5.024 Vapour Pressure (VP): 0.0161mmHg @25 ⁰ c Henry's Constant (HK): 6.34x10 ⁻⁵ atm m ³ /mol.
Lindane		Colourless solid with a musty Odour Molecular Formula: C ₆ H ₆ Cl ₆ CAS: 58-89-9 Mol. Weight: 290.830 g/mol Melting Point: 56.98 ⁰ C Boiling Point: 304.35 ⁰ C Octanol/Water: Log (K _{ow}) 4.26 Water Solubility: 4.044 mg/L@25 ⁰ c Soil Adsorption Coefficient (K _{oc}): 3380 (LogK _{oc})=3.529 Vapour Pressure (VP) :0.000506 mmHg@25 ⁰ c Henry's Constant (HK): 4.788x10 ⁻⁵ atm m ³ /mol.

Dichlorvos		<p>Colourless to Amber Liquid with a mild chemical odour. Molecular Formula: C₄H₇Cl₂O₄P CAS: 62-73-7 Mol. Weight: 220.976 g/mol Melting Point: 18.07⁰C Boiling Point: 251.76⁰C Octanol/Water: Log (K_{ow}) 0.60 Water Solubility: 1889 mg/L@25⁰c Soil Adsorption Coefficient (K_{oc}): 40.2 (LogK_{oc})=1,604 Vapour Pressure (VP) :0.0631 mmHg@25⁰c Henry's Constant (HK): 9.713x10⁻⁶ atm· m³/mol.</p>
Dimethoate		<p>White Crystalline solid with a camphor like odour, while to grayish crystals for technical products Molecular Formula: C₅H₁₂NO₃PS₂ (CAS:60-51-5) Mol. Weight: 229.257g/mol Melting Point: 86.01⁰C Boiling Point: 360.80⁰C Octanol/Water: Log (K_{ow}) 0.28 Water Solubility: 6626 mg/L@25⁰c Soil Adsorption Coefficient (K_{oc}): 24.52 (LogK_{oc})=1,389 Vapour Pressure (VP): 4.12x10⁻⁵ mmHg@25⁰c Henry's Constant (HK): 1.876x10⁻⁹ atm m³/mol.</p>
Diazinon		<p>Colourless liquid with a faint ester like odour, Tech, Grade is pale to dark brown. Molecular formula: C₁₂H₂₁N₂O₃PS CAS: 333-41-5 Mol. Weight: 304.345g/mol Melting Point: 87.58⁰C Boiling Point: 366.20⁰C Octanol/Water: Log (K_{ow}) 3.86 Water Solubility: 6.456 mg/L@25⁰c Soil Adsorption Coefficient (K_{oc}): 1337 (LogK_{oc})=3.126 Vapor Pressure (VP): 5.43x10⁻⁵ mmHg@25⁰c Henry's Constant (HK): 3.368x10⁻⁶ atm m³/mol.</p>
Chlorpyrifos		<p>Colorless to white crystalline solid with a mild mercaptan-like odor Molecular Formula: C₉H₁₁C₁₃NO₃PS</p>

		<p>CAS 2921-88-2 Mol. Weight: 350.586g/mol Melting Point: 82.93⁰C Boiling Point:377.43⁰C Octanol/Water: Log (K_{ow}) 4.66 Water Solubility: 0.357 mg/L@25⁰c Soil Adsorption Coefficient (K_{oc}): 6829 (Log K_{oc}) =3.834 Vapor Pressure (VP): 2.05x10⁻⁵ mmHg 25⁰c Henry's Constant (HK): 2.649x10⁻⁵ atm m³/mol.</p>
<p>Permethrin</p>		<p>Colourless crystal to a viscous liquid; white to pale yellow. Molecular Formula: C₁₂H₂₀Cl₂O₃ CAS:52645-53-1 Molecular. Weight: 391.288 g/mol Melting Point: 164.97⁰C Boiling Point:437.63⁰C Octanol/Water: Log (K_{ow}) 7.43 Water Solubility: 0.009747 mg/L@25⁰c Soil Adsorption Coefficient (K_{oc}): 1.784x10⁵ (Log K_{oc}) =5.251 Vapor Pressure (VP): 8.26x10⁻⁷ mmHg 25⁰c Henry's Constant (HK): 4.363x10⁻⁵ atm m³/mol</p>
<p>Cypermethrin</p>		<p>Yellow viscous liquid or semi solid with characteristic odour Molecular Formula: C₂₂H₁₉Cl₂NO₃ CAS: 52315-07-8 Molecular. Weight: 416.297g/mol Melting Point: 82.07 ⁰C Boiling Point:450.48⁰C Octanol/Water: Log (K_{ow}) 6.38 Water Solubility: 0.0088 mg/L@25⁰c Soil Adsorption Coefficient (K_{oc}): 1.08x10⁵ (Log K_{oc}) =5.034 Vapor Pressure (VP): 1.3x10⁻⁷ mmHg 25⁰c Henry's Constant (HK): 8.092x10⁻⁶ atm m³/mol</p>

*Physicochemical properties presented were obtained from the Royal Society of Chemistry⁵⁷ and are predicted data from the USEPA's EPISuite™

3 RESULTS AND DISCUSSION

The results obtained from the strategies employed at the methodology design phase are presented under three main sections as follows:

- Pesticide (Plant Protection Products) Regulations
- Nigeria Pesticide Trade Data
- Analytical Results of Pesticide Residues

3.1 Plant Protection Products Regulations

The comparative assessments of Regulations concerned with the placement of PPPs on the market of the three regions (EU, USA FRN) are tabulated in Table 3.1 and Table 3.2 below.

Table 3.1 Comparative Assessments of Plant Protection Products Regulations

REGULATIONS	EU	USA	FRN
Authorization and Placement of PPPs on the Market	√	√	√
Data Requirements for AS, Adjuvants, Synergists, Co-formulants	√	√	X
Data Requirements for PPPs	√	√	√
CLP regulations for Dangerous Preparations	√	√	X
Labelling Regulations	√	√	√
Legal Limits	√	√	Adopts CODEX MRLs
Sustainable/Responsible Use of Pesticides (SUP/RUP) (Involves certification/training of applicators)	√	√	X
Pesticides Use in Organic Agriculture	√	√	X
Environmental Liability and Endangered Species	√	√	X
Statistics on Pesticides	√ (Sale and Use- Eurostat)	√	√ (Import & Export Data available but no consumption data)
Inspection and Maintenance of machinery for pesticide Applications	√	√	X
Pesticide Limit in Drinking Water	√	√	√
Surface and Groundwater Quality	√	√	√
Disposal of Pesticides	√	√	√ (No harmonized documented data)

Table 3.2 Assessments of PPPs Authorisation Indicators

Indicator	EU	USA	FRN
Classification of Pesticides	1. Plant Protection Products 2. Biocides: Group 1-Disinfectants Group 2-Preservatives Group 3-Pest Control Group 4-Other Biocidal Products	1. Conventional 2. Antimicrobial 3. Biopesticides: Antimicrobials, Biochemical, Plant Incorporated Protectants (PIPs)	1. Chemical Pesticides 2. Biopesticides: Antimicrobials, Biochemical, Plant Incorporated Protectants (PIPs)
Ingredients Classification	Active Substance (AS), Adjuvants, Safeners, Synergists, Co-formulants	Active substances + Adjuvants	Formulations
Approval procedure (PPP)	Three stages: -Approval of AS -Authorization of Pesticides (MS & EC) -Monitoring (MS)	Three stages: -Approval of Active substance (USEPA) -Authorization of Pesticides (USEPA) -Monitoring (USEPA)	Three stages: -Efficacy Assessments -Authorization of pesticides (NAFDAC) -Monitoring (NAFDAC)
Approval of AS	Risk Assessment of AS by EFSA Approval by EC (Union level)	Risk Assessment and Approval by US-EPA	Efficacy Assessment and Approval by NAFDAC
Risk Based Registration (Highly Hazardous pesticides (HHP))	Registered as low/high risks (eg. Candidate for substitution)	Registered as General Use Pesticide (GUP) or Restricted Use Pesticide (RUP)	registered as "Restricted" but no regulatory restriction between high or low risks pesticides
Initial Registration	10years	10 Years	5years
Renewal	15years	15years	5years

Table 3.1 above revealed that Nigeria's current Pesticide Regulations does not include comprehensive data requirements for AS, Adjuvants, Synergists, co-formulants and national Legal limits. The adoption of Codex or EU MRL may not be adequate for Nigeria as there are variances in the climatic conditions of both regions, dietary intake (consumption data) and agricultural practices. Therefore, the MRL set in one country or continent might not be appropriate or totally suitable for adoption by another country having different climatic conditions and dietary exposures. Regulations on setting data requirements for active substances and other ingredients usually through comprehensive human and environmental risk assessments studies are highly essential in ensuring continuous safety and efficacy of PPPs.

Regulations on statistics of pesticide is key to determining the trade, distribution, use and final sinks of these pesticides. The regulation on the disposal of pesticide is not adequate as harmonised documented data on disposal of pesticide was not available which is critical in

determining the potential metabolites and environmental fate of the disposed pesticides and its potential effects on human health and the environment. Regulations of the FRN has no working technical regulations on use of PPPs in Organic agriculture and Responsible or Sustainable use of pesticides. Organic farming is globally gaining prominence and the need to restrict the use of certain pesticides in organic farming is highly imperative. The inclusion of sustainable use of pesticides either in the regulations or nations Directive (Guidelines) will help promote Integrated Pest Management (IPM), Integrated Vector Management (IVM) and promote capacity building initiatives on safety use of PPPs. Certification of pesticide applicators and application equipment are also activities under the sustainable use of pesticides. Also, indicators geared towards promoting the protection of non-target species is another important factor to be considered as some of the endangered species are beneficial either as pollinators or pest control.

Table 3.2 summarises the similarities and differences in the authorisation processes of PPPs in the EU, USA and FRN. The EU differentiates completely pesticides use on Agriculture (PPP) from non-Agricultural applications (Biocides) while the USA and FRN employs general groupings in terms of chemical and biopesticides. The EU and USA **conducts comprehensive human and environmental risk assessments on both AS and final pesticide products** before final authorisation while FRN focus more on efficacy assessments of the final formulation. Depending on the hazardous properties of pesticides, the EU and USA considers its authorization as either **candidate for substitution** (in order to gradually phase out or replace HHP with safer alternatives), **restricted** (Not available to general public) or **General use** (available to the public) while all registered pesticide products in Nigeria are currently available to the public and are sold freely without regulatory restrictions even though it is presumed to be registered as restricted products.

3.2 Nigeria Pesticide Trade Data

A. Imports and Exports

Data on the amount of pesticides imported into Nigeria was obtained from the Custom excel data^{58,53} and was available on triennial basis. Over 9million tons of pesticides were imported into Nigeria from 2013-2018 as seen in Table 3.3.

Table 3.3 Quantities (Tons) of Imported Pesticides

Pesticides	Imported Qty (Tons) 2013-2015	Imported Qty (Tons) 2016-2018	Total (Tons) 2013-2018
Herbicides	4,296,327.55	3,199,428.90	7,495,756.45
Insecticides	459,391.03	17,384.92	476,775.95
Fungicides	38,633.72	14,774.44	53,408.16
Disinfectants	5,100.78	0.24	5,101.02
Others	339,071.12	1,100,645.05	1,439,716.17
Total	5,138,524.21	4,332,233.55	9,470,757.75

Out of over 9million tons of pesticides imported into Nigeria between 2013-2018, about 5million and 4million tons were imported between 2013-2015 and 2016-2018 respectively (Table 3.3). This data is represented in Figure 3.1 below

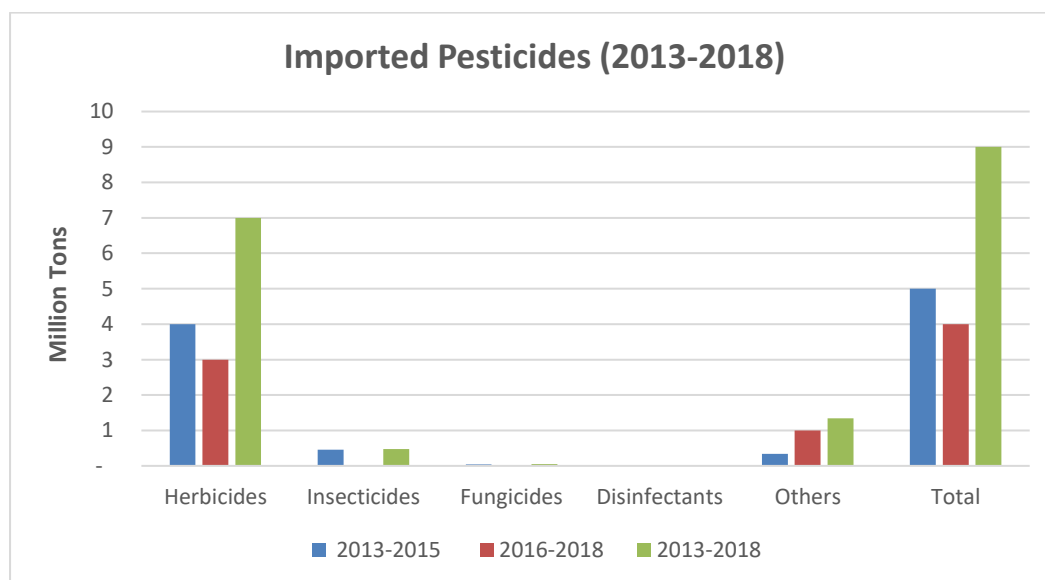


Figure 3.1 Quantities (kg) of Pesticides imported from 2013-2018

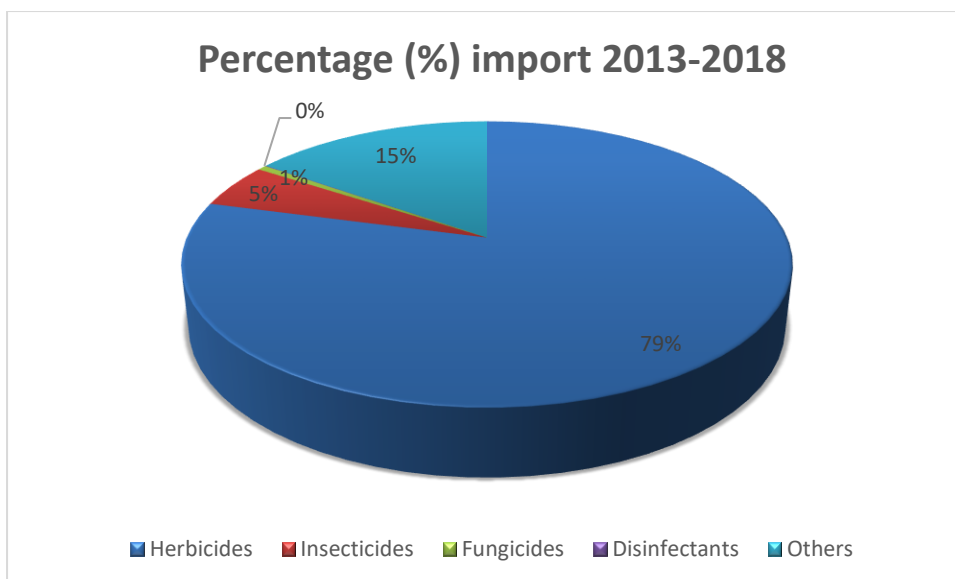
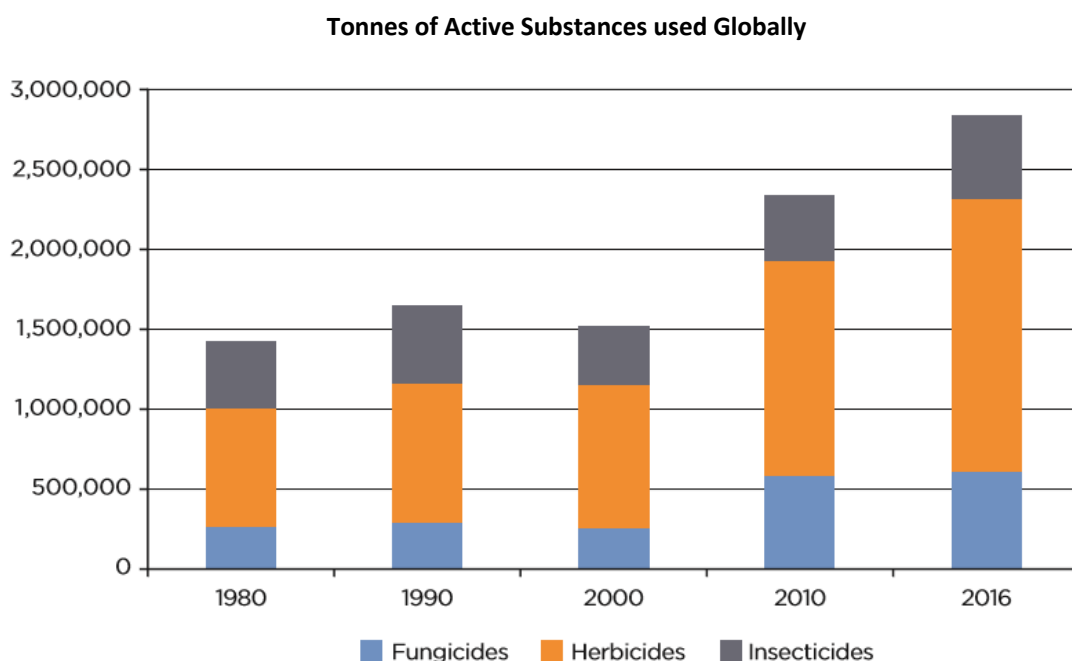


Figure 3.2 Percentage of Imported pesticides from 2013-2018.

Of the four major types of pesticides imported into Nigeria between 2013-2018, Percentage of imported Herbicides (79%), was much higher compared to the other group of pesticides as seen in Figure 3.2 above. The percentage of imported Herbicides quadruples the other classes of pesticides. This however agrees with the report on tonnes of Active substances used globally which reported high herbicide utilisation^{59,60} compared to other pesticides as illustrated in Figure 3.3 below



Philip McDoughall (2018). Evolution of the crop Protection Industry since 1960⁶⁰

Figure 3.3 Tonnes of Active Substances (AS) used globally

The high herbicides consumption compared to other classes of pesticides may be partly due to the rapid increase in no-till farming which involves planting a new crop without ploughing into the stubble of the previous crop. Intrinsic to the no-till is the use of herbicides as weed control

The top 15 pesticide exporting countries to Nigeria and their corresponding quantities from 2013-2018 are tabulated in Table 3.4 below.

Table 3.4 Top 15 Pesticides Exporting countries to Nigeria 2013-18

Countries	Qty (Tons) 2013-2018
China	9,086,848.08
India	205,441.16
United Kingdom	25,193.72
Belgium	19,971.79
Malaysia	18,160.27
United states	18,133.46
United Arab Emirate	13,464.06
South Africa	11,555.37
Germany	9,932.40
Indonesia	7,657.94
Singapore	7,055.86
Cameroon	5,150.36
Spain	5,033.70
Switzerland	4,896.28
Portugal	4,652.69

Table 3.4 above revealed that Nigeria imports bulk of its pesticides from China.

Countries	Qty (Tons) 2013-2018
China	9,086,848.08
India	205,441.16
United Kingdom	25,193.72
Belgium	19,971.79
Malaysia	18,160.27
United states	18,133.46
United Arab Emirate	13,464.06
South Africa	11,555.37
Germany	9,932.40
Indonesia	7,657.94
Singapore	7,055.86
Cameroon	5,150.36
Spain	5,033.70
Switzerland	4,896.28
Portugal	4,652.69

Import and Export Value (€)

The total Pesticide Import and Export values from 2013-2018 were equivalent of: €1.9 billion and €144 million respectively⁵⁸. Figure 3.4 and Figure 3.5 below illustrates the yearly pesticide import and export values from 2013-2018

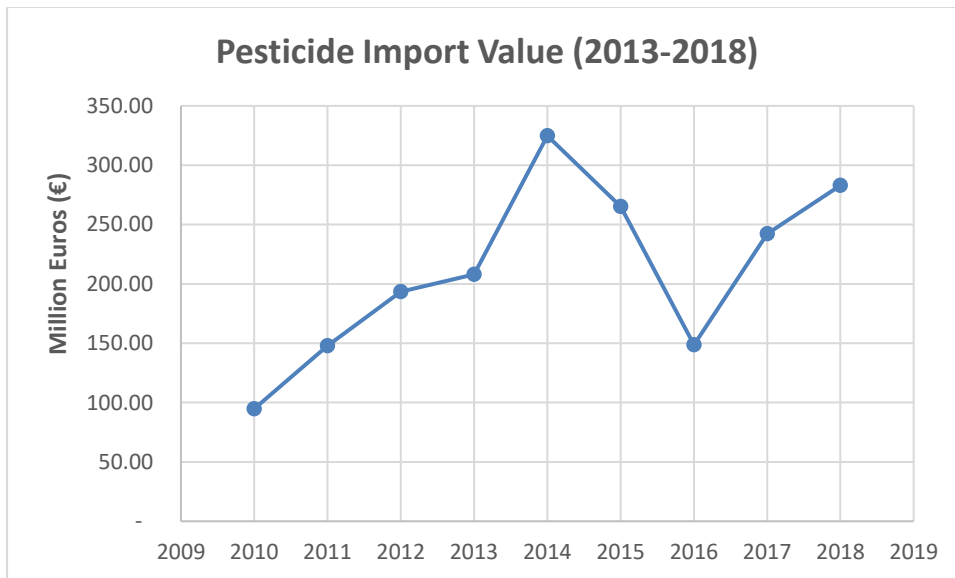


Figure 3.4 Pesticide import value 2013-2018

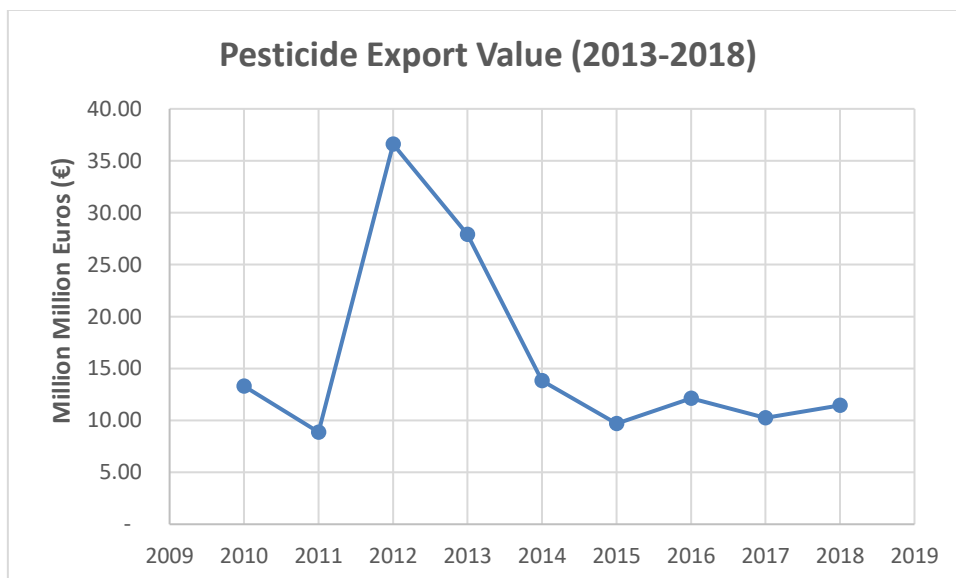


Figure 3.5 Pesticide Export Value 2013-2018

Figure 3.4 indicated a sharp import value increase in 2014 while export value experienced a sharp value decrease (Figure 3.5) in same 2014. This might interpret to mean high pesticide consumption and utilisation in 2014 compared to volumes sold out in the same year. A situation

that can be compared with the high pesticide use in beans crops from Nigeria between 2014-2015 (alerted by the EU) leading to the ban on beans export to the EU since June 2015.

Table 3.5 Imported pesticides (€) from other African Countries from 2013-2017

Countries	Herbicides (€)	Insecticides (€)
Cameroon	161,574.65	119,066.10
South Africa	929,487.46	671,161.38
Algeria	154,408.39	160,163.76
Cote d'Ivoire	325,814.07	192,122.52
Egypt	167,914.61	202,097.55

From the values obtained in FAOSTAT⁶¹ of the United Nations 2019 in Table 3.5 above, the five African countries considered had lower import pesticides values compared to Nigeria. Although, Nigeria pesticide import values were from 2013-2018 while those in Table 3.5 were from 2013-2017. The higher pesticides import values in Nigeria might be related to its large population (over 200million) compared to South Africa (58 million), Cameroon (25.3million), Algeria (42.6million), Cote D'Ivoire (26million) and Egypt (96Million). None of these other African countries were halved the population of Nigeria.

B. Manufacturing Industries in Nigeria

The different manufacturing industrial sectors in Nigeria ^{52, 62} as at January 2019 are represented in Table 3.6 and Figure 3.6 below

Table 3.6 Manufacturing Sectors in Nigeria

Industrial Sectors	Total (%)
Food, Beverage & Tobacco	27.2
Basic Metal	9.4
Vehicles Miscellaneous Assembly	7
Electrical/Electronics	3.9
Textile	4
Chemical/Pharmaceutical	14.6
Agrochemical	0.2
Plastic Rubber & Foam	11.3
Non-Metals & Minerals	6.5
Pulp Paper & Printing	13
Wood & Wood Prod	2.9

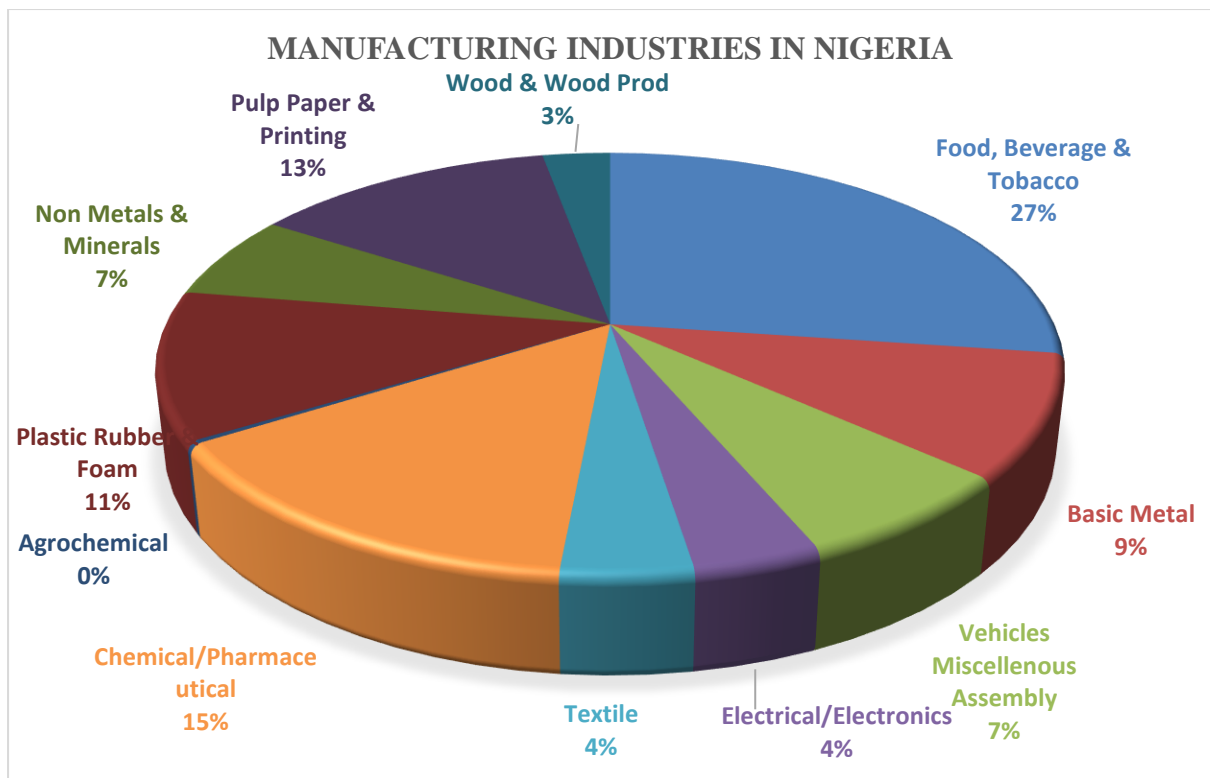


Figure 3.6 Manufacturing Industries in Nigeria January. 2019

From Figure 3.6 above, it is obvious that the Agrochemical manufacturing sector is only about 0.2% of the entire manufacturing sectors in Nigeria. This, however, also account for one of the reasons why high amounts of pesticides were imported into the country due to the limited national agrochemical manufacturing capacities to meet up with its growing population.

3.3 Analytical Results of Pesticide Residues

ORGANOCHLORINES

Table 3.7 Organochlorine concentrations (mg/kg) in Beans samples from all Locations

PESTICIDES (mg/kg)	LOCATIONS											MEAN±SD	RANGE (mg/kg)
	L1		L2		L3		L4		L5		L6		
	WB	BB	WB	BB	WB	BB	WB	BB	WB	BB	WB		
Lindane	0.17	0.04	ND	0.04	<LOQ	0.17	0.14	0.12	0.03	<LOQ	<LOQ	0.07±0.07	ND-0.17
Aldrin	0.06	0.03	0.02	0.02	0.02	0.88	0.03	0.05	<LOQ	0.04	0.02	0.11±0.3	0.01-0.88
DDT	0.05	0.06	0.09	0.06	0.04	0.23	ND	0.08	ND	0.08	0.03	0.07±0.06	ND-0.23

In Table 3.7 above, the OCPs residues in the Beans samples were present in concentrations ranging from ND-0.88mg/kg. Although, white beans (WB) from L3, L6 and brown beans from L5 were <LOQ for lindane while white beans from L5 was <LOQ for Aldrin pesticides residues. DDT was not detected in white beans from Locations L4 & L5 while Lindane was not also detected in white beans from L2 (Figure 3.7).

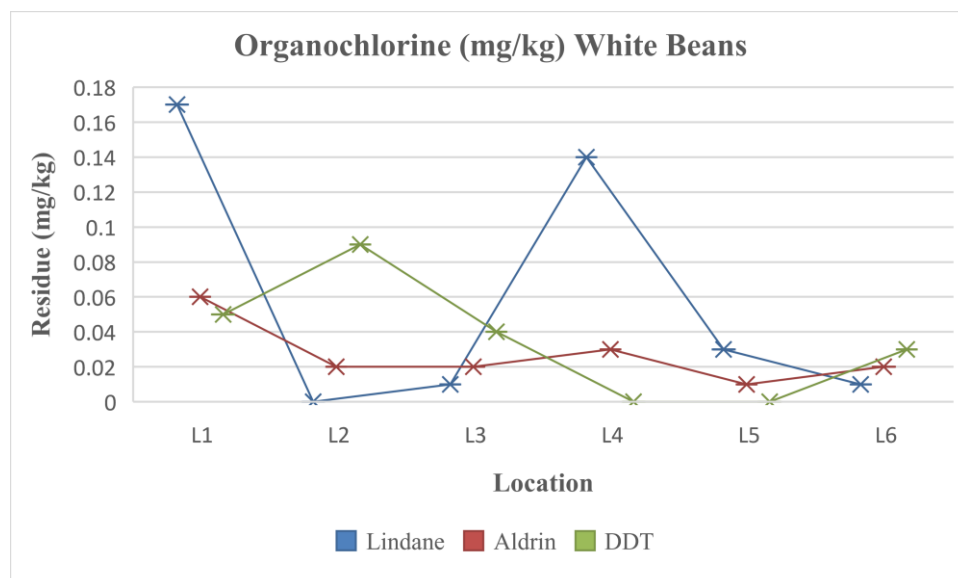


Figure 3.7 Organochlorine Concentrations (mg/kg) in White Beans Samples

Highest concentration of OCPs were detected in Brown Beans (BB) at location 3 (Figure 3.8).

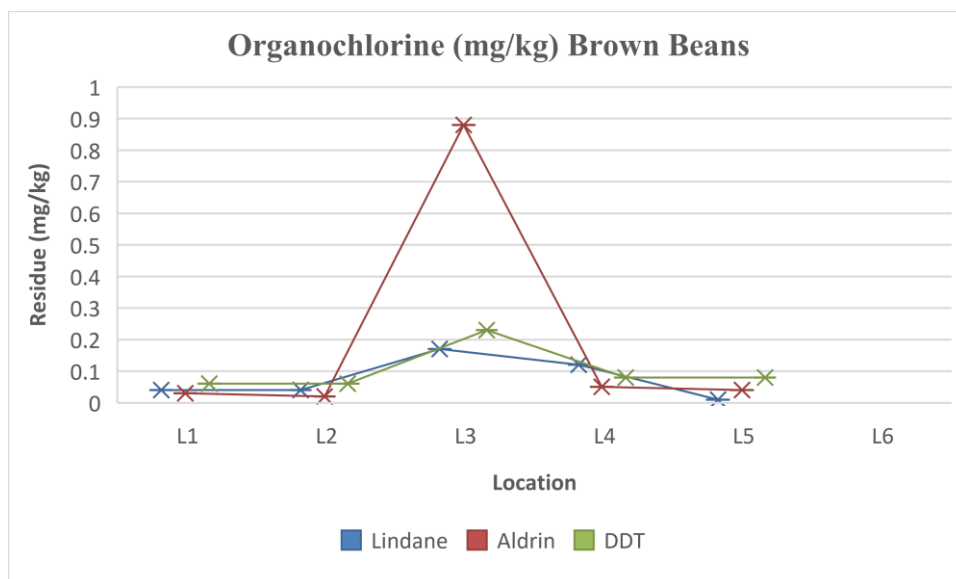


Figure 3.8 Organochlorine Concentrations (mg/kg) Brown Beans Samples
No Brown Beans was available for analysis at L6 (Figure 3.8)

Figure 3.13 showed that: 91% of the samples were above the EU-MRL (0.01mg/kg) for Aldrin, while 64% and 55% samples were also above the EU-MRL of 0.01mg/kg and 0.05mg/kg for Lindane and DDT respectively.

The detection of high concentrations of persistent OCPs (Lindane, Aldrin and DDT) in crops have previously been reported³¹ in Nigeria whereby, Nigerian farmers deliberately mix several pesticides including Aldrin, DDT and Lindane to formulate local insecticides on crops and also directly apply Aldrex (Aldrin dust) to crops to control pests³¹. This factor might be responsible for over the 91% of samples analysed in this study being above the EUMRL for Aldrin pesticide residues (Figure 3.13). The OCPs concentrations obtained can be compared to the range (mg/kg) of 0.043-0.509 and 0.001-0.274 obtained from other studies^{37,39}. The OCPs analysed in this project have been banned by the Stockholm Convention on Persistent Organic Pollutants because of its persistence, high tendency to bioconcentrate and bioaccumulate in humans. Though the use of DDT is still restricted to the treatment of malaria in some African countries⁶³ which might also be responsible for its detection on agricultural crops in Nigeria. The use of organochlorine pesticides by Nigerian Farmers have continued to experience widespread application due to easy availability, efficacy, and affordability³¹.

ORGANOPHOSPHATES

Table 3.8 Organophosphates concentrations (mg/kg) in Beans samples from all Locations

PESTICIDES (mg/kg)	LOCATIONS											MEAN±SD	RANGE (mg/kg)
	L1		L2		L3		L4		L5		L6		
	WB	BB	WB	BB	WB	BB	WB	BB	WB	BB	WB		
Dichlorvos	<LOQ	5.25	0.09	<LOQ	<LOQ	0.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.54±1.6	<LOQ(0.01)-5.25
Dimethoate	ND	ND	0.23	ND	ND	ND	<LOQ	0.06	<LOQ	0.03	0.14	0.05±0.07	ND-0.23
Diazinon	ND	ND	ND	ND	ND	0.03	0.04	0.08	<LOQ	0.02	ND	0.02±0.03	ND-0.08
Chlorpyrifos	0.07	ND	0.76	0.12	0.16	1.78	0.04	0.05	0.05	0.12	ND	0.29±0.5	ND-1.78

Table 3.8 indicated that the overall range of organophosphates concentrations in the Beans samples were from ND-5.25mg/kg. Dimethoate was not detected in all samples obtained from L1 and L3. Diazinon was not also detected in all samples from L1, L2, and L6. Chlorpyrifos was not detected in the sample obtained from L6 but had the highest concentration in white Beans from L2 (Figure 3.9).

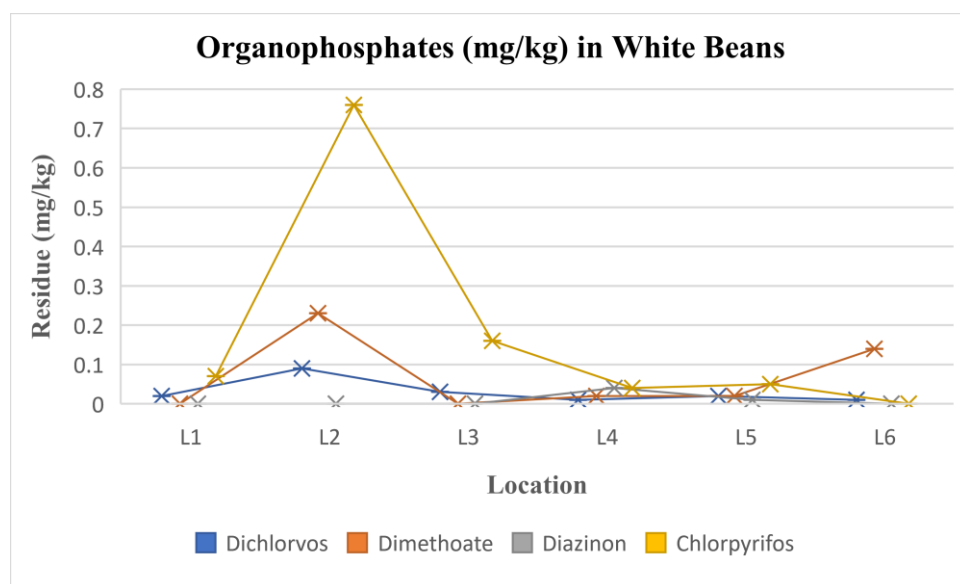


Figure 3.9 Organophosphates Concentrations (mg/kg) in white Beans samples

The highest concentration of Dichlorvos (5.25mg/kg) was in brown beans from L1 (Figure 3.10) but all samples from L4, L5 & L6 were <LOQ for Dichlorvos residues (Table 3.8).

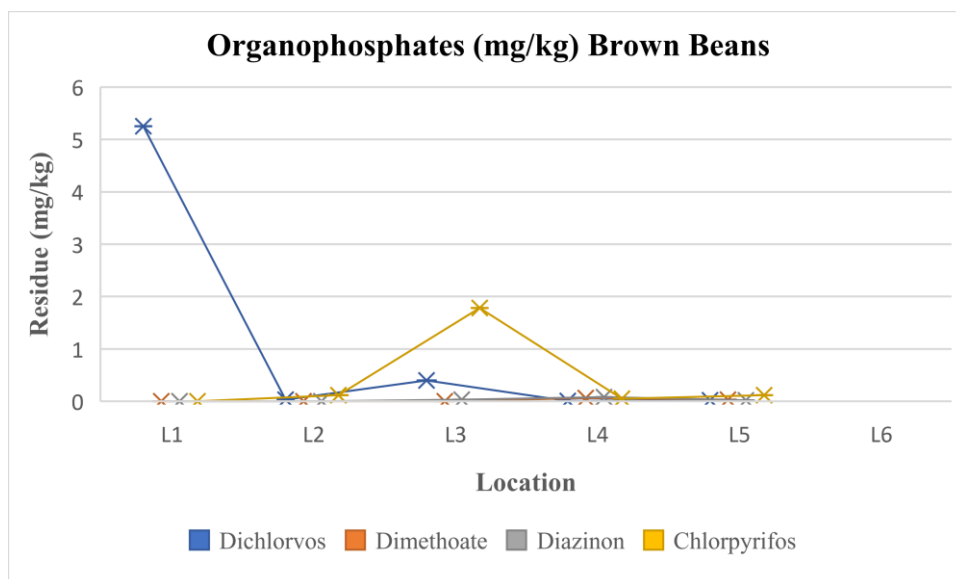


Figure 3.10 Organophosphates Concentrations (mg/kg) in Brown Beans samples
 No Brown Beans was analysed for Organophosphates at L6 as seen in Figure 3.10

The highest concentration of Dichlorvos (5.25mg/kg) detected in the brown beans samples from L1(Figure 3.10) indicated high use of Dichlorvos for post-harvest storage in the area because, L1 is the main city centre of Abuja (Figure 2.4), occupied mostly by high income earners who prefers the high-quality brown beans over the white beans. High use of Dichlorvos pesticides for the postharvest storage of beans in Nigeria have been well documented^{34, 49, 51} The proliferation of Dichlorvos in Nigeria as a major component of locally formulated insecticides known as “Ota Piapia” was also well reported⁶⁴ with its use in food preservation. The highest concentration of Dichlorvos in this study agrees with the results (4.68mg/kg, 6.8mg/kg and 10.8mg/kg) reported⁵¹ by the EU on RASFF. High values of OPs in beans samples have also been reported⁴⁰.

The range of Dimethoate concentrations (ND-0.23mg/kg) in this study were below the range (0.037-1.9)mg/kg published on the EU RASSF Portal as shown in Table 1.6 while the range of chlorpyrifos concentrations (ND-1.78mg/kg) were above EU RASFF values (0.069 mg/kg - 0.41 mg/kg) reported⁵¹. Diazinon residues showed least concentration levels compared to other organophosphate pesticides analysed, although, low levels of diazinon in beans samples compared to other organophosphates has been documented³⁹. High levels of organophosphates pesticides (above the EUMRL) in beans samples from Nigeria have also been reported³⁸ and of all the OPs analysed, chlorpyrifos had the highest percentage of samples (82%) above the EUMRL (Figure 3.13). The organophosphate pesticides have been reported to be more acutely toxic than the organochlorines but are comparatively less persistent⁶⁵

PYRETHROIDS

Table 3.9 Pyrethroids Concentrations (mg/kg) in Beans Samples from all Locations

PESTICIDES (mg/kg)	LOCATIONS											MEAN +STDEV	RANGE (mg/kg)
	L1		L2		L3		L4		L5		L6		
	WB	BB	WB	BB	WB	BB	WB	BB	WB	BB	WB		
Permethrin	0.74	ND	0.55	0.46	ND	0.64	2.01	ND	ND	0.56	0.56	0.5±0.5	ND-2.01
Cypermethrin	ND	0.07	ND	0.09	ND	4.55	2.83	ND	ND	0.63	0.63	0.8±1.5	ND-4.55

The overall concentration range of the pyrethroids in the samples were from ND-4.55mg/kg (Table 3.9). No pyrethroids was detected in white beans from L3, L5, and brown beans from L4. The highest concentration of pyrethroids was cypermethrin found in brown beans at L3 (Figure 3.12), while white beans had highest concentration of both pyrethroids at L4 (Figure 3.11).

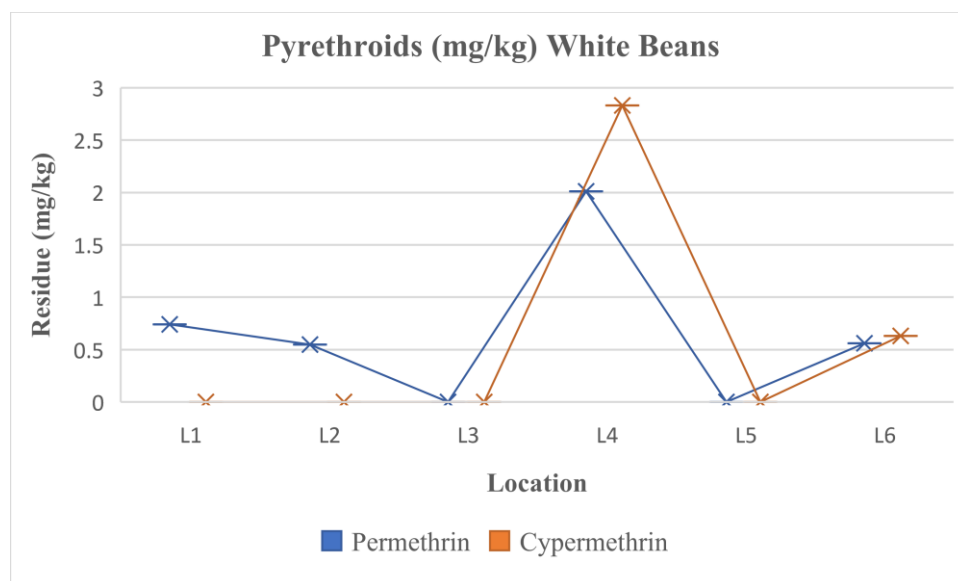


Figure 3.11 Pyrethroids Concentrations (mg/kg) in white beans samples

Figure 3.13 showed that 82% of samples were below the EU- MRL (0.7mg/kg) for cypermethrin while 64% were above the EU MRL (0.05mg/kg) for Permethrin.

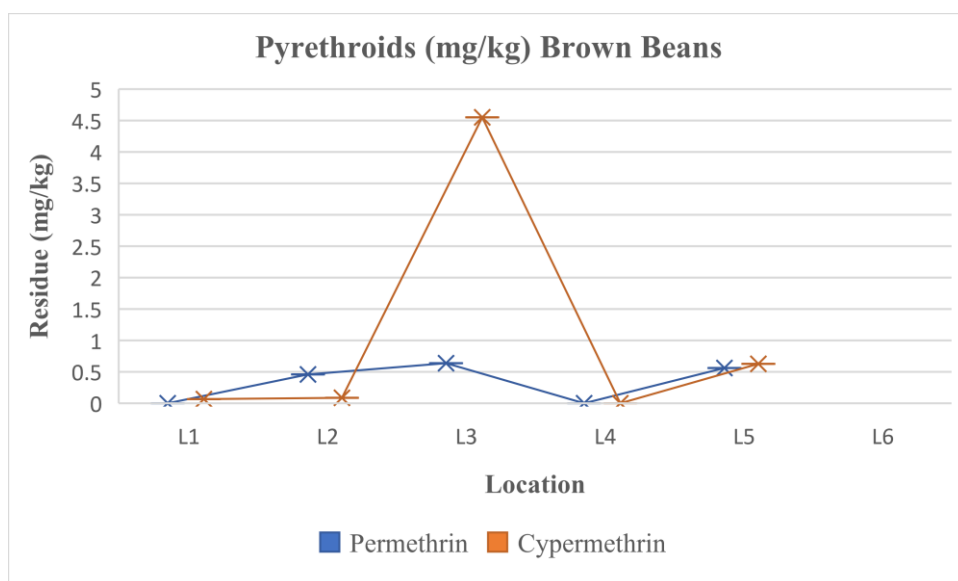


Figure 3.12 Pyrethroids Concentrations (mg/kg) in Brown Beans samples
No Brown Beans was analysed for Pyrethroids at L6 as seen in Figure 3.12

The high concentration of both pyrethroids in white Beans at L4 indicated its high use in white beans in L4 compared to other locations. The highest concentration of cypermethrin (4.55mg/kg) found in brown beans from L3 (Figure 3.12) indicated very high utilisation of the pesticide for postharvest storage purpose as pyrethroids were developed to mimic natural occurring pyrethrins and are readily subjected to photolysis, microbial (Enzymatic) degradation and degrades faster than OPs and OCPs⁶⁶. The overall range of pyrethroids concentrations (ND-4.55 mg/kg) were higher than the range 0.024-0.86mg/kg reported in the EU RASFF portal (Table 1.6). Pyrethroid concentrations above the EUMRL in beans samples from Nigeria is well documented³²

Table 3.10 Overall concentration (mg/kg) range of pesticide residues and EU-MRLs

PESTICIDES	RANGE WHITE BEANS (WB) Mg/kg	RANGE BROWN BEANS (BB) Mg/Kg	Overall range in WB & BB	TOTAL MEAN OF PEST. CONC.	EU MRL Mg/Kg
Lindane	ND-0.17	<LOQ (0.01) -0.17	ND-0.17	0.07±0.07	0.01
Aldrin	<LOQ (0.01) -0.06	0.02-0.88	<LOQ (0.01)-0.88	0.11±0.26	0.01
DDT	ND-0.09	0.06-0.23	ND-0.23	0.07±0.06	0.05
Dichlorvos	<LOQ (0.01)-0.09	<LOQ (0.01)-5.25	<LOQ (0.01)-5.25	0.54±1.57	0.01
Dimethoate	ND-0.23	ND-0.06	ND-0.23	0.05±0.07	0.01
Diazinon	ND-0.04	ND-0.08	ND-0.88	0.02±0.03	0.01
Chlorpyrifos	ND-0.76	ND-1.78	ND-1.78	0.29±0.54	0.01
Permethrin	ND-2.01	ND-0.64	ND-2.01	0.5±0.5	0.05
Cypermethrin	ND-2.83	ND-4.55	ND-4.55	0.8±1.5	0.7

Percentage Pesticides Below/Above MRL

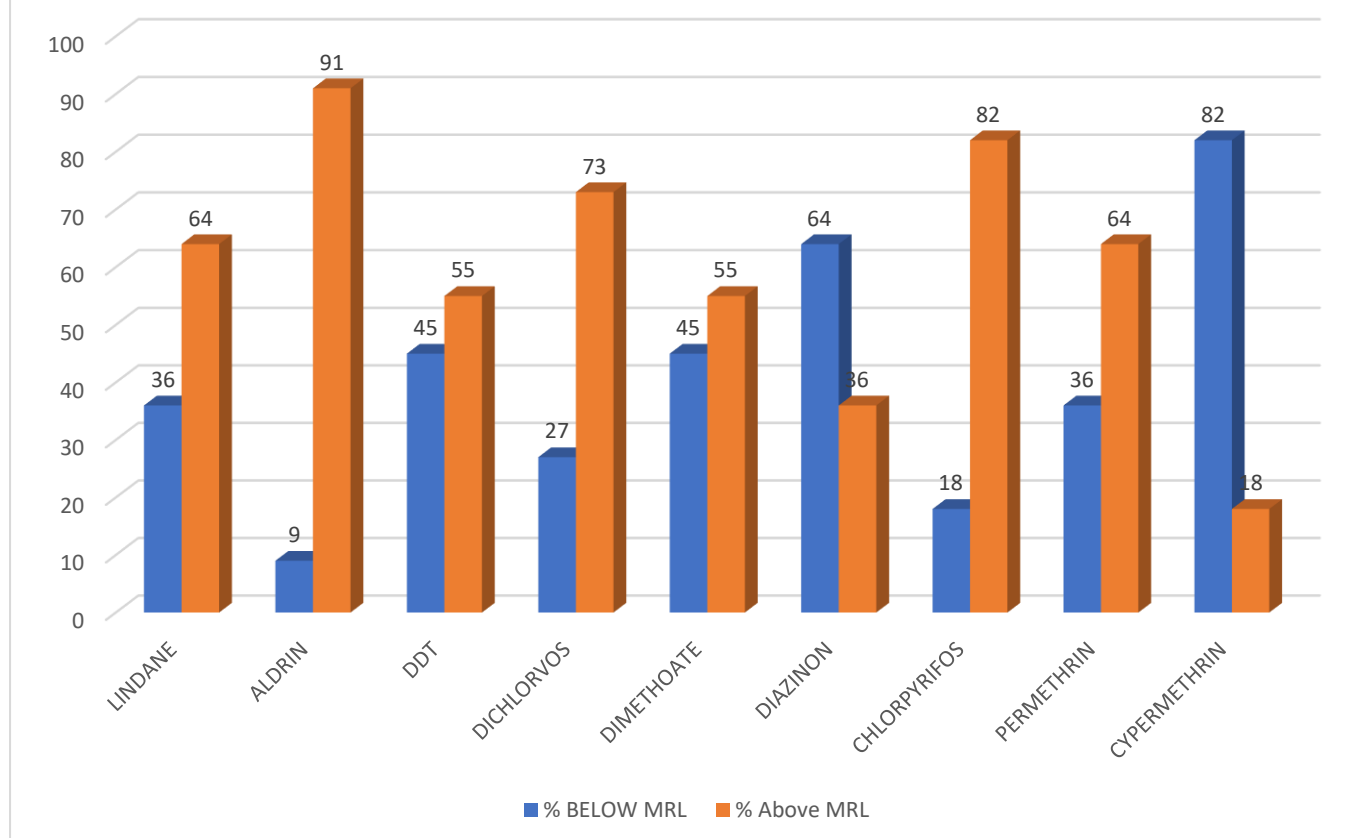


Figure 3.13 Percentage of Pesticides below and above MRL

Key:

L1=Location 1 Abuja (AMAC)

L2=Location 2 Bwari (BWR)

L3=Location 3 Kuje (KUJ)

L4=Location 4 Gwagwalada (GWL)

L5=Location 5 Kwali (KWL)

L6=Location 6 Abaji (ABJ)

WB=White Beans

BB=Brown Beans

It was established that not all the classes of pesticides (organochlorines, organophosphates and pyrethroids) analysed were detected in the bean samples. However, this does not necessarily mean that the Not detected (ND) pesticides were not used during cultivation, pre or post-harvest storage. The Non detection might be as a result of low residue concentrations, i.e. below the detection limit (LOD). A factor which is often influenced by prevailing environmental conditions such as: Temperature, photo and bacterial degradation, volatilisation which affects the environmental fate of these pesticides. It is also possible that pesticides were not applied prior to sampling as some residues were also found below the limits of quantification (LOQ).

The brown beans were found to be contaminated with higher pesticide residues compared to the white beans. The relative higher residue levels in brown beans compared to white might be because brown beans are often believed to be of higher nutritional value compared to the white beans in Nigeria. It is also more expensive and hence, the probable need to preserve it with more pesticides in order to retain its market value and quality. Although, brown beans was not found on the market at Location 6 (ABJ) at the time of sampling. This might be because L6 is a remote region, located on the outskirts of the state capital (Figure 2.4). L6 is mostly dominated by very low-income earners, hence, habitats may not really be able to afford the brown beans because it is more expensive compared to the white beans.

Limitation

The Pesticide excel import data which was obtained from the NCS and analysed for this research study had group captions like: “Agricultural Pesticides” or “Pesticides” which was a challenge during data analysis because, some of these generic names may actually fall within the broad classes of either Insecticides, Herbicides, Fungicides or Disinfectants. This factor may influence data numerical grouping during data analysis which may underrepresent certain groups of Pesticides. It may also result in obvious challenges when considering studies like environmental fate and consumption data of imported pesticides in Nigeria.

Pesticide export and consumption data were not available to be included in this study.

4 CONCLUSION

It was discovered that 88% of the samples having residue concentrations above the LOQ showed high levels of pesticide residues contaminations. The high levels of pesticide residues and use of banned or unauthorised PPPs in Nigeria are due to easy and cheap availability of the PPPs in the public domain (street stores and markets) without regulatory restrictions on its distribution and sale. Lack of critical safety indicators in the current pesticide regulations may also be a leading factor in the current proliferation and indiscriminate use of the PPPs.

Additionally, the high quantities of pesticide imports into Nigeria as a result of low national manufacturing capacities has inspired the environmental concern on the end of life and final sinks of these pesticides. This is because most actors (importers, distributors, marketers, users) involved in the pesticide distribution chain may not consider pesticide disposal facilities an important safety factor in its life cycle. The need for more robust and effective regulations with safety control and monitoring schemes has become highly imperative in Nigeria.

Therefore, the recommendations towards improved environmental safety and sustainable use of Plant Protection Products in Nigeria are highlighted under two main headings viz:

Regulations and Safety Controls/Monitoring.

A. Regulations

The following topics were found to be lacking in the existing pesticide regulations in Nigeria and are considered highly desirable.

Regulations on:

1. Maximum Residue Limits in Nigeria
2. Data Requirements for Active substances, Adjuvants, Synergists, Co-formulants and safeners
3. Pesticides use in Organic Agriculture
4. Risk Based Registration
5. Statistics on Pesticides- (design to include accurate and concise pesticide grouping data on import Export, use and disposal)

B. Safety Controls and Monitoring

1. Identify Highly Hazardous Pesticides (HHP) already in use (Review of registered Pesticides database and national surveys to identify unauthorised HHPs in circulation)
2. Conduct Risk and Need Assessments of the identified HHP. (Risk may be evaluated as a function of hazard and exposure assessments).
3. Employ risk reduction strategies (Restrictions, Elimination of HHP, substitution, change in formulation, compulsory use of appropriate PPEs)
4. Conduct cost benefit analysis (considering whether to continue the use of certain HHP or choose safer/less hazardous pesticides).
5. Institutionalise Sustainable Use of Pesticides (differentiate Restricted Use Pesticides (RUP) from General Use Pesticides (GUP) at evaluation/authorisation stage, RUP available only on prescription, potential lists of candidates for substitution, policy on protection of endangered species, certification of applicators alongside application machineries, capacity building programs on IPM and IVM)
6. Develop Policy and Administrative measures including financial incentives to promote availability and distribution of low risk (Biological) alternatives (eg. Subsidy on taxation).
7. Institutionalise residue compliance levels on fresh agricultural produce before placement on the market.
8. Evaluate end of life of the different categories of pesticides during authorisation process (disposal plans of pesticides, empty containers and obsolete stocks)
9. Information sharing with other countries (on pesticide incidents, Regulatory Actions and alternatives to HHP may be developed and promoted).
10. Clear and credible information on pesticides risks and safety may be communicated to the general public with feedback on perception of chemical risks

Conclusion:

It is worthy of note that: conducting a holistic review of the current pesticide regulations in Nigeria is not sufficient to ensure environmental safety protocols and Sound Management of pesticides. Adequate implementation regimes and enforcement strategies of the reviewed regulation is imperative in ensuring continuous human and environmental safety towards sustainable futures.

5 BIBLIOGRAPHY

- ¹ Peshin, R. (2002). Economic Benefits of Pest Management; Encyclopaedia of Pest Management, pages 224-227, Pub. Marcel Dekker
- ² Pretty, J., & Bharucha, Z. (2015). Integrated Pest Management for Sustainable Intensification of Agriculture in Asia and Africa. *Insects*, 6(1),152–182. doi:10.3390/insects6010152
- ³ Ojo, Joshua (2016). Pesticides Use and Health In Nigeria. *Ife Journal of Science* 18(4)
- ⁴ Unsworth, J. (2010). History of pesticide use. International Union of pure and applied chemistry (IUPAC).
https://agrochemicals.iupac.org/index.php?option=com_sobi2&sobi2Task=sobi2Details&catid=3&sobi2Id=31 (Accessed May 7, 2019)
- ⁵ Smith A.E. and Secoy, D.M. (1975) Forerunners of Pesticides in Classical Greece and Rome; *J. Ag. Food Chem.* 23 (6) 1050
- ⁶ Bernardes, M. F. F., Pazin, M., Pereira, L. C. & Dorta, D. J. (2015). Impact of Pesticides on Environmental and Human Health. *Toxicology Studies - Cells, Drugs and environment*. doi:10.5772/59710
- ⁷ Katherine, P., Johanna, S., & Anne, F. (2012). Pyrethroid Insecticides: Use, Environmental Fate, and Ecotoxicology, *Insecticides - Advances in Integrated Pest Management*, Dr. Farzana Perveen (Ed.), ISBN: 978-953-307-780-2, InTech, Available from: <http://www.intechopen.com/books/insecticides-advances-in-integrated-pest-management/pyrethroidinsecticides-use-environmental-fate-and-ecotoxicology>
- ⁸ McKnight, U. S., Rasmussen, J. J., Kronvang, B., Binning, P. J., & Bjerg, P. L. (2015). Sources, occurrence and predicted aquatic impact of legacy and contemporary pesticides in streams. *J. Environmental Pollution*, 200, 64-76. <https://doi.org/10.1016/j.envpol.2015.02.015>
- ⁹ European Commission, “Pesticides” https://ec.europa.eu/food/plant/pesticides_en) Accessed 7th May, 2019.
- ¹⁰ Harvard University (2015). GMOs and Pesticides: Helpful or Harmful <http://sitn.hms.harvard.edu/flash/2015/gmos-and-pesticides/>
- ¹¹ Food and Agricultural Organisation of the United Nations. “Pesticide Registration Toolkit”. <http://www.fao.org/pesticide-registration-toolkit/tool/page/pret/rs01-pesticide-registration-strategies> Accessed 24th June 2019
- ¹² Official Journal of the European Union (2009), Regulations: REGULATION (EC) No 1107/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC
- ¹³ USA 40 CFR Parts 150 to 189 “Electronic code of Federal Regulations”. - Chapter I, Subchapter E—Pesticide Programs (contained in Volume 23, 40 CFR Parts 150 to 189) https://www.ecfr.gov/cgi-bin/text-idx?SID=aeda156f44d1a0da941ef63ac1afb865&mc=true&tpl=/ecfrbrowse/Title40/40cfrv26_02.tpl#0
- ¹⁴ National Agency for Food and Drug Administration and Control (NAFDAC), NAFDAC Regulations. NAFDAC Acts, Regulations and Government Notices. https://www.nafdac.gov.ng/wp-content/uploads/Files/Resources/Regulations/CHEMICAL_REGULATIONS/Pesticide-Registration-Regulations-2019.pdf
- ¹⁵ Biopesticide Registration Regulations (2014 Draft). http://www.nlipw.com/wp-content/uploads/Bio-Pesticides_Registraton_Regulations.pdf
- ¹⁶ Chemsafety PRO (2018). A quick guide to international Chemical Conventions

-
- https://www.chemsafetypro.com/Topics/Convention/international_chemical_conventions.html
- ¹⁷Food and Agricultural Organization of the United Nations (FAO).
<https://www.ippc.int/en/structure/>
- ¹⁸OECD Pesticide Programme <https://www.oecd.org/env/ehs/pesticides-biocides/agriculturalpesticidesprogramme.htm>. Accessed 21st May 2019
- ¹⁹ World Health Organization & International programme on Chemical safety. (2010). The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification 2009. WHO. <http://www.who.int/iris/handle/10665/44271>
- ²⁰World Health Organization (2019) “Food safety”
https://www.who.int/foodsafety/areas_work/chemical-risks/jmpr/en/ (Accessed 21st June, 2019.)
- ²¹ Pesticide Action Network (PAN). https://en.wikipedia.org/wiki/Pesticide_Action_Network. (Accessed 21st June 2019)
- ²² National Pesticide Information Center (NIPC), (2019). Pesticide Statistics <http://npic.orst.edu/ingred/stats.html> Accessed 23rd June 2019.
- ²³ Erhunmwunse, N. O., Dirisu, A., Olomukoro, J. O. (2012). *Implications of pesticide usage in Nigeria. J. Tropical Freshwater Biology*, 21(1)15-25
- ²⁴ Munees, A., Mohammad, S.K. (2013) Pesticides as Antagonists of Rhizobia and the Legume-Rhizobium Symbiosis: A Paradigmatic and Mechanistic Outlook. *Journal of Biochemistry & Molecular Biology*1(4):63-75 DOI: 10.12966/bmb.12.02.2013
- ²⁵ Victor, A.S., Elvis, A.B., Lawrence, K., John A.M. (2015). Pesticide use, practice, and perceptions of vegetable farmers in the cocoa belts of the Ashanti and Western regions of Ghana. *J. Advances in crop science and Technology*. 03(03). doi: 10.4172/2329-8863.1000174
- ²⁶ Stadlinger, N., Mmochi, A.J., Dobo, S. (2011). Pesticide use among smallholder rice farmers in Tanzania. *J. Environ. Dev. Sustain.* 13, 641–656
- ²⁷ Mengistie, B.T., Mol, A.P.J., Oosterveer, P. (2017). Pesticide use practices among smallholder vegetable farmers in Ethiopian Central Rift Valley. *J. Environ. Dev. Sustain.* 19, 301–324.
- ²⁸ Hashemi, S.M., Damalas, C.A. (2011). Farmers' Perceptions of Pesticide Efficacy: Reflections on the importance of pest management practices adoption. *J. Sustain. Agric.* 35, 69–85.
- ²⁹ Khan, M., Mahmood, H.Z., Damalas, C.A. (2015). Pesticide use and risk perceptions among farmers in the cotton belt of Punjab, Pakistan. *Crop. Prot.* 67, 184–190
- ³⁰ Ogah, C.O., Jettey J., Coker, H.B., Adepoju-Bello, A.A. (2012) Analysis of Organochlorine pesticide residues in beans from markets in Lagos State, Nigeria. *West African Journal of Pharmacy* 23 (1), 60 – 68
- ³¹ Oyekunle, J.A.O., Akindolani, O.A., Sosan, M.B., Adekunle, A.S. (2017). Organochlorine pesticide residues in dried cocoa beans obtained from cocoa stores at Ondo and Ile-Ife, Southwestern Nigeria. *J. Toxicology Reports*, 4,51–159. doi:10.1016/j.toxrep.2017.03.001
- ³² Isegbe, V., Habib, M., Obaje, J., Ekor, S., Solomaon, S., (2016)^a. Organophosphate Pesticide Residues Analysis Sampled From Containerized Beans Repatriated from European Union. *International Journal of Innovative Food, Nutrition & Sustainable Agriculture* 4(4):31-35
- ³³ Isegbe, V., Habib, M., Obaje, J., Ekor, S., Solomaon, S., (2016)^b. Residues of Organochlorine Pesticide in Dried Beans (*Vigna unguiculata*) Originating from Nigeria. *International Journal of Innovative Food, Nutrition & Sustainable Agriculture* 4(4):25-30
- ³⁴ Gwary, M. O., Hati. S. S., Dimari, A. G., Ogugbuaja, O. V. (2012). Pesticide Residues in Bean Samples from Northeastern Nigeria. *ARPN Journal of Science and Technology* (2) 2. 79-84.

- ³⁵ Anzene, J.S., Tyohemba, R.L., Ahile, U.J., Emezi, K.S.A. (2014). Organochlorine pesticide residues analysis of postharvest cereal grains in Nasarawa State, Nigeria. *International Journal of Agronomy and Agricultural Research*, 5(5), 59-64.
- ³⁶ Ibigbami, O., Aiyesanmi, A., Adeyeye, E., Adebayo, A., & Aladesanwa, R. (2017). Multi-residue levels of organophosphorus pesticides in cocoa beans from some cocoa farms in Ekiti state, Nigeria. *Bangladesh Journal of Scientific and Industrial Research*, 52(4), 281-288. <https://doi.org/10.3329/bjsir.v52i4.34769>
- ³⁷ Olufade, Y.A., Sosan, M.B., Oyekunle, J.A.O (2014). Levels of Organochlorine Insecticide Residues In Cowpea Grains and Dried Yam Chips From Markets In Ile-Ife, Southwestern Nigeria: A Preliminary Survey. *Ife Journal of Science*, 16 (2), 161-170.
- ³⁸ Akinneye, J.O., Adedolapo, A.O., Adesina, F.P. (2018) Quantification of Organophosphate and Carbamate residue on stored grains in Ondo State Nigeria. *Journal of biology and medicine* 2(1), 1-6.
- ³⁹ Akoto, O., Andoh, H., Darko, G., Eshun, K., Osei-Fosu, P. (2013). Health risk assessment of pesticides residue in maize and cowpea from Ejura, Ghana. *Chemosphere*, 92(1), 67–73. doi:10.1016/j.chemosphere.2013.02.057
- ⁴⁰ Jean, S. (2013). *Contamination of cowpea and by-products by organophosphorous pesticide residues in Ngaoundere markets: Dietary risk estimation and degradation study*. *African Journal of Food Science*, 7(5), 92–102. doi:10.5897/ajfs2013.1013
- ⁴¹ Kailas, K. (2016). Multiple Pesticide Residue determination from Bean and Brinjal using HPLC. *International Journal of Research in Engineering and Applied Sciences*, 6 (5), 15-21
- ⁴² The Expert Committee on Pesticide Residues in Food (PRiF) (2017) Report on the pesticide residues monitoring programme: Quarter 2 2017. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/664814/pesticide-residues-quarter2-2017-report.pdf
- ⁴³ Mahmood, I., Imadi, S. R., Shazadi, K., Gul, A., & Hakeem, K. R. (2016). *Effects of Pesticides on Environment*. *Plant, Soil and Microbes*, 253–269. doi:10.1007/978-3-319-27455-3_13
- ⁴⁴ Oyeyiola, A.O., Fatunsin, O.T., Akanbi, L.M., Fadahunsi, D.E., Moshood, M.O. (2017) Human Health Risk of Organochlorine Pesticides in Foods Grown in Nigeria. *Journal of Health and Pollution*: 7(15), 63-70. <https://doi.org/10.5696/2156-9614-7.15.63>
- ⁴⁵ Mazlan, N., Ahmed, M., Muharam, F. M., Alam, M. A. (2017). Status of Persistent Organic Pesticide Residues In Water And Food And Their Effects On Environment And Farmers: A Comprehensive Review In Nigeria. *Semina: Ciências Agrárias*, 38(4), 2221. doi:10.5433/1679-0359.2017v38n4p2221
- ⁴⁶ Peters, K., Bundschuh, M., Schaefer, R.B. (2013). Review on the effects of toxicants on freshwater ecosystem functions. *J. Environ. Pollut.* 180, 324-329. <http://dx.doi.org/10.4314/tfb.v21i1.2>
- ⁴⁷ Beketov, M., Kefford, B.J., Schaefer, R.B., Liess, M., (2013). Pesticides reduce regional biodiversity of stream invertebrates. *Proceedings of National Academy of Science*. 110 (27), 11039-11043. doi:10.1073/pnas.1305618110 .
- ⁴⁸ Hassan, Y., Zamani, H., Varshney, D. (2018). Preserving or Poisoning: A case of Dried-Beans from Nigeria. *International Journal of Management Technology and Engineering*, 8(7): 473-484
- ⁴⁹ Nigerian Institute of Food Science and Technology (NIFST) (2019) HARMFUL EXPORTS: EU BANS NIGERIA FROM EXPORTING BEANS, MELON, OTHERS. <https://nifst.org/harmful-exports-eu-bans-nigeria-from-exporting-beans-melon-others/> (Accessed 7th May 2019)

-
- ⁵⁰ United Nations Development Organisation (UNIDO), (2017). UNIDO's Fourth Donor Meeting presents the Conduits of Excellence project in Nigeria <https://www.unido.org/search?keys=Ban+on+Nigeria+Beans>
- ⁵¹ European Commission, RASFF PORTAL: <https://webgate.ec.europa.eu/rasff-window/portal/?event=notificationsList&StartRow=44201>
- ⁵² Federal Ministry of Industry, Trade and Investment (FMITI). Chemical Division, Abuja, Federal Capital Territory, 2019.
- ⁵³ National Bureau of Statistics (2019). Pesticide Trade Data (2010-2019). Plot 762, Independence Avenue, Central Business District, Abuja, FCT. www.nigerianstat.gov.ng
- ⁵⁴ Federal Capital Territory, Nigeria, (2019). https://en.wikipedia.org/wiki/Federal_Capital_Territory,_Nigeria
- ⁵⁵ Maps.google.com, July 2019
- ⁵⁶ European Standard CSN EN 15662. (2019). Food of Plant Origin-Multimethod for determination of Pesticide residues using GC- and LC-based analysis following acetonitrile extraction/partitioning and clean-up by dispersive SPE-Modular QuEChERS-method. <https://www.en-standard.eu/csn-en-15662-foods-of-plant-origin-multimethod-for-the-determination-of-pesticide-residues-using-gc-and-lc-based-analysis-following-acetonitrile-extraction-partitioning-and-clean-up-by-dispersive-spe-modular-quechers-method/>
- ⁵⁷ Royal society of Chemistry "Chemspider Predicted Episuit" US environmental Protection Agency's EPISuite™. <http://www.chemspider.com/Chemical-Structure.2928.html?rid=76ab7f63-5183-44e9-a15d-c16bb86d692a>. Assessed 18th June 2019.
- ⁵⁸ Nigeria Custom Service (NCS), "Custom pesticide Excel" Abuja, Federal Capital Territory, 2019
- ⁵⁹ Wenjun Zhang (2019). Global Pesticide Use: Profile, Trend, Cost/Benefit and More. Proceedings of the international Academy of Ecology and Environmental Sciences, 8(1):1-27
- ⁶⁰ Philip McDoughall (2018). Evolution of the crop Protection Industry since 1960. <https://croplife.org/wp-content/uploads/2018/11/Phillips-McDougall-Evolution-of-the-Crop-Protection-Industry-since-1960-FINAL.pdf> Accessed 21st June 2019.
- ⁶¹ Food and Agricultural Organisation (FAO), 2019. Pesticides Trade. <http://www.fao.org/faostat/en/#data/RT/visualize>
- ⁶² Manufacturers Association of Nigeria, "Number of companies of Sub sectorial groups as at January 2019", Ikeja, Lagos, 2019
- ⁶³ Van den Berg, H., Manuweera, G., Konradsen, F. (2017). Global Trends in the production and use of DDT for control of Malaria and other vector-borne diseases. *Malaria Journal*, 16(1). Doi:1186/s12936-017.2050-2
- ⁶⁴ Musa U.F., Hati S.S., Mustapha A. & magaji G. (2010). Dichlorvos Concentrations in Locally formulated pesticide (Ota Piapia) utilized in Northeastern Nigeria. *Scientific Research Essay*, 5 (1): 049-054
- ⁶⁵ Model, K. J., Sampaio, S. C., Remor, M. B., Mercante, E., & Boas, M. A. V. (2018). Organochlorinated And Organophosphorus Pesticides In The Pelotas River Sediment. *Engenharia Agrícola*, 38(1), 124–134. doi:10.1590/1809-4430-eng.agric.v38n1p124-134/2018
- ⁶⁶ Hénault-Ethier, L. (2015). Health and environmental impacts of pyrethroid insecticides: What we know, what we don't know and what we should do about it. Executive Summary and Scientific Literature Review. Prepared for Équiterre. Montreal, Canada. 68pp. <http://www.equiterre.org/publication/revue-delitterature-sur-les-impacts-des-insecticides-pyrethrinoides-sur-la-sante-et-len>