KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI, GHANA

COLLEGE OF SCIENCE

PESTICIDE RESIDUES AND POTENTIAL HEALTH RISK THROUGH THE CONSUMPTION OF FISH FROM IBADAN, OYO STATE, NIGERIA.

BY

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A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY,

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF

DEGREE OF

MASTER OF PHILOSOPHY (MPHIL.) IN ENVIRONMENTAL CHEMISTRY

JUNE, 2015.

DECLARATION

I hereby declare that this thesis is the result of my own original research towards the Mphil. degree and that to the best of my knowledge, no part of it has been previously published by another person nor presented for the award of another degree in the university or elsewhere except where due acknowledgement has been made in the text.

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DEDICATION

This thesis is dedicated to OSO, JOEL OMOKARO. You left too early………

ACKNOWLEDGEMENT

May God's name be highly exalted. To him I give all glory and adoration for the success of this work. I'm most thankful to God for its completion.

My utmost gratitude goes to my Parents Mr. Godspower Oso and Mrs. Josephine Oso for their prayers, love, financial and moral support. Also to my siblings: Blessing Oghogho, John Oghenemaro and Emmanuel Ogagaoghene for being there.

I would like to appreciate the efforts and support of my Supervisor; Dr. E. E. Kwaansa-Ansah, I pray that God will grant you your heart's desires and bless you beyond your imagination.

I want to thank the following people for their contributions and help rendered along the way no matter how little: Dr. Omoniyi Moses, Dr. Ogunremi (University of Ibadan), Professor Ajani (Fisheries Dept. University of Ibadan), Mr. Samuel Afful (Ghana Atomic Energy Commission), Dr. and Mrs Babatunde Duduyemi, Dr. Lawrence Boakye, Uncle Lawson Okukulabe, Uncle Douglas and Aunt Nkechi, Miss Adenike Ige, my able colleagues; Mr. Olusegun Salawu, Mr. Seyram Adzibolosou, Miss Joy Ogedegbe, Miss Princess Amadi, Mr. Dominique Amuzu and my classmates.

God bless you all.

ABSTRACT

This study was conducted to determine the concentration of organochlorine, organophosphorus and pyrethroid pesticide residues present in some selected fish species (*Oreochromis niloticus, Clarias gariepinus, Trachurus trachurus, Sardinella madenrensis and Scomber japonicus*) from markets in Ibadan, Oyo state, Nigeria. Further studies were carried out to determine the health risk posed on the human population from the consumption of the selected fish species. The extraction procedure and clean-up was done using Hexane/Acetone solvent system. The five fish species were analyzed for pesticide residues by gas chromatography equipped with electron capture detector. Nine (9) organophosphorus pesticides (Methamidopho, Phorate, Fonofos, Primiphos-methyl, Chlorpyrifos, Malathion, Fenithrothion, Parathion-ethyl and Profenofos), nine (9) pyrethroid pesticides (Allenthrin, Bifenthrin, Fenpropathrin, Lambda-cyhalothrin, Cyfluthrin, Cypermethrin, Fenvalerate, Delta-methrin and Permethrin) and thirteen (13) organochlorine pesticides (β-HCH, δ-HCH, Heptachlor, γ-Chlordane, α-endosulfan, β-endosulfan, p,p'-DDE, Dieldrin, Endrin, p,p'DDD, p,p'-DDT, Methoxychlor and Aldrin) were detected. The mean concentrations detected for organophosphorus pesticides ranged from 0.0024±0.0002 μg/g to 0.0076±0.0031 μg/g, pyrethroids ranged from 0.2154±0.0066 μg/g to 7.6504±0.0259 μg/g and organochlorine pesticides ranged from 0.1048±0.0079 μg/g to 3.2062±0.0348 μg/g. The health risk assessment analysis performed on the samples had health index of less than 1 (HI<1) for pyrethroids and organophosphorus pesticides in all fish species analyzed, indicating that their intake through fish consumption may pose no danger or harm to its consumers. On the other hand, health index was less than 1 (HI<1) for most organochlorines, with the exception of heptachlor, dieldrin and

aldrin which had HI greater than 1 (HI>1) in some fish species, indicating that there may be harm in continuous consumption of such fish which could result in detrimental chronic effects on the consumer.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Human population across the globe keeps increasing at an alarming rate and is dependent on practices like mining, farming, forestry, fish farming, oil exploitation, structural developments, rural development and industrialization for survival. These practices involve the manipulation, degradation and destruction of the environment leaving undesirable effects on both land and the aquatic environment.

One of human's major dependence for survival and means of livelihood is on agricultural resources and products. Nigeria is a densely populated country with a vast land size on which farmers cultivate a wide range of crops for public consumption and as a source of income. Intensive agricultural activities are a major threat to Nigerian fishery, wildlife and marine resources. Most farmers, in order to increase their yields, use agrochemicals, which can enter surface and ground waters through runoff from treated soils, leaching processes, aerial drift and inappropriate disposal methods thus changing water chemistry (Olanike, 2003; Joseph, *et. al*., 2013). On entry into water bodies (lakes and rivers), pesticides cause immediate toxic effects on aquatic life (flora and fauna).

Pesticide is a general name used to classify herbicides, rodenticides, fumigants, fungicides, garden chemicals, wood preservatives, household disinfectants and insecticides. They provide a wide range of benefits from their usage to control, destroy and prevent damage from insects, weeds and other pests thereby leading to high farm yield and reduced insect-borne diseases (Robert and Pixie, 2006). Their usage became increasingly popular with time due to the steady increase in pest population and decrease in soil fertility (Zacharia, 2011).

Although they may be selectively toxic to pests, pesticides may still be toxic to humans if pesticide-contaminated food is ingested. They are non-biodegradable as some pesticides may not be reused for many years after application, but are long lasting and are likely to accumulate in sediments and soils (FDA, 2011).

Fish could be obtained from water which has been polluted and these pollutants could have accumulated in fish up to levels that may pose threats to the health of consumers (e.g. reproductive disorders, carcinogenicity, teratogenicity and mutagenic effects). Biomagnifications and bioaccumulation move up the food chain until a toxic level is reached as other edible zooplanktons apart from fish present in the water also ingest these toxic chemicals.

These residues in fish tend to build up in the fatty tissues at varying concentrations and is dependent on issues such as fat content, age, fish size and gender of the fish (FDA, 2011).

Pesticides differ in characteristics, physical and chemical properties and are usually classified in three major ways: based on the pesticide composition, mode of action and targeted pest species (Zacharia, 2011). By chemical classification, pesticides can be grouped into four major groups: Organochlorine, Carbamates, Pyrethroids and Organophosphorus.

Organophosphorus pesticides are commonly toxic to both vertebrates and invertebrates alike and may lead to paralysis and death if ingested. Unlike organochlorines, organophosphorus pesticides are not persistent in the environment. They decompose easily under various chemical and biological conditions.

The synthetic pyrethroids are known to be one of the most effective groups of pesticides that account for a large percentage of the world's usage of pesticides. Their low toxicity to birds and mammals has promoted their extensive usage in agriculture as very effective agents for combating pests (Smith and Stratton, 1986; Glickman and Lech, 1982; Casida *et. al*., 1983; Kenan, 2004)

Organochlorines are a group of compounds also called chlorinated hydrocarbons with the most important of them being DDT (Dichlorodiphenyltrichloromethane) (Afful *et. al.*, 2010). OCPs which as ever-present environmental contaminants have constantly been detected in certain food commodities, sediments, drinking water and fish globally (Mott and Snyder 1987; Ize-Iyamu, *et. al*., 2007; Tanabe *et. al*. 1994). Various studies have shown how toxic organochlorine pesticides could be to humans and animals including also certain health effects such as immune system dysfunction, cancer, birth defect and reproductive failures. (Bouman, *et. al.*, 1990; Brassow, *et. al.*, 1981; Olea, *et. al., 1998*; Winter, *et. al.*, 1992).

As a class of compounds, organochlorines have exceptional physical and chemical properties that control their persistence, fate, and transport in the environment. Although these properties may be different amongst the various organochlorine compounds, they all possess the abilities to:

a) Resist most chemical and microbial degradation and remain in the environment.
b) Associate with sediments or other solids.
c) Accumulate in the fatty tissue of invertebrates, mammals, fish and other living organisms with the possibility of damaging internal organs.
d) Affect reproduction of birds, fish e.t.c especially weakening the shells of eggs.

In fact, it is their exceptional properties that have contributed to both their efficiency as pesticides and their persistence and accretion in the environment (USEPA, 2002).

The high application of pesticides to the environment has caused contamination of soils and water globally. Once pesticides are introduced into the environment whether through direct application to the soil surface, disposal or spill, they may move away from their point of application or discharge (FDA, 2011) through runoff, leaching, volatilization, adsorption or crop removal thereby escalating environmental pollution.

Factors like climate, soil properties (e.g. presence of organic matter, pH and clay materials), physico-chemical properties of the pesticide, biological factors, properties of the water systems and other environmental factors influence the fate of pesticides in both soil and water environments. Increased usage of pesticides has therefore caused a lingering pollution of soils and water worldwide.

1.2 PROBLEM STATEMENT

One major negative impact of Agriculture to the environment is pollution by pesticides. The use of pesticides to control weeds, insects and other pests has resulted in a series of benefits (increased farm yield and decline of insect-borne diseases) but also raises questions concerning probable unpleasant effects on the environment. (Robert and Pixie, 2006). Organochlorine Pesticides (OCPs), Pyrethroids and Organophosphorus Pesticides (OPs) are widely used ignorantly and improperly in insect control (e.g. mosquito and tsetse fly control) and Agriculture in Nigeria. However, this continued abuse is of international concern because of their long term residual effect on the environment and resistance to most chemical and microbial degradation. Their persistence and high toxicity along with considerable bioaccumulation and biomagnification along the food chain makes them toxicants that should be given due consideration.

1.3 OBJECTIVES

1.3.1 GENERAL OBJECTIVE

The main objective of this work is to determine the potential health risk of pesticides through the consumption of fish from Ibadan, Oyo state, Nigeria.

1.3.2 SPECIFIC OBJECTIVES

The following were the specific objectives of the study:

1. To determine the presence and concentrations of Organochlorine pesticides in fish collected from markets in Ibadan.
2. To determine the presence and concentrations of Organophosphorus pesticides in fish collected from markets in Ibadan.
3. To determine the presence and concentrations of Pyrethroid pesticides in fish collected from markets in Ibadan.
4. To evaluate the hazard index in order to estimate the potential risk of health hazards of the pesticides to the population from the consumption of fish.

1.4 JUSTIFICATION

The consumption of fish is steadily increasing globally, especially in Nigeria because of its high nutritional value and its being a readily available cheap source of protein. Because of the high consumption of fish by Nigerians, determining the levels of pesticides residues in fish is essential in order to make sure that the exposure of humans to these contaminants particularly through dietary consumption does not surpass tolerable levels for health. Subsequently, this study may aid the evaluation of the potential health risk of pesticide residues detected in specific fish species on the population of the people of Ibadan.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 HISTORICAL BACKGROUND

The earliest use of pesticides can be traced to the beginning of agriculture. But contemporary use of pesticides in areas like public health and agriculture can be dated to the 19^{th} century involving the control of pests such as insects (mosquitoes, blackflies e.t.c), fungi and bacteria using a fumigant hydrogen cyanide, arsenic and other toxic compounds before their nonusage due to their toxic nature and ineffectiveness (Zacharia, 2011).

In Africa because of farming and the prevalence of mosquitoes, pesticides have become major chemicals used in homes and agriculture. Due to the high specific effectiveness and reliability, pesticides are currently used throughout the world in agriculture, horticulture and forestry as well as for domestic, hygiene and veterinary purposes. Pesticides are the only compounds which are prepared to be harmful and then introduced directly to the environment. (Danso *et. al*., 2002).

In 1873, a German scientist Ziedler synthesized dichlorodiphenyltrichloroethane (DDT) and in 1939, its effect on pests was made known by Paul Muller. It rapidly spread worldwide due to its affordability and efficacy at controlling pests. DDT was also used for other nonagricultural purposes (Zacharia, 2011).

Pyrethrins were initially extracted from the flower heads of *Chrysanthemum cinerariaefolium* for use as insecticides. However, Pyrethroids (synthetic analogues) were developed because of the noticeable rapid decomposition of pyrethrins by light. Hence, allenthrin, the first pyrethroid pesticide was identified in 1949 (Bradberry *et. al.,* 2005).

Pyrethroids have long been widely used as insecticides for domestic/commercial purposes and for treating head lice and scabies. In most tropical regions, part of their anti-malarial tactics is to soak mosquito nets in solutions of δ-methrin. Hence, net users of all age group and state of health as well as those who dip the nets face long-term exposure (Barlow *et. al*., 2001).

Pyrethroids, organochlorine and organophosphorus pesticides as well as many other organic trace pollutants have been manufactured and released into the environment over the past century (Van der Oost *et. al.,* 2003). Many of these contaminants eventually end up in the aquatic environments either through direct discharges or due to atmospheric and hydrological processes (Stegeman and Hahn, 1994).

However, these chemicals, most times do not constitute a hazard to organisms in the forms which they are found in the environment. Once the organism has been exposed and the chemicals are readily bio-available, a series of biological interactions may occur. In view of the fact that their means of approach is by targeting the system or enzymes of pests; which are quite similar to the system or enzymes of humans, these organochlorine pesticides also pose threats to human health. (Ghidini, *et. al*., 2005; Bennet, *et. al*., 1997).

In Nigeria and Africa at large, unprecedented population growth accompanied by an intense urbanization leading to increase in agricultural and industrial development (Biney *et al.*, 1987, 1994; Saad *et al.*, 1990) have caused a wide diversification in the types of pollutants that reach inland bodies of water (Olanike, 2003) giving rise to very undesirable effects and a major threat on fishes, other aquatic organisms and the entire aquatic environment.

With malaria, which is a major global infectious disease of concern spread by mosquitoes, it has become quite obvious that pesticide discovery was a necessity for the safety and welfare of mankind. DDT has been continually used to reduce the growth of mosquitoes and as an antifouling agent in some developing countries (Covaci, *et. al*., 2004; Tao, *et. al*., 2009). Although, pests can develop resistance to pesticides when a particular type of pesticide is used repeatedly over a period of time. In this case, control will be achieved with greater difficulty. However, other control strategies could be adopted such as; alternating pesticides used occasionally by switching from one type of pesticide to another and testing the targeted insect population for resistance (Eric *et. al.,* 2000).

2.2 SOME TERMS ASSOCIATED WITH PESTICIDES

i. **Toxicity**: this is a measure of the potential of a pesticide to cause harm to living organisms. It is used to compare how poisonous one pesticide is to another.

ii. **Target organism**: this is the particular pest specifically intended to control.

iii. **Persistence**: a measure of a continuous or connected period of time that a pesticide remains in the environment in its toxic state.

iv. **Concentration**: this is the amount of a pesticide in a specified medium (e.g. soil, sediment, water, biota or air).

v. **Chronic**: refers to the effect of long term exposure to the chemical substance that do cause immediate death of the exposed organism. Chronic effects of pesticides include cancer, undesirable genetic conditions, delayed growth rate, reproductive disorders and eventual death.

vi. **Broad spectrum**: refers to a pesticide that is extremely toxic to various organisms. It targets a wide range of pests.

vii. **Active ingredient**: this is the chemical component of a pesticide that controls and causes the pesticidal effect to the target pest.

viii. **Acute**: refers to the harmful effects of a pesticide on an organism from short term exposure.

ix. **Accumulate**: this is the potential of a pesticide to amass within the tissues of an organism. The build-up can reach levels that are many times higher than concentrations in the environment and along the food chain, bioaccumulation and biomagnification results.

2.3 CLASSIFICATION OF PESTICIDES

Pesticides can be classified in so many ways but are best classified by: their mode of action, the chemical composition and targeted pest species (Drum, 1980).

2.3.1 PESTICIDE CLASSIFICATION BASED ON THEIR MODE OF ACTION

Based on this, pesticides are classified according to how they act to bring about the required results. Pesticides can be classified as systemic and non-systemic pesticides. Systemic pesticides are the pesticides that successfully move through the tissues of the plant to bring about the required effects. Non-systemic pesticides, also known as contact pesticides, are pesticides that do not penetrate the tissues of the plants. They only yield the desired effects when in contact with the targeted pest (Buchel, 1983).

2.3.2 PESTICIDE CLASSIFICATION BASED ON THE TARGETED PEST SPECIES

Here, pesticides are classified based on the targeted pest species as shown in Table 2.1 below:

Table 2.1: Pesticide classification based on the targeted species

Types of pesticide	**Target organism**
Insecticides	Insects
Herbicides	Weeds
Rodenticides	Rodents
Fungicides	Fungi
Acaricides and miticide	Arachnids e.g. ticks and mites
Molluscicides	Molluscs
Bactericides	Bacteria
Avicides	Birds
Virucides	Virus
Algaecides	Algae

2.3.3 PESTICIDE CLASSIFICATION BASED ON THEIR CHEMICAL COMPOSITION

This has been the most helpful classification to researchers based on the type of the active ingredient. This classification gives indication of the efficiency, physical and chemical property of the pesticide. A knowledge which is significant for precautions needed during application (in order to know the mode of application, application rate and safety measures to be adopted).

The four major groups of pesticides are organophosphorus, organochlorines, pyrethroids, and carbamates. (Buchel, 1983).

2.3.4 PESTICIDE CLASSIFICATION BASED ON FORMULATION

Another means of classifying pesticides is based on how it is formulated. This includes: liquid formulation, powder formulation, baits, dust, smoke, ultra-low volume (ulv) liquids and granules.

2.3.5 PESTICIDE CLASSIFICATION BASED ON TOXICITY CLASS

The World Health Organisation (WHO) developed a system of grouping pesticides based on toxicity classes. They are as follows:

- Class IA: Extremely hazardous
- Class IB: Highly hazardous
- Class II: moderately hazardous
- Class III: slightly hazardous
- Class IV: Product unlikely to present acute hazard in normal use

Another means of classifying pesticides is based on whether it is authorized to be used. This includes:

- Registered pesticides
- Banned pesticides

Pesticides are also classified according to their persistence, their concentration, how they are used and their container size (OPAC, 2010).

2.4 GENERAL PHYSICAL PROPERTIES OF PESTICIDES

Molecular weight: this is an intrinsic quality that differentiates a pesticide from another excluding stereo-isomeric pesticides that have same molecular weight but differs just on the group spatial orientations at specific chiral centres.

Vapour pressure: this is a measure of how easily the pesticide volatilizes and vapourizes. For a pesticide, this can be beneficial and a disadvantage at the same time. If a pesticide's mode of action is fumigant, it would be advantageous to have elevated levels of vapour pressure although; this can lead to environmental pollution due to vapour drift. However, pesticides with low vapour pressure can accumulate in water, soil or biota.

Solubility: this is a measure of how easily the pesticide dissolves in a given solvent. It depends on factors such as pH, temperature, polarity of the pesticide and molecular size.

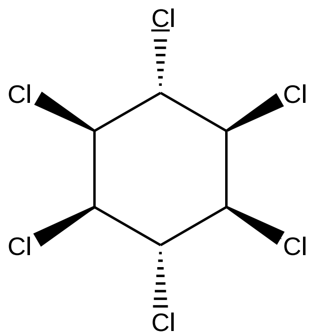
2.5 GENERAL CHEMICAL PROPERTIES OF PESTICIDES

A pesticide released into the environment undergoes a sequence of interdependent processes which determine their persistence, distribution and fate in the environment. Some of these processes include degradation, transportation, biota uptake and retention

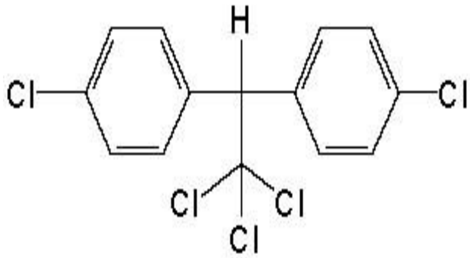
Degradation involves chemical transformation or breakdown of pesticides into other forms. This could be further categorized into Chemical and Biological degradation. Biodegradation involves pesticide breakdown by microbes, leading to the formation of new compounds which may be more toxic than the parent compounds comparatively (Joseph *et. al*., 2013; Linde, 1994). Chemical degradation of pesticides may involve all or some of the following chemical processes: reduction, oxidation, photodegradation and hydrolysis.

2.6 ORGANOCHLORINE PESTICIDES

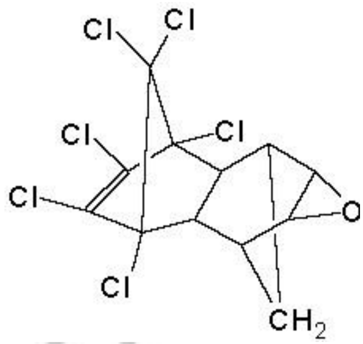
Organochlorine compounds are substances that contain carbon and chlorine elements and in most cases also contain hydrogen. They are also referred to as chlorinated organic compounds. They are higly lipophilic and stable and these characteristics make them bioaccumulate in the environment.



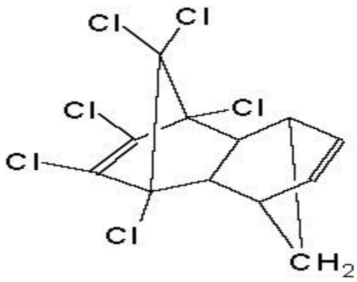
Lindane



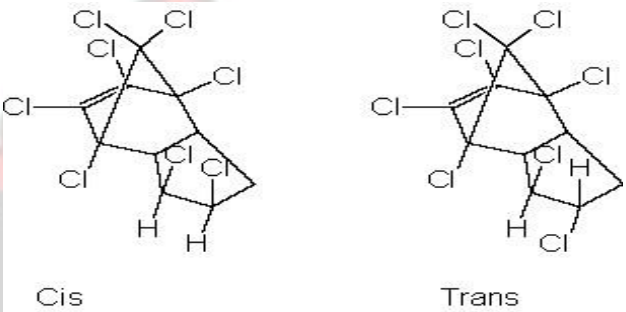
Dichlorodiphenyltrichloroethane



Dieldrin



Aldrin



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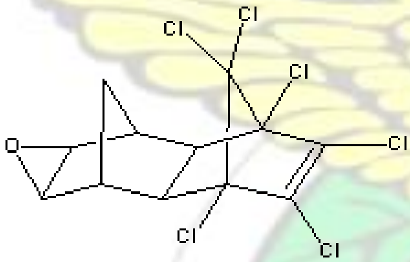
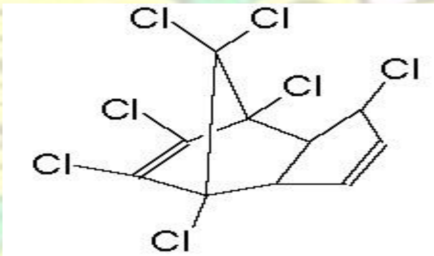


Endrin



Heptachlor

Figure 2.1: Examples of some organochlorines.

Dichlorodiphenyltrichloroethane (DDT) was an effective insecticide used for the control of pesticide before its ban. It degrades to two metabolites: DDE (Dichlorodiphenyldichloroethylene) and DDD (1,1-dichloro-2,2-bis(p-chlorophenyl)ethane). DDT accumulates in plants and in the fatty tissues of fish, birds and animals. Aldrin and dieldrin have similar structures; dieldrin is converted to aldrin in the presence of sunlight and bacteria. In 1987, usage of both aldrin and dieldrin were entirely banned by the EPA because of their potential harm to human health (USEPA, 2002).

Chlordane and Endrin are cyclodienes. Endrin is more extremely toxic than the other cyclodienes but has less persistence in the environment.

2.7 ORGANOPHOSPHORUS PESTICIDES

Organophosphates (OPs) are general terms used in describing all the phosphorus-containing insecticides. They are commonly the deadliest pesticides to vertebrate animals, often exercising their toxic action by slowing down the cholinesterase enzymes of the nervous system which result in the accumulation of acetylcholine. This then interferes with neuromuscular junctions producing rapid twitching of the voluntary muscles and eventually paralysis. Examples of some organophosphates include:

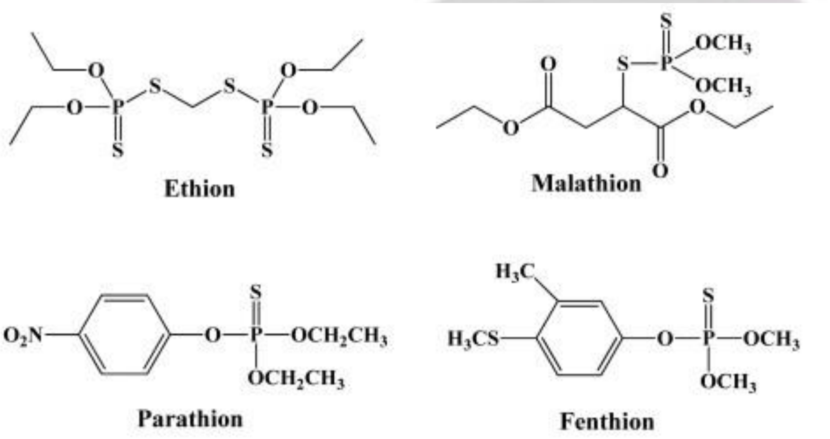
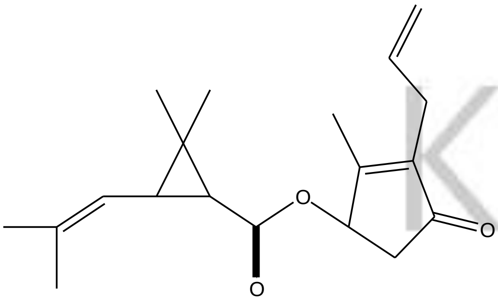


Figure 2.2: Examples of some organophosphorus

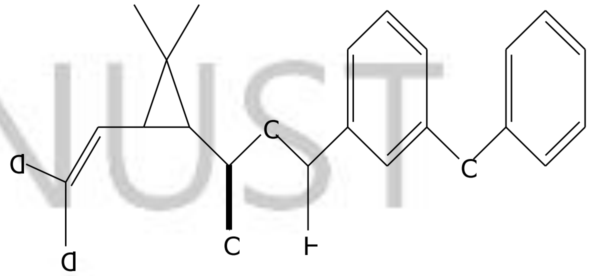
2.8 PYRETHROIDS

Pyrethroids are less lethal to mammals than insects because of characteristics such as low dermal adsorption and fast breakdown of non-toxic metabolites which protects mammals while insects have lower body temperature, higher sodium channel sensitivity and smaller body size. Pyrethroids have toxic mechanisms that make them complex but this turns out to be more complicated when they are put together (co-formulated) with an organophosphorus insecticide or piperonyl butoxide as these are compounds which inhibit the metabolism of pyrethroids

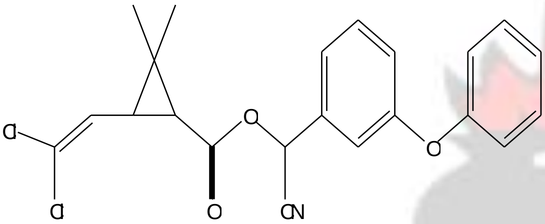
(Bradberry *et. al*., 2005; Bradbury and Coats, 1989; Narahashi *et. al*.., 1995; Narahashi *et. al*., 1996; Song and Narahashi, 1996).



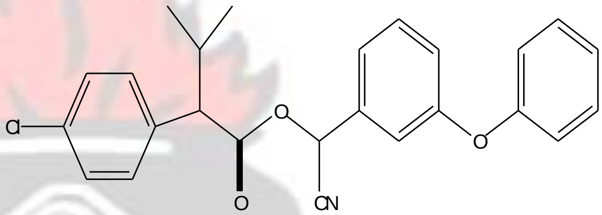
Allenthrin



Permethrin



Cypermethrin



Fenvalerate

Figure 2.3: Some examples of pyrethroids,

2.9 HARMFUL FARMING AND FISHING PRACTISES

Fish contributes about 55% of the protein intake in Nigeria, with per capita consumption of 7.52 Kg per annum and a total consumption of 1.2 million metric tons (Adewuyi, 2010). African Catfish (*Clarias gariepinus*), Nile Tilapia (*Oreochromis niloticus*), Sardine (*Sardinella maderensis*), Atlantic Horse Mackerel (*Trachurus trachurus*), and Chub Mackerel (*Scomber japonius*) are some of the common species of fishes that are of high commercial value in Nigeria and are consumed fresh, smoked or salted.

Fishes have frequently been reported to suffer massive kill and to contain higher concentration of pesticide residues than those allowable by various environmental bodies due to the release of pesticides into the aquatic environment. Aquatic pollution by agrochemicals results mainly from their widespread use in agriculture and in vector control campaigns. (Olanike, 2003)

leaving the waters unsuitable for drinking, irrigation, fish cultivation and other household purposes. Despite their toxicity, persistence and other negative environmental effects, their relatively low cost, affordability and lack of appropriate enforcement of national regulations have led to their increased and continued usage in
Nigeria and most developing countries of the world (Calamari, 1985; Biney *et al.*, 1987; Osibanjo and Bamgbose, 1989; Saad *et al.*, 1990).

2.9.1 INCIDENCE OF ORGANOCHLORINE, ORGANOPHOSPHORUS AND PYRETHROID PESTICIDES IN FISH

In Africa and many countries all over the world, it is a known fact that pesticides are being used indiscriminately and ignorantly for various purposes (Ize-iyamu, 2007). This is an ongoing threat that poses a big challenge to human health not only in Africa but to the entire human population worldwide.

For several reasons, fish species have attracted significant interest in studies that assess biological and biochemical response to environmental contaminants (Powers, 1989).

In a study carried out by Gitahi *et. al.,* (2002) analysis was carried out for some selected organochlorine and organophosphorus pesticides residues in water, red swamp crayfish (*Procambarus Clarkii*), sediment and black bass (*Micropterus Salmoides*) from Lake Naivasha. Even though organophosphate pesticides were found to be the most commonly applied pesticides in the lake's catchment, none was detected in any of the samples analysed. Organochlorine pesticides like p,p'-DDT, o,p'-DDT and p,p'-DDE residue levels in black bass and crayfish were higher than previously recorded. Lindane, dieldrin, β-endosulfan and aldrin concentrations were detected at lower concentrations in crayfish. The higher residue concentration was significant for black bass due to their higher fat content.

In Lagos, Nigeria, organochlorine pesticide residues; transnonachlor, DDD, DDT, DDE, Dieldrin, HCH and HCB were measured in three fish species: *Ethmalosa fimbriata*, *Tilapia zilli and Chrysichthys nigrodigitatus*. Mean concentrations of organochlorine pesticides were found to range from 0.01-8.92 ppm (David *et. al*., 2008). OCP concentrations (except for HCHs) detected in the fish species were detected below the FAO-WHO 1997 codex alimentarious commission set limit but higher than the allowed Federal Ministry of Environment limit.

In one study, analysis was carried out to determine the levels of organochlorine pesticide residues in fish and water samples from some rivers in Edo state, Nigeria. Extraction was done using Soxhlet extraction (Osibanjo and Adeyeye, 1995; Osibanjo and Tongo, 1985; Saleh and Lee, 1978). In fish, the organochlorine residues detected were also the same as those detected in fish but were of higher concentrations. Lindane was detected at levels 63 µg/g, 54 µg/g and 39 µg/g in fish from Ovia, Ogba and Ikoro rivers respectively. While Aldrin was found present at 59 and 27 µg/g in the bottom and top feeders from Ovia river (Ize-iyamu, 2007). The levels were noted to be higher than the allowable Federal Environmental Protection Agency limits (FEPA, 1991).

In a study by Afful, *et. al*. (2010), investigation was done to assess the organochlorine levels in six fish species from the Densu basin (*Chrysichthys nigrodigitatus, Clarias gariepinus, Tilapia zilli, Hepsetus odoe, Channa obscura and Heterotis niloticus*). The concentrations of organochlorine pesticide residues detected ranged from 0.3-71.3 µg/kg which was below the 50-1000 µg/kg Australian Maximum Residue limit for fresh water fish

A study by Kuranchie-Mensah *et. al*. (2013) in Ghana carried out to determine the levels of organochlorine residues in five fish species: *Chrysichthys nigrodigitatus, Tilapia zilli, Hepsetus odoe, Oreochromis niloticus and Heterotis niloticus* from the Densu river basin

(Weja). Detectable OCPs were γ-HCH, dieldrin, δ-HCH, and aldrin. The others investigated were endosulfan sulphate, α-endosulfan, p,p'-DDT and its metabolites endrin aldehyde and endrin ketone. α-endosulfan was the highest Organochlorine pesticide residue recorded in the study while dieldrin was the least at levels which were below the Maximum Residue Limits fixed by EU, FAO, USFDA, Australia and Italy and thus were said to be safe for human consumption.

A market survey was conducted by Dogheim *et. al*., (1996) to monitor organochlorine and organophosphorus pesticide residues in fish and some other foods and fruits. None of the detected organophosphorus residues exceeded their maximum residue limit; this could have been due to degradation. However, some of the organochlorine residues exceeded their maximum residue limits set by Codex Committee on pesticide residues.

In Bornu state, Nigeria, the levels of some Organophosphorus pesticides (Dichlorvos, Diazinon, Chlorpyrifos and Fenitrothion) residues were determined in the gills, liver, flesh and stomach of four commercial fish species (*Clarias gariepinus, Hetrotis niloticus, Oreochromis niloticus* and *Tilapia zilli*) from Alau Dam, Konduga Local Government Area, Borno State. Concentrations of all pesticides detected were noted to be higher than the maximum residue limit and the acceptable daily intake values set by the European Union (EU). With this level of organophosphorus pesticide residues, it was suggested that the dams were polluted due to human activities such as farming activities (Joseph *et. al*., 2013).

δ-methrin, a synthetic pyrethroid was studied for toxic effects on the larvae of common carp and their embryos. The numbers of dead embryos were noted to have increased with increasing concentration of δ-methrin while the lowest concentration produced a significant decline in the amount of dead larvae. The results provided evidence that δ-methrin pollution may yield negative effects on the reproduction and development of carp suggesting that consideration should be given during application of this chemical in agricultural areas near aquatic ecosystems.

A study carried out by Akan, *et. al.* (2014) to determine the levels of some organochlorine and organophosphorus pesticide residues in organs of *Tilapia zilli*, *Hetrotis niloticus, Clarias anguillaris* and *Oreochromis niloticus* from Lake Chad, Baga, Borno State, Nigeria. Organs of *Oreochromis niloticus* analysed had the highest organophosphorus pesticide concentrations, while *Heterotis niloticus* showed the least concencentrations. The organs of *Tilapia zilli* had the highest organochlorine pesticide concentrations, while *Heterotis niloticus* had the least. However, concentrations of pesticide in the fish species studied exceeded permissible limits set by FAO and FEPA.

2.9.2 POTENTIAL HEALTH EFFECTS OF PESTICIDES

The existence of pesticides in the environment may not automatically be a problem, but may be a source of exposure. Just like for every toxic substance, the tendency of the exposure to cause harm depends on: the dose, the sensitivity of an individual to the toxin, the exposure and the toxicity of the pesticide (CDPR, 2008).

The toxicological properties for some of these chemicals have been assessed by the US Agency for Toxic Substances and Disease Registry (U.S. ATSDR) and WHO. The regulatory assessment documents are published as separate toxicological profiles for the individual chemicals of concern (U.S. ATSDR, 2000).

The toxicity of a pesticide is its ability to cause damage to health and the amount required to cause damage depends on the toxicity of the pesticide. Some pesticides are more toxic than others and often times, the longer the time of exposure, the greater the chance of harm. Exposure can be either through breathing, ingestion (e.g. by eating or drinking), or by direct contact with the skin or eyes. Factors like age, gender, individual sensitivity or other factors put some people more at risk than others.

Pesticides are widely known for their toxic nature (Ademoroti, 1996) and most pesticides have been classified as possible human carcinogens which induce toxic effects on several body systems such as the liver, kidneys, immune, reproductive, endocrine and nervous systems. Some symptoms of pesticide poisoning include dizziness, chronic convulsion and irritation (Winter, 1992). Short term side effects include nausea, headaches, abdominal cramps, vertigo, dermatopathies, diplopia and ocular disturbances. Adverse effects include long terms ones like nervous defects, infertility, depression, prostate cancer, leukaemia and increased likelihood of respiratory failures (Joseph, *et. al*., 2013).

Health effects connected with organochlorine pesticides include birth defect, reproductive failures, endocrine disruption, cancer, neonatal damage and immune system dysfunction (Saxena *et. al*., 1981; Bouman *et. al*., 1990; Brassow *et. al*., 1981; Olea *et. al*. 1998 and Winter 1992).

Organophosphorus pesticides are known to have side effects on living organisms such as inhibiting cholinesterase activity and making the central nervous system (CNS) functional disturbances (Joseph, *et. al*., 2013).

Research has shown pyrethroids to be tremendously lethal to aquatic life such as fish (Balint *et. al*. 1995; Datta and Kaviraj, 2003; Delistraty, 2000; Eells *et. al*., 1993; Svobodova *et. al*., 2003; Szegletes *et. al*., 1995 and Viran *et. al*., 2003), zooplankton population (Gliwiez and Sieniauwska, 1986; Kaushik *et. al*., 1985 and Tidou *et. al*., 1992) and some valuable aquatic arthropods e.g. shrimp and lobster (Bradbury and Coats, 1989; Srivastav *et. al*., 1997). Studies have shown these pesticides to alter the development of the larvae of oysters (Davis and Hidu, 1969) and the filtration and pumping activity of freshwater mussel (Kontreczky *et. al*., 1997).

Despite their widespread universal application, there are quite a few numbers of reports of poisoning by pyrethroids (He *et. al*., 1989; Peter *et. al*., 1996). Occupationally, the main route of pyrethroid absorption is through the skin which occurs with liquid formulations. Although, this can be avoided through the use of protective clothing; the major undesirable effect of dermal exposure is paraesthesiae. Exposure by inhalation which occurs mostly with dust and powder formulations and not as vapours because pyrethroids are not volatile is a far less significant route (Adamis *et. al*., 1985; Chen *et. al*., 1991; Zhang *et. al.*, 1991) as it may only give rise to nasal and respiratory irritation but its danger amplifies when pyrethroids are used in confined spaces (Llewellyn *et. al*., 1996).

Pyrethroid ingestion has been reported to give rise to abdominal pain, queasiness; nausea, vomiting, sore throat, mouth ulceration, increased secretions and/or dysphagia (He *et. al*., 1989; Yang, *et. al*., 2002).

2.9.3 HEALTH RISK FROM CONSUMING CONTAMINATED FISH

Seafood is not only a global commodity (FAO, 2004) but also a valuable and cheap food item that forms an important part of our healthy diet. It contains high quantities of complete protein (which is the main component of our muscles, organs, and glands), polyunsaturated fats, and other quality nutrients (e.g., minerals). Unfortunately, people do not get to consume fish for its nutritional values alone. Nowadays, many fish and shellfish are found to be contaminated with very toxic agents at some level. They are frequently at the peak of aquatic food chain and therefore concentrate huge quantity of these toxic chemicals which bioaccumulate in their tissues and hence, are finally transmitted to other animals through the food chain (Ukoha, 2014) thereby endangering communal health through consumption of contaminated sea food. Major examples of these toxic contaminants are the highly *persistent* organochlorine compounds (*P*OCs); which include PCBs, dioxins (PCDDs and PCDFs), organochlorine pesticides (e.g., chlordane, DDT, dieldrin, mirex) and organophosphorus pesticides. Fish and shellfish are contaminated mainly due to these chemicals' pollution to the aquatic system which builds up on the particles that are suspended in an aquatic system or settled on the sediment. Numerous bottom-dwelling organisms will feed on these contaminated particles. The contaminated microbes in turn will serve as food for aquatic biota. People consuming fish can also be exposed to contaminants present in these aquatic systems, in that they can become increasingly concentrated in bigger fish up the food chain. These persistent chemicals can accumulate in the fats of contaminated fish and later build up in a fish consumer's body, usually for a fairly long time (Michael, 2007).

As an effort to prevent the severe health consequences from exposure to these contaminants from the consumption of fish, some health regulatory authorities have established health advisories or legal tolerances. Because these residue levels are intended more for health risk prevention purposes, they are each set equal to or lower than their mostly out-dated international legal limits compiled by FAO, which were primarily or initially for trade purposes. These tolerance limits are largely expressed as mg of contaminant per kg of fish tissue on wet weight basis (i.e., parts per million = ppm). Different countries or regions have interpreted or used these tolerance limits differently, whether for legal action or for health advisory purposes.

In the United States, tolerances for pesticide residues in fisheries products are referred to and enforced by the U.S. Food and Drug Administration (USFDA, 2011) as *action* levels, which are typically those recommended by the U.S. Environmental Protection Agency (U.S.E.P.A). These federal action levels are residue limits at or above which U.S. Food and Drug Administration has authority to make lawful steps to eliminate the product from the market. Local authorities frequently adopt these levels in making decisions for choosing whether to issue consumption advisories or to seal water bodies from commercial harvesting of fish.

Several countries have used U.S. FDA action levels as reference standards in setting their own national limits (Micheal, 2007).

CHAPTER THREE

3.0 METHODOLOGY

3.1 SAMPLING AREA

Ibadan is a densely populated city, the capital of Oyo state, Nigeria, the largest city in West Africa and the second largest in Africa, with land size covering an area of 240 km2. The city is located on geographic grid reference longitude 305 E, latitude 7020 N (Filani, 1994).

(a) (b)

Figure 3.1(a) Map of Africa showing Nigeria and (b) Map of Nigeria showing Ibadan, the study area (Olanike, 2008)

3.2 SAMPLING

Five fish species were selected for analysis in this study; two freshwater fish species (Nile Tilapia and African Catfish) and three saltwater fish species (Atlantic horse mackerel, Sardine and Chub Mackerel). The fish species were bought from the market to assess the pesticide residues in them. Their weight, length and width were measured, and then the fish samples were kept in a thermo insulator box and transported to the laboratory at KNUST where they were kept in the freezer pending time for analysis.

3.3 CLEANING OF GLASSWARE

All the glasswares used for extraction and cleaning were rigorously cleaned with soapy water. The glasswares were rinsed three times with tap water and further rinsed twice with distilled water. They were rinsed again with acetone (99%). The glasswares were placed in an oven overnight at 100ºC and kept in clean cabinets.

3.4 REAGENTS

Pesticide grade ethyl acetate, G.C/Analytical grade acetone from Labscan (Dublin, Ireland), Sodium hydrogen carbonate and Sodium sulphate from E. Merck (Germany) and Disposable solid-phase florisil cartridges (500 mg/8 mL) from Sigma-Aldrich Chemicals USA. Pesticide reference standards were gotten from Ehrenstofer GmbHm (Germany) and stored in the freezer.

3.5 APPARATUS

Apparatus used for laboratory analysis includes the following: Gas Chromatograph (GC): Helwet Packard 5890 series ii with Electron Capture Detector, nickel source and Gas Chromatograph (GC): Helwet Packard 5890 series ii with Nitrogen Phosphorus Detector, Column: 30 m capillary column, 0.53 mm ID, fused silica coated with DB-5, Integrator: Hewlett Packard 3396, Weighing balance: Metler Toledo Type BD1201, Ultrasonic bath (US Bransonic 220), Rotary vacuum evaporator: Buchi Rotavapor R-200 (Buchi Labortechnic AG, Postfach, Switzerland), Graduated pipettes, Round bottom flasks (250ml and 100ml), Aluminum foils, Oven, Auto sampler vials (2ml) ,Chromatographic columns.

3.6 EXTRACTION

The muscle tissues of the fish samples were ground using a glass blender to obtain a homogenous composite sample. 20 g of the fish sample was placed into an extraction flask. 5.0 g of sodium hydrogen carbonate was added to neutralize the acid content and 20 g of anhydrous sodium sulphate was added to absorb the moisture content. The mixture was extracted with 100 ml of 3:1 Hexane/Acetone solvent system and sonicated in a US Bransonic 220 ultrasonic bath for 1 hour. The extract was filtered and concentrated to 5 ml using Büchi Rotavapor R-200 vacuum rotary evaporator.

3.7 SOLID-PHASE EXTRACTION (SPE) CLEAN-UP

The clean-up column was packed with 2 g of activated silica gel and 3 g anhydrous sodium sulphate. The packed column was clamped with a retort stand and conditioned using 10 ml of hexane (99%). The extract was passed through the conditioned column with a receiving flask beneath the column. The sample (analyte) put in the column was eluted with 10 ml hexane (99%) and eluted further with 20 ml 2:1 Hexane:Acetone to recover the pesticide residues. The sample was collected into a round bottomed flask and concentrated using a rotary evaporator fitted to a vacuum pump to almost dryness and 2 ml ethyl acetate (99%) was added. The mixture was then transferred to an auto sampler vials ready for Gas Chromatographic analysis.

3.8 CALIBRATION CURVE

The stock solutions containing each individual pesticide standards were used to prepare calibration curves in order to check for the linearity of the system. Ethyl acetate (9975 µl) was added to 25 µl of pesticide standards solution (2 µg/ml). Serial dilutions of concentrations of 0.20 µg/ml, 0.02 µg/ml, 0.01 µg/ml and 0.005 µg/ml were prepared. 1.0 µl of each concentration was injected into the injection port of the G.C and the responses were recorded. A calibration curve was constructed by plotting the concentration against their respective peak areas.

3.9 GC ANALYSIS

Analysis was performed using a Gas Chromatograph model CP-3800 (Varian) equipped with 63Ni Electron Capture Detector (ECD) and Nitrogen Phosphorus Detector (NPD) of activity 15 mCi with an auto sampler were used for the analysis of organochlorine, organophosphorus and pyrethroid pesticides. Injected volume of the extract was 1.0 µL. The operating conditions of the fused silica gel capillary column were: VF-5 ms, 30 m x 0.25 mm x 0.25
µm, temperature programme: 700C (2 min) to 1800C (1 min) 250C/min to 3000C 50C/min, Injection temperature: 2700C, Detector temperature: 3000C, Carrier gas: Nitrogen at 1.0 mL/min. 0.1 ppm mixed standard solutions of organochlorine and pyrethroid pesticides were analyzed and 1.0 ppm mixed standard solution of organophosphorus pesticide was analyzed in a similar manner for identification. Peak identifications were conducted by comparing the retention time of authentic standards and those obtained from the extracts. Calculation of concentration was done by using a four point calibration curve.

3.10 QUANTIFICATION OF PESTICIDES RESULTS

To determine the quantities of residues in the sample extracts, an external standard method was used. A standard mixture containing known amounts of pesticides was run and the response of the detector for each compound was determined. The area of the corresponding peak in the sample was compared with that of the known standard.

3.11 QUALITY ASSURANCE AND QUALITY CONTROL

Inclusion of quality control and quality assurance was done to the analytical method. Samples were handled cautiously to avoid contamination. G.C grade reagents were used for the G.C analysis, Analytical grade reagents were used in sample preparations, treatments and deionised water was used all through the study.

3.12 RECOVERY TEST

Loss of target compounds could occur during sample preparation, extraction and analysis. The extent of analyte loss especially during extraction was assessed by performing a recovery test. This was done by spiking the samples with 0.5ppm of an internal standard (isodrin) before extraction to evaluate the recovery of the compounds. The recovery was determined using the formula:

$$\% \text{ Recovery} = \frac{\text{Pesticide (ppm) recovered from fortified sample} \times 100}{\text{Amount of pesticide (ppm) added}}$$

3.13 LIMIT OF DETECTION (LOD)

The extracts of the fortified samples were serially diluted by a factor of two to give different concentrations. 1.0μL of each concentration was injected and the least concentration that gave response was noted. The limit of detection was calculated by the formula:

$$\text{LOD} = \frac{V1\ (\mu l) \times \text{Concentration fortified}}{V2\ (\mu l)}$$

Where V1=volume injected and V2=final volume of fortified extract

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 CHARACTERISTICS OF FISH SPECIES USED FOR ANALYSIS.

The types of species, body weight, length and feeding habits of the fish analyzed in this study are presented in Table 4.1.

Table 4.1: Characteristics of fish species used for analysis

Fish species	Total Weight(g)	Standard Length(cm)	Total length(cm)	Feeding Habit
Nile Tilapia (*Oreochromis niloticus*)	200 190 190 200 110	20.2 20.2 19.2 20.4 16.0	24.4 25.0 23.3 24.7 20.0	Phytoplanktons, detritus, algae
African Catfish (*Clarias gariepinus*)	600 700 800 600 700	40.5 44.5 40.7 42.5 43.5	45.2 48.3 46.4 45.4 47.2	Zoobenthos, insects, crustaceans, mollusk, worms, rotifers, detritus
Atlantic horse mackerel (*Trachurus trachurus*)	500 500 400 600 400	36.3 36..8 34.5 37.8 34.0	41.0 42.0 39.7 43.2 40.0	Polychaeta, crustacean, mollusc, chaetognatha, osteichthytes. Toleosts,capepods and mysids.*
Sardine (*Sardinella maderensis*)	300 210 200 200 210	26.0 26.5 26.3 26.0 26.2	29.3 31.5 31.4 31.0 30.5	Phytoplanktons, zooplankton.
Chub mackerel (*Scomber japonicus*)	300 300 300 200 200	28.4 29.0 29.3 28.0 28.8	32.4 33.3 33.4 32.3 32.9	copepods and rotifers (as larvae), zooplankton (as juveniles) and mysids and euphausids (as adults).

Harriet, *et. al*, 2011; *Bahar, *et. al*., 2009.

Thirteen organochlorine residues, nine organophosphorus and nine pyrethroid residues were detected in all the fish species analyzed. δ-HCH, Heptachlor and α-endosulfan were the predominant organochlorine pesticides detected and were present in all fish samples analyzed. Predominant OPs were metamidopho, fonofos, pirimiphos-methyl and chlorpyrifos and the predominant pyrethroids were cyfluthrin, cypermethrin, permethrin and δ-methrin. The residue levels of each pesticide were present in varying amount in each species of fish analyzed.

Organochlorine and pyrethroid residues occurred in all the five fish species analyzed while organophosphorus residues were detected in only three out of all five species. Mean concentrations of organochlorine, organophosphorus and pyrethroid pesticides detected in the fish samples are presented in table 4.2a, 4.3 and 4.4.

4.2 OCCURRENCE OF ORGANOCHLORINE PESTICIDES IN FISH SAMPLES

Mean concentrations of some Organochlorine pesticide residues detected in the fish samples analyzed (*Clarias gariepinus, Oreochromis niloticus, Trachurus trachurus, Sardinella madenrensis and Scomber japonicus*) are presented in Table 4.2a.

Table 4.2a illustrates show individual organochlorine pesticides and their respective mean concentrations when the fish samples were analyzed. Organochlorine residues were detected in all the fish species. The predominant pesticides were δ-HCH, Heptachlor and αendosulfan, they were present in all the fish species. In all, thirteen organochlorines (β-HCH, δ-HCH, Heptachlor, γ-Chlordane, α-endosulfan, β-endosulfan, p,p'-DDE, Dieldrin, Endrin, p,p'-DDD, p,p'-DDT, Methoxychlor and Aldrin) were detected in the samples. The detection of the organochlorines in the fish samples indicates the wide use of these chemicals in the study area.

Organochlorine pesticides contaminated all fish samples analysed in this study with a concentration ranging from the detection limit to 3.2062±0.0348 μg/g which is higher than results reported by Harriet, *et. al*. (2011) but lower than those reported by Ize-Iyamu *et. al*. (2007). Relatively high concentrations of heptachlor were detected in all fish samples. αendosulfan was also detected at high concentrations in all the fish species as compared to the other organochlorine pesticides detected.

The Mean concentration of heptachlor detected in Nile Tilapia, African Catfish, Atlantic horse mackerel, Sardine and Chub Mackerel were 3.2062±0.0348 μg/g, 3.1476±0.0529 μg/g, 2.6926±0.0354 µg/g, 1.5324±0.1389 µg/g and 3.1086±0.0503 µg/g respectively. These concentrations were much higher than the EU set maximum residue limit (MRLs) of 0.2 µg/g.

β-HCH was detected only in Nile Tilapia with a mean concentration of 0.2884±0.0535 µg/g. β-HCH (Lindane) whose occurrence might be connected to its extensive use by farmers for agricultural purposes marketed as 'Gammalin 20'. δ-HCH was detected in all five fish species with a mean concentration of 0.4228±0.2155 µg/g in Nile Tilapia, 0.4220±0.0153 µg/g in Catfish, 0.1908±0.0096 µg/g in Atlantic horse mackerel, 0.4414±0.0433 µg/g in Sardine and 0.1474±0.0082 µg/g in Chub Mackerel. γ-chordane, occurred in one fish species with a mean concentration of 0.1578±0.0158 µg/g in Nile Tilapia. The concentrations of these pesticides were much higher than the WHO and FAO (2009) set maximum residue limit (MRLs) of 0.01 µg/kg for β-HCH and δ-HCH.

Like DDT, chlordane compounds which are resistant to metabolism, have a strong affinity for lipid, and biomagnify in aquatic food webs. α-endosulfan was detected in all five fish species. The mean concentrations detected were 1.4090±0.0139 µg/g in Nile Tilapia, 2.3240±0.0716 µg/g in African Catfish, 1.3870±0.1134 µg/g in Atlantic horse mackerel, 3.0832±0.2696 µg/g in Sardine and 1.4032±0.2155 µg/g in Chub Mackerel. β-endosulfan occurred in Atlantic horse mackerel with a mean concentration of 1.0686±0.0611 µg/g and in Sardine with a mean concentration of 1.3092±0.0348 µg/g. Concentrations which are much higher than the WHO and FAO (2009) set maximum residue limit (MRL) 0.1 µg/kg and the Acceptable Daily Intake value (ADI) of 0.006 µg/kg for endosulfan.

p,p'-DDD, p,p'-DDE and p,p'-DDT were detected in Nile Tilapia with mean concentrations of 0.1048±0.0079 µg/g, 0.1864±0.0164 µg/g and 0.5962±0.0252 µg/g respectively. However, in Catfish, only p,p'-DDE was detected with a mean concentration of 0.2696±0.0082 µg/g and none of the residues were detected in the other three fish species. Concentrations of these DDT metabolites detected were much lower than the WHO and FAO (2009) set maximum residue limit (MRL) of 1.0 µg/kg, showing that there is still the danger of bioaccumulation up the food chain. Sericano *et. al*. (1990) gave the estimated environmental half-life of DDT to be between 10-20 years. In the process, DDT is transformed to DDE and DDD. In this study, p,p'-DDD and p,p'-DDE could have occurred in the fish samples as a product of the breakdown and metabolism of DDT as they are also produced in most animals when the body tries to rid itself of the pesticide. Commercial DDT (mixtures of p,p'-DDT, o,p'-DDT, p,p'DDE and p,p'-DDD) are imported into Nigeria and marketed as zerdane, anofex, chlorophenoethane for control of mosquitoes and other insect-borne diseases (David *et. al*., 2008).

Dieldrin and Endrin were detected only in Nile Tilapia with mean concentrations of 0.2496±0.0130 µg/g and 0.1198±0.0037 µg/g respectively while Aldrin occurred in only Sardine with a mean concentration of 0.2996±0.00889 µg/g. With the similiarities between aldrin and dieldrin and considering the fact that sunlight and bacteria can change aldrin to dieldrin, dieldrin detected in Nile Tilapia could be as a result of the breakdown of aldrin. Although in 1987, EPA banned all uses because of concerns about potential harm to human health, results show that they are either still being used or are persistent in the environment. The concentrations of aldrin and dieldrin detected were much higher than the WHO and FAO (2009) set maximum residue limit (MRL) of 0.2 µg/kg and the Acceptable Daily Intake values (ADIs) of 0.0001 µg/kg. While endrin exceeded the EU maximum residue limit of 0.05 µg/g suggesting possibility of potential health effect to consumers.

Methoxychlor was detected in catfish with a mean concentration of 1.3452±0.0495 µg/g and in Chub Mackerel with a mean concentration of 0.9598±0.0716 µg/g. Methoxychlor like DDT, binds strongly to fatty tissues. With the high fat content of Catfish and Chub Mackerel, they may take several months to break down.

Table 4.2a: Mean Concentrations of Organochlorine Pesticide Residues Detected in Fish Samples.

FISH SPECIES	ORGANOCHLORINE PESTICIDES													
		B-HCH	δ-HCH	Heptachlor	γ-Chlordane	α-Endosulfan	p,p'-DDE	Dieldrin	Endrin	P,P'-DDD	P,P'-DDT	Methoxychlor	β-Endosulfan	Aldrin
Nile Tilapia *(Oreochromis niloticus)*	Mean	0.2884	0.4228	3.2062	0.1578	1.4090	0.1048	0.2496	0.1198	0.1864	0.5962	BD	BD	BD
	SD	0.0535	0.2155	0.0348	0.0158	0.0139	0.0079	0.0130	0.0037	0.0164	0.0253	BD	BD	BD
	Range	0.2506-0.3262	0.2704-0.5752	3.1816-3.2308	0.1466-0.1690	1.3992-1.4188	0.0992-0.1104	0.2404-0.2588	0.1172-0.1224	0.1748-0.1980	0.5784-0.6140	BD	BD	BD
African Catfish (*Clarias gariepinus)*	Mean	BD	0.422	3.1476	BD	2.324	0.2696	BD	BD	BD	BD	1.3452	BD	BD
	SD	BD	0.0153	0.0529	BD	0.0716	0.0082	BD	BD	BD	BD	0.0495	BD	BD
	Range	BD	0.4112-0.4328	3.1102-3.1850	BD	2.2734-2.3746	0.2638-0.2754	BD	BD	BD	BD	1.3102- 1.3802	BD	BD
Atlantic Horse Mackerel (*Trachurus trachurus)*	Mean	BD	0.1908	2.6926	BD	1.3870	BD	BD	BD	BD	BD	BD	1.0686	BD
	SD	BD	0.0096	0.0354	BD	0.1134	BD	BD	BD	BD	BD	BD	0.0611	BD
	Range	BD	0.1840-0.1976	2.6676-2.7176	BD	1.3068-1.4672	BD	BD	BD	BD	BD	BD	1.0254-1.1118	BD
Sardine (*Sardinella madenrensis)*	Mean	BD	0.4414	1.5324	BD	3.0832	BD	BD	BD	BD	BD	BD	1.3092	0.2997
	SD	BD	0.0433	0.1389	BD	0.0088	BD	BD	BD	BD	BD	BD	0.2696	0.0348
	Range	BD	0.4108-0.4720	1.4342-1.6306	BD	0.2934-0.3059	BD	BD	BD	BD	BD	BD	2.1218-2.5030	1.2846-1.3338
ChubMackerel (*Scomber japonicus)*	Mean	BD	0.1474	3.1086	BD	1.4032	BD	BD	BD	BD	BD	0.9598	BD	BD
	SD	BD	0.0082	0.0503	BD	0.2155	BD	BD	BD	BD	BD	0.0716	BD	BD
	Range	BD	0.1416-0.1532	3.0730-3.1442	BD	1.2508-1.5556	BD	BD	BD	BD	BD	0.9092-1.0104	BD	BD
SD: Standard Deviation; Limit of detection: 0.01ug/g; BD: Below Detection														

Table 4.2b: Maximum Residue Limits (MRLs) stipulated by various statutory agencies

Compound	EU (µg/g)	Italian (µg/g)	FDA, 2001(µg/g)	FAO, 1983 (µg/g)
Chlordane	0.05	0.05	-	-
DDT	1	1	5	0.3
Dieldrin	0.2	0.2	0.3	0.3
Heptaclor	0.2	0.2	0.3	0.3
HCB	0.2	0.2	-	-
alpha-HCH	0.2	0.2	**-**	**-**
beta-HCH	0.1	0.1	0.3	0.3
gamma-HCH	1	1	0.3	0.3
Endrin	0.05	0.05	0.3	0.3

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4.3 OCCURRENCE OF ORGANOPHOSPHORUS PESTICIDES IN FISH SAMPLES

The mean concentration of some organophosphorus pesticides (Methamidopho, Phorate, Fonofos, Primiphos-methyl, Chlorpyrifos, Malathion, Fenithrothion, Parathion-ethyl and Profenofos) detected in the fish species analyzed (*Clarias gariepinus, Oreochromis niloticus, Trachurus trachurus, Sardinella madenrensis and Scomber japonicus)* are presented in Table 4.3.

Organophosphorus pesticide residues detected in all the fish samples ranged from 0.0024±0.0002 µg/g to 0.0076±0.0031 µg/g. The highest concentration recorded was of profenofos detected in Chub Mackerel. While chlorpyrifos which was detected in Chub Mackerel and fonofos which was detected in Atlantic Horse Mackerel recorded the lowest values of 0.0024±0.0004 µg/g and 0.0024±0.0002 µg/g respectively. Metamidopho was detected in two out of the five fish species analyzed. It was detected in Nile Tilapia with a mean concentration of 0.0052±0.0011 µg/g and in Atlantic horse mackerel with a mean concentration of 0.0050±0.0025 µg/g. Phorate was detected in only one fish species with a mean concentration of 0.0048±0.0004 µg/g in Nile Tilapia. Fonofos occurred in two of the fish species at a mean concentration of 0.0036±0.001 µg/g and 0.0024±0.0002 µg/g in Nile Tilapia and Atlantic Horse Mackerel respectively. Pirimiphos-methyl was detected in Nile Tilapia with a mean concentration of 0.0044±0.0007 µg/g and in Chub Mackerel with a mean concentration of 0.0036±0.0013 µg/g. Chlorpyrifos was detected in Nile Tilapia with a mean concentration of 0.0026±0.0006 µg/g and Chub Mackerel with 0.0024±0.0004 µg/g which were both higher than the WHO and FAO (2009) set maximum residue limits (MRLs) of 0.30 µg/kg for Chlorpyrifos. Malathion, Fenithrothion, Parathion-ethyl and Profenos were all detected in only one fish species Chub Mackerel with mean concentrations of 0.0072±0.0021 µg/g, 0.0072±0.0023 µg/g, 0.0044±0.0016 µg/g and 0.0076±0.0031 µg/g respectively. With Fenitrothion detected above the WHO and FAO (2009) set maximum residue limits (MRLs) of 0.01 µg/kg.

Metamidopho, Chlorpyrifos and Fonofos were the most frequently detected residues in all the samples, each occurring in two different species each while all other residues were detected in one fish species each.

Six, five and two pesticide residues were found in Chub Mackerel, Nile Tilapia and Atlantic Horse Mackerel respectively. Methamidopho and Fonofos were found in two fish species (Nile Tilapia and Atlantic Horse Mackerel*)* with the exception of the three other fish species. Pirimiphos-methyl was detected in Chub Mackerel and Nile Tilapia.

Although Catfish contains a high level of fat, no organophosphorus residues were detected as compared to Nile Tilapia and Chub Mackerel. This could be due to degradation of the pesticides or variation in feeding patterns as well as variation in metabolic characteristics of these fish species. African Catfish feeds on Zoobenthos, insects, worms, rotifers and detritus.

Tilapia is primarily herbivorous; it feeds on phytoplankton or benthic algae and detritus while the Chub Mackerel consumes copepods and rotifers (as larvae), zooplankton (as juveniles) and mysids and euphausids (as adults).

Table 4.3: Mean Concentrations of Organophosphorus Pesticide Residues Detected in Fish Samples

FISH SPECIES		ORGANOPHOSPHORUS PESTICIDES								
		Methamidipho	Phorate	Fonofos	Pirimiphos-m	Chlorpyrifos	Malathion	Fenitrothion	Parathion-et	Profenofos
Nile Tilapia *(Oreochromis niloticus)*	Mean	0.0052	0.0048	0.0036	0.0044	0.0026	BD	BD	BD	BD
	SD	0.0011	0.0004	0.0010	0.0007	0.0006	BD	BD	BD	BD
	Range	0.0040-0.0062	0.0044-0.0052	0.0026-0.0046	0.0036-0.0050	0.0020-0.0032	BD	BD	BD	BD
African Catfish (*Clarias gariepinus)*	Mean	BD	BD	BD	BD	BD	BD	BD	BD	BD
	SD	BD	BD	BD	BD	BD	BD	BD	BD	BD
	Range	BD	BD	BD	BD	BD	BD	BD	BD	BD
Atlantic-Horse Mackerel (*Trachurus trachurus)*	Mean	0.0050	BD	0.0024	BD	BD	BD	BD	BD	BD
	SD	0.0025	BD	0.0002	BD	BD	BD	BD	BD	BD
	Range	0.0032-0.0078	BD	0.0022-0.0026	BD	BD	BD	BD	BD	BD
Sardine (*Sardinella madenrensis)*	Mean	BD	BD	BD	BD	BD	BD	BD	BD	BD
	SD	BD	BD	BD	BD	BD	BD	BD	BD	BD
	Range	BD	BD	BD	BD	BD	BD	BD	BD	BD
Chub Mackerel (*Scomber japonicus)*	Mean	BD	BD	BD	0.0036	0.0024	0.0072	0.0072	0.0044	0.0076
	SD	BD	BD	BD	0.0013	0.0004	0.0021	0.0023	0.0016	0.0031
	Range	BD	BD	BD	0.0026-0.0050	0.0020-0.0028	0.0060-0.0096	0.0054-0.0098	0.0030-0.0062	0.0042-0.0102

SD: standard deviation; Limit of detection: 0.001ug/g; BD: Below Detection

4.4 OCCURRENCE OF PYRETHROIDS PESTICIDES IN FISH SAMPLES

The mean concentration of some Pyrethroids (Allenthrin, Bifenthrin, Fenpropathrin, Lambdacyhalothrin, Cyfluthrin, Cypermethrin, Fenvalerate, Delta-methrin and Permethrin) detected in the fish samples analyzed (*Clarias gariepinus, Oreochromis niloticus, Trachurus trachurus, Sardinella madenrensis and Scomber japonicus)* are presented in Table 4.4.

Pyrethroid residues were detected in all the fish species. The most commonly occurring pyrethroids were Cyfluthrin, Cypermethrin, Permethrin and δ-methrin, and occurred in at least three out of the five fish species. In all, nine pyrethroids were detected in the samples which includes Allenthrin, Bifenthrin, Fenpropathrin, Lambda-cyhalothrin, Cyfluthrin, Cypermethrin, Fenvalerate, Delta-methrin and Permethrin

Allethrin was detected in Nile Tilapia with a mean concentration of 0.6920±0.0156 µg/g. Bifenthrin was detected in two fish species with mean concentrations of 1.2596±0.0024 µg/g and 1.5174±0.1196 µg/g in Nile Tilapia and African Catfish respectively. Fenpropathrin was detected in one fish species with a mean concentration of 3.2708±0.06557 µg/g in Nile Tilapia. λ-cyhalothrin was detected in two out of the five fish species; mean concentrations detected were 0.2844±0.00398 µg/g in Nile Tilapia and 0.2558±0.0333 µg/g in Sardine. Cyfluthrin was detected in all five species with mean concentrations of 2.3798±0.1667 µg/g in Nile Tilapia, 1.9738±0.0253 µg/g in African Catfish, 5.2678±0.1322 µg/g in Atlantic Horse Mackerel, 1.3924±0.0632 µg/g in Sardine and 4.5514±0.0758 µg/g in Chub Mackerel.

Cypermethrin was detected in four fish species with mean concentrations of 2.4678±0.0220 µg/g in Nile Tilapia, 6.7454±0.0587 µg/g in Atlantic Horse Mackerel, 7.6504±0.0259 µg/g in Sardine and 6.1078±0.0253 µg/g in Chub Mackerel. Fenvalerate occurred in Nile Tilapia with a mean concentration of 0.7458±0.0058 µg/g and in African Catfish with 1.1890±0.0016 µg/g. Delta-methrin occurred in Nile Tilapia, African Catfish and Atlantic Horse Mackerel with mean concentrations of 1.2542±0.0668 µg/g, 1.8018±0.0211 µg/g and 0.2154±0.0066 µg/g respectively. Permethrin was detected in three fish species with mean concentrations of 1.8212±0.0216 µg/g, 0.3994±0.0367 µg/g and 1.2432±0.0259 µg/g in Atlantic Horse Mackerel, Sardine and Chub Mackerel respectively.

Table 4.4: Mean Concentrations of Pyrethroid Pesticide Residues Detected in Fish Samples

FISH SPECIES	PYRETHROID PESTICIDES									
		Allenthrin	Bifenthrin	Fenpropathrin	λ-Cyhalothrin	Cyfluthrin	Cypermethrin	Fenvalerate	δ-Methrin	Permethrin
Nile Tilapia *(Oreochromis niloticus)*	Mean	0.6290	1.2596	3.2708	0.2844	2.3798	2.4678	0.7458	1.2542	BD
	SD	0.0156	0.0024	0.0656	0.0040	0.1667	0.0220	0.0058	0.0668	BD
	Range	0.6192-0.6470	1.2574-1.2622	3.1972-3.323	0.2798-0.2868	2.1874-2.4802	2.4442-2.4878	0.7418-0.7524	1.1874-1.321	BD
African Catfish (*Clarias gariepinus)*	Mean	BD	1.5174	BD	BD	1.9738	BD	1.1890	1.8018	BD
	SD	BD	0.1196	BD	BD	0.0253	BD	0.0016	0.0211	BD
	Range	BD	1.3974-1.6366	BD	BD	1.9498-2.0002	BD	1.1874-1.1906	1.7794-1.8212	BD
Atlantic-Horse Mackerel (*Trachurus trachurus)*	Mean	BD	BD	BD	BD	5.2678	6.7454	BD	0.2154	1.8212
	SD	BD	BD	BD	BD	0.1321	0.0587	BD	0.0066	0.0216
	Range	BD	BD	BD	BD	5.1166-5.3612	6.6804-6.7944	BD	0.2078-0.2192	1.8006-1.8436
Sardine (*Sardinella madenrensis)*	Mean	BD	BD	BD	0.2558	1.3924	7.6504	BD	BD	0.3994
	SD	BD	BD	BD	0.0333	0.0633	0.0259	BD	BD	0.0367
	Range	BD	BD	BD	0.2318-0.2418	1.3196-1.4324	7.6340-7.6802	BD	BD	0.3682-0.4398
Chub Mackerel (*Scomber japonicus)*	Mean	BD	BD	BD	BD	4.5514	6.1078	BD	BD	1.2432
	SD	BD	BD	BD	BD	0.0758	0.0253	BD	BD	0.0259
	Range	BD	BD	BD	BD	4.5036-4.6388	6.0900-6.1368	BD	BD	1.2136-1.2614
SD: standard deviation; Limit of detection: 0.01ug/g; BD: Below Detection										

4.5 HEALTH RISK ASSESSMENT OF PESTICIDES ASSOCIATED WITH THE CONSUMPTION OF FISH IN IBADAN.

The health risk posed by the consumption of fish from Ibadan by the pesticides under studied (Organochlorine, Organophosphorus and Pyrethroids) was assessed. Nile Tilapia (*Oreochromis niloticus*), African Catfish (*Clarias gariepinus*), Atlantic Horse Mackerel (*Trachurus trachurus*), Sardine (*Sardinella madenrensis*) and Chub Mackerel (*Scomber japonicus*) are major commercial aquatic products in Ibadan. Hence, assessing the potential human health risk from the consumption of these fishes is an extremely important step towards public health safety. Health risk assessment is a very important tool to evaluate the consequences of human action and it measures the adverse effect to public health (Ukoha, 2014).

The health effect of organochlorine, organophosphorus and pyrethroid pesticides cannot be underestimated, this has led food safety experts to regulate and monitor the consumption of these toxic chemicals by developing the concept of the maximum residue limits. The Maximum Residue Limits (MRL) can be defined as the maximum concentration of a pesticide residue (µg/g) which if found in food substances is considered to have no significant and toxicological health effect or hazard. It also represents the maximum concentration authorized and recommended in food products and animal feeds by the Codex Alimentarius Commision (Gerken *et al*., 2001; Darko and Akoto, 2008). MRL (maximum residue limit) and ADI (acceptable daily intake) can be defined as the estimated quantity of a substance in food that can be consumed over a lifetime without evident health risk to the consumer.

It can also be used to predict the dietary intake of pesticide residues. The estimated dietary intake of a pesticide residue in a given food is obtained by multiplying the residue level in the food by the amount of that food consumed. The Estimated Average Daily Intake (EADI) of pesticide residues should be less than its established ADI (WHO, 1997).

4.6 POTENTIAL HUMAN HEALTH RISK ASSESSMENT

To assess the risk of pesticide contained in each fish species on the consumers, USEPA guidelines for potential risk assessment were used. Estimated Average Daily Intake (EADI) was found by multiplying the average residual pesticide concentration (mg/kg) in each fish specie by the fish consumption rate in Nigeria (kg/day) and divided through by the average body weight (kg) (WHO, 1997). The estimated hazard indices for children and adults were obtained by estimating the ratios between the EADI (mg/kg/day) by their corresponding values of WHO/FAO acceptable daily intakes, ADI. In this study, the fish consumption rate for an adult was calculated from the annual per capita consumption of fish to be 0.0366 kg/day and for the child to be one third of the adult consumption which is 0.0122 kg/day. The average body weights of adult and child used are 70 kg and 16 kg respectively (Ukoha *et. al.*, 2014).

4.7 ESTIMATED DAILY INTAKE (mg/kg/day) OF PESTICIDES ASSESSED FOR FISH CONSUMPTION BY THE POPULATION OF IBADAN

The estimated daily intakes (EDI) of the pesticides detected in this study by humans are shown in Table 4.5 (adult) and 4.6 (child). The estimated daily intakes of all organophosphorus and pyrethroid pesticides in the five fish samples were within the acceptable daily intakes (i.e. EDI<ADI). While organochlorine levels in most of the fish species analysed were within the permissible limits except for heptachlor whose EDI for all fish samples were higher than the acceptable daily intakes. Dieldrin occurring in Nile Tilapia, aldrin in Sardine and α-endosulfan occurring in African Catfish also had their EDIs above the permissible limits. Thereby, suggesting a high probability of adverse health effect on consumers.

Table 4.5: Estimated daily intake (mg/kg/day) of pesticides assessed for fish consumption by the population of Ibadan for an adult (70 kg).

Type of pesticide	Estimated Daily Intake of Fish				
	Oreochromis niloticus	*Clarias gariepinus*	*Trachurus trachurus*	*Sardinella madenrensis*	*Scomber japonicus*
ORGANOPHOSPHORUS	($x10^{-6}$)	($x10^{-6}$)	($x10^{-6}$)	($x10^{-6}$)	($x10^{-6}$)
Methamidopho	2.7188	-	2.6143	-	-
Phorate	2.5097	-	-	-	-
Fonofos	1.8823	-	1.2549	-	-
Primiphos-M	2.3006	-	-	-	1.8823
Chlorpyrifos	1.3594	-	-	-	1.2549
Malathion	-	-	-	-	3.7646
Fenithrothion	-	-	-	-	3.7646
Parathion-Et	-	-	-	-	2.3006
Profenofos	-	-	-	-	3.9737
Type of pesticide	Estimated Daily Intake of Fish				
	Oreochromis niloticus	*Clarias gariepinus*	*Trachurus trachurus*	*Sardinella madenrensis*	*Scomber japonicus*
PYRETHROIDS	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)
allenthrin bifenthrin	3.2888	-	-	-	-
fenpropathrin λ-	6.5859	7.9338	-	-	-
cyhalothrin	17.1016 1.4870	-	-	-	-
cyfluthrin	12.4429	-	-	1.3375	-
cypermethrin	12.9030	10.3201	27.5415	7.2803	23.7973
fenvalerate δ-	3.8995	-	35.2688	40.0006	31.9351
methrin permethrin	6.5577	6.2168	-	-	-
	-	9.4208	1.1262	-	-
		-	9.5223	2.0883	6.5002
ORGANOCHLORINES	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)
β-HCH	1.5079	-	-	-	-
δ-HCH	2.2106	2.2064	0.9976	2.3079	0.7707
heptachlor γ-	16.7638	16.4575	14.0784	8.0123	16.2504
chlordane α-	0.8251 7.3671	-	-	-	-
endosulfan β -	-	12.1512	7.2520	12.1219	7.3367
endosulfan	1.3051 0.6264	-	5.5873	6.8452	-
dieldrin	0.5480 0.9746	-	-	-	-
endrin p,p’-	3.1173	-	-	-	-
DDE p,p’-DDD	-	1.4096	-	-	-
p,p’-DDT	-	-	-	-	-
methoxychlor aldrin		-	-	-	-
		7.0335	-	-	5.0184
		-	-	1.5665	-

Table 4.6: Estimated daily intake (mg/kg/day) of pesticides assessed for fish consumption by the population of Ibadan for a child (16 kg).

	Estimated Daily Intake Of Fish

TYPE OF PESTICIDE	*Oreochromis Niloticus*	*Clarias Gariepinus*	*Trachurus Trachurus*	*Sardinella Madenrensis*	*Scomber Japonicus*
Organophosphorus	(10^{-6})	(10^{-6})	(10^{-6})	(10^{-6})	(10^{-6})
Methamidopho	3.965 3.66	-	3.8125	-	-
Phorate	2.745	-	1.83	-	-
Fonofos	3.355	-	-	-	-
Primiphos-M	1.9825	-	-	-	2.745
Chlorpyrifos	-	-	-	-	1.83 5.49
Malathion	-	-	-	-	5.49
Fenithrothion	-	-	-	-	3.355
Parathion-Et	-	-	-	-	5.795
Profenofos		-	-	-	
Pyrethroids	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)
Allenthrin	4.7961	-	-	-	-
Bifenthrin	9.6044	11.570	-	-	-
Fenpropathrin	24.940	-	-	-	-
Λ-Cyhalothrin	2.1686	-	-	1.9505	-
Cyfluthrin	18.146	15.050	40.1646	10.6171	34.7044
Cypermethrin	18.817	-	51.4336	58.3343	46.5719
Fenvalerate	5.6867	9.0661	-	-	-
Δ-Methrin	9.5633	13.739	1.6424	-	-
Permethrin	-	-	13.8866	3.0454	9.4794
Organochlorines	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)	($x10^{-4}$)
B-HCH δ-	2.1991	-	-	-	-
HCH	3.2239	3.2178	1.4549	3.3657	1.1239
Heptachlor γ-	24.4473	24.0005	20.5311	11.6846	23.6985
chlordane α-	1.2032	-	-	-	-
endosulfan β-	10.7436	17.7207	10.5759	17.6778	10.6994
endosulfan	-	-	8.1481	9.9827	-
Dieldrin Endrin	1.9032	-	-	-	-
p,p'-DDE p,p'-	0.9135	-	-	-	-
DDD p,p'-	0.7991	2.0557	-	-	-
DDT	1.4213	-	-	-	-
Methoxychlor	4.5460	-	-	-	-
Aldrin	-	10.2572	-	-	7.3185
	-	-	-	2.2845	-

Table 4.7: Health risk assessment based on average daily intake of Pyrethroid pesticide residues detected in fish samples.

Pyrethroids	Pesticide	Residual concn. (ug/g)	ADI (mg/kg/day)	16 kg			70 kg		
				EADI ($x10^{-4}$)	HI-Child	Health risk	EADI ($x10^{-4}$)	HI-Adult	Health risk

Nile Tilapia	Allethrin Bifenthrin Fenpropathrin λ-cyhalothrin Cyfluthrin Cypermethrin Fenvalerate δ- methrin	0.6290 1.2596 3.2708 0.2844 2.3798 2.4678 0.7458 1.2542	NO ADI 0.01 0.03 0.02 0.04 0.02 0.02 0.01	4.7961 9.6044 24.940 2.1686 18.146 18.817 5.6867 9.5633	- 0.096 0.083 0.012 0.05 0.094 0.03 0.096	- NO NO NO NO NO NO NO	3.2888 6.5859 17.1016 1.4870 12.4430 12.9030 3.8995 6.5577	- 0.0659 0.0570 0.0074 0.0311 0.0645 0.0195 0.0656	- NO NO NO NO NO NO NO
African Catfish	Bifenthrin Cyfluthrin Fenvalerate δ- methrin	1.5174 1.9738 1.1890 1.8018	0.01 0.04 0.02 0.01	11.570 15.050 9.0661 13.739	0.115 0.038 0.045 0.14	NO NO NO NO	7.9338 10.3200 6.2168 9.4208	0.0793 0.0026 0.0311 0.0094	NO NO NO NO
Atlantic Horse Mackerel	Permethrin Cyfluthrin Cypermethrin δ-methrin	1.8212 5.2675 6.7454 0.2154	0.05 0.04 0.02 0.01	13.8866 40.1646 51.4336 1.6424	0.28 0.1 0.26 0.016	NO NO NO NO	9.5223 27.5420 35.2690 1.1262	0.02 0.07 0.2 0.0112	NO NO NO NO
Sardine	λ-cyhalothrin Permethrin Cyfluthrin Cypermethrin	0.2558 0.3994 1.3924 7.6504	0.02 0.05 0.04 0.02	1.9505 3.0454 10.6171 58.3343	0.010 0.0061 0.027 0.292	NO NO NO NO	1.3375 2.0883 7.2803 40.0010	0.0067 0.0042 0.02 0.2000	NO NO NO NO
Chub Mackerel	Permethrin Cyfluthrin Cypermethrin	1.2432 4.5514 6.1078	0.05 0.04 0.02	9.4794 34.7044 46.5719	0.019 0.087 0.233	NO NO NO	6.5002 23.7970 31.9350	0.013 0.06 0.16	NO NO NO

Table 4.8: Health risk assessment based on average daily intake of Organochlorine pesticide residues detected in fish samples.

OCs	Pesticide	Residual concn. (ug/g)	ADI (mg/kg/day)	16 kg			70 kg		
				EADI ($x10^{-4}$)	HI-Child	Health risk	EADI ($x10^{-4}$)	HI-Adult	Health risk
Nile Tilapia	B-HCH δ- HCH heptachlor γ- chlordane α- endosulfan p,p'-DDE dieldrin endrin p,p'- DDD p.p'- DDT	0.2884 0.4228 3.2062 0.1578 1.4090 0.1048 0.2496 0.1198 0.1864 0.5962	0.005 NO ADI 0.0001 0.0005 0.006 0.01 0.0001 0.0002 0.01 0.01	2.1991 3.2239 24.4473 1.2032 10.7436 0.7991 1.9032 0.9135 1.4213 4.5460	0.0440 - 24.450 0.2410 0.1790 0.0080 1.9032 0.4560 0.0140 0.0450	NO - YES NO NO NO YES NO NO NO	1.5079 2.2106 16.7638 0.8251 7.3671 0.5480 1.3051 0.6264 0.9746 3.1173	0.03 - 16.7638 0.1650 0.1228 0.0055 1.3051 0.3132 0.01 0.0311	NO - YES NO NO NO YES NO NO NO
African Catfish	δ-HCH heptachlor α- endosulfan p,p'-DDE Methoxychlor	0.4220 3.1476 2.3240 0.2696 1.3452	NO ADI 0.0001 0.006 0.01 0.1	3.2178 24.0005 17.7205 2.0557 10.2572	- 24.001 0.295 0.021 0.01	- YES NO NO NO	2.2064 16.4575 12.1512 1.4096 7.0335	- 16.4575 0.2025 0.0141 0.0070	- YES NO NO NO

Atlantic Horse Mackerel	δ-HCH	0.1908	NO ADI	1.4549	-	-	0.9976	-	-
	heptachlor	2.6926	0.0001	20.531	20.5311	YES	14.0784	14.0784	YES
	α-endosulfan	1.3870	0.006	10.576	0.18	NO	7.2520	0.1209	NO
	β-endosulfan	1.0686	0.006	8.1481	0.136	NO	5.5873	0.0931	NO
Sardine	δ-HCH	0.4414	NO ADI	3.3657	-	-	2.3079	*	*
	Heptachlor	1.5324	0.0001	11.6846	11.685	YES	8.0123	8.0123	YES
	Aldrin	0.2996	0.0001	2.2845	2.2845	YES	1.5665	1.5665	YES
	α-endosulfan	2.3184	0.006	17.6778	0.295	NO	12.1219	0.2020	NO
	β-endosulfan	1.3092	0.006	9.9827	0.1664	NO	6.8452	0.1140	NO
Chub Mackerel	δ-HCH	0.1474	NO ADI	1.1239	-	-	0.7707	-	-
	Heptachlor	3.1080	0.0001	23.6985	22.699	YES	16.2504	16.2504	YES
	α-endosulfan	1.4032	0.006	10.6994	0.18	NO	7.3367	0.1222	NO
	Methoxychlor	0.9598	0.1	7.3185	7.32	YES	5.0184	0.0050	NO

Table 4.9: Health risk assessment based on average daily intake of Organophosphorus pesticide residues detected in fish samples.

OP	Pesticide	Residual concn. (ug/g)	ADI (mg/kg/day)	16 kg			70 kg		
				EADI ($x10^{-6}$)	HI-Child	Health risk	EADI ($x10^{-6}$)	HI-Adult	Health risk
Nile Tilapia	Metamidopho	0.0052	0.004	3.965	0.00099	NO	2.7188	0.0007	NO
	Phorate	0.0048	0.0007	3.66	0.00523	NO	2.5097	0.0036	NO
	Fonofos	0.0036	NO ADI	2.745	-	-	1.8823	-	-
	Pirimiphos-m	0.0044	0.03	3.355	0.00011	NO	2.3006	0.00008	NO
	Chlorpyrifos	0.0026	0.01	1.9825	0.0002	NO	1.3594	0.0001	NO
Atlantic Horse Mackerel	Metamidopho	0.0050	0.004	3.8125	0.00095	NO	2.6143	0.0006	NO
	Fonofos	0.0024	NO ADI	1.83	-	-	1.2549	-	-
Chub Mackerel	Pirimiphos-m	0.0036	0.03	2.745	0.00009	NO	2.6143	0.00006	NO
	Chlorpyrifos	0.0024	0.01	1.83	0.0002	NO	1.2549	0.0001	NO
	Malathion	0.0072	0.3	5.49	0.00002	NO	3.7646	0.00001	NO
	Fenithrothion	0.0072	0.006	5.49	0.00092	NO	3.7646	0.0006	NO
	Parathion-et	0.0044	0.004	3.355	0.00084	NO	2.3006	0.0006	NO
	Profenofos	0.0076	0.03	5.795	0.0002	NO	3.9737	0.0001	NO

Table 4.7, 4.8 and 4.9 represents the estimated dose values and health hazards connected with pyrethroids, organochlorine and organophosphorus pesticide residues respectively in fish from markets in Ibadan. Hazard indices were computed for children (average weight, 16 kg) and adults (average weight, 70 kg). Calculations of the risk associated with the consumption of fish from markets in Ibadan were carried out to ascertain whether eating fish poses a threat to human

consumers. It has been reported that if the hazard index is greater than 1 (HI>1), the chemical has exceeded the maximum acceptable level and may cause harm to humans (Tsakiris *et. al*., 2011). For cases where the HI<1, the pesticides involved are unlikely to cause harm to human consumers.

Table 4.7 reports the health risk assessment for the intake of pyrethroids from the consumption of the fish samples analyzed. It showed that the hazard estimates for Allenthrin, Bifenthrin, Fenpropathrin, λ-cyhalothrin, Cyfluthrin, Cypermethrin, Fenvalerate, δ-methrin and Permethrin in all fish species analyzed were below one for both groups (child and adult), indicating a low health risk and no human health hazard.

In table 4.8, health risk estimates for intake of organochlorine residues in adults indicated that γ-chlordane, β-HCH, α-endosulfan, δ-HCH, p,p'-DDT, Methoxychlor and p,p'-DDE may pose no direct human health hazard even though present in the fish samples. This is due to the fact that their HI for most of the samples were all less than unity (i.e. HI<1) as a result of their comparatively small concentrations in the fish tissues.

The hazard index estimations computed for Heptachlor, Dieldrin and Aldrin indicated that they may be of particular concern. They were found to pose health risk to adults since their estimated doses surpassed the recommended reference dose. Results of this study revealed heptachlor to be the major contaminant discovered in the fish tissues. Heptachlor had HI extremely high for all five fish species (*Oreochromis niloticus:* HI=16.7638, *Clarias gariepinus:* HI=16.4575, *Trachurus trachurus:* HI=14.0784, *Sardinella madenrensis:* HI=8.0123 *and Scomber japonicus:* HI= 16.2504), Dieldrin (*Oreochromis niloticus:* HI=1.3051), and Aldrin (*Sardinella madenrensis:* HI=1.5665). Suggesting that a high health risk is associated with the intake of Heptachlor through the consumption of all five fish species, Dieldrin through the consumption of Nile Tilapia and Aldrin through the consumption of Sardine analyzed in this study.

In children, although Methoxychlor occurred only in African Catfish and Chub Mackerel, it had HI less than unity (HI<1) in Catfish while in Chub Mackerel it had HI higher than unity (HI>1) signifying that exposure on a daily basis to this contaminant (methoxychlor) through Chub Mackerel consumption has a health risk for children. Heptachlor had its HI extremely high in all fish samples (*Oreochromis niloticus:* HI=24.450, *Clarias gariepinus:* HI=24.001, *Trachurus trachurus:* HI=20.5311, *Sardinella madenrensis:* HI=11.685 *and Scomber japonicus:* HI=22.699). Dieldrin had its HI above 1 in Nile Tilapia (HI=1.9032) while Aldrin also had its HI>1 (HI=2.2845).

Table 4.9 reported the health risk from the intake of organophosphorus pesticides from the consumption of the fish samples analysed. It showed that the hazard estimates for Methamidopho, Phorate, Fonofos, Primiphos-methyl, Chlorpyrifos, Malathion, Fenithrothion, Parathion-ethyl and Profenofos in all fish samples analysed were below one for both groups (children and adults), indicating a low health risk and no human health hazard.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This study confirms some degree of contamination of fish sold in markets in Ibadan from pesticide residues. Pesticide intake and health risk/hazard for the fish consumers is however still low for the pyrethroids and organophosphorus pesticides detected and there is no immediate risk. Organochlorine pesticides are the contaminants of concern in this study. Organochlorine pesticides contaminated all fish species analyzed in this study at concentrations ranging from the detection limit to 3.2062±0.0348 µg/g. Health risk was reported for heptachlor through the consumption of all five fish species analyzed, dieldrin through the consumption of Nile Tilapia and aldrin through the consumption of Sardine. With the high levels of these organochlorine pesticides detected in the fish species, the continuous use of these pesticides will definitely lead to a high concentration of these 'not easily metabolized' chemicals in the body.

5.2 RECOMMENDATIONS

1. Further research can be carried out on this study for improvement.
2. Sampling can be extended to more fish species, more markets in Ibadan and other cities in Nigeria.
3. Source of fish sold in the markets can be investigated.
4. Other pesticides not included in this study could be investigated e.g carbamates.

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APPENDICES

APPENDIX ONE

RESULTS OF LABORATORY ANALYSIS

Table A1.1: Concentrations (μg/g) of organophosphorus pesticide residue in fish.

FISH SPECIES	ORGANOPHOSPHORUS PESTICIDE			
		1 (μg/g)	2 (μg/g)	3 (μg/g)

Nile Tilapia (*Oreochromis Niloticus*)	Methamidopho Ethoprophos Phorate Diazinon Fonofos Dimethoate Pirimiphos-m Chlorpyrifos Malathion Fenitrothion Parathion-ethyl Chlorfenvinp Profenofos	0.0062 BD 0.0048 BD 0.0036 BD 0.0046 0.0020 BD BD BD BD BD	0.0040 BD 0.0044 BD 0.0026 BD 0.0050 0.0032 BD BD BD BD BD	0.0054 BD 0.0052 BD 0.0046 BD 0.0036 0.0026 BD BD BD BD BD
African Catfish (*Clarias Gariepinus*)	Methamidopho Ethoprophos Phorate Diazinon Fonofos Dimethoate Pirimiphos-m Chlorpyrifos Malathion Fenitrothion Parathion-ethyl Chlorfenvinp Profenofos	BD BD BD BD BD BD BD BD BD BD BD BD BD	BD BD BD BD BD BD BD BD BD BD BD BD BD -	BD BD BD BD BD BD BD BD BD BD BD BD BD
Atlantic Horse Mackerel (*Trachurus Trachurus*)	Metamidopho Ethoprophos Phorate Diazinon Fonofos Dimethoate Pirimiphos-m Chlorpyrifos Malathion Fenitrothion Parathion-ethyl Chlorfenvinp Profenofos	0.0078 BD BD BD 0.0022 BD BD BD BD BD BD BD BD	0.0032 BD BD BD 0.0024 BD BD BD BD BD BD BD BD	0.0040 BD BD BD 0.0260 BD BD BD BD BD BD BD BD

Sardine	Metamidopho	BD	BD	BD
(*Sardinella*	Ethoprophos	BD	BD	BD
Maderensis)	Phorate	BD	BD	BD
	Diazinon	BD	BD	BD
	Fonofos	BD	BD	BD
	Dimethoate	BD	BD	BD
	Pirimiphos-m	BD	BD	BD
	Chlorpyrifos	BD	BD	BD
	Malathion	BD	BD	BD
	Fenitrothion	BD	BD	BD
	Parathion-ethyl	BD	BD	BD
	Chlorfenvinp	BD	BD	BD
	Profenofos	BD	BD	BD
Chub Mackerel	Metamidopho	BD	BD	BD
(*Scomber*	Pirimiphos-m	0.0050	0.0026	0.0032
Japonicus)	Ethoprophos Phorate	BD	BD	BD
	Diazinon	BD	BD	BD
	Fonofos	BD	BD	BD
	Dimethoate	BD	BD	BD
	Pirimiphos-m	BD	BD	BD
	Chlopyrifos	0.0020	0.0024	0.0028
	Malathion	0.0060	0.0060	0.0096
	Fenitrothion	0.0098	0.0064	0.0054
	Parathion-ethyl	0.0040 BD	0.0030 BD	0.0062 BD
	Chlorfenvinp	0.0042	0.0102	0.0084
	Profenofos			

BD: Below detection

Table A1.2: Concentrations (µg/g) of pyrethroid pesticide residue in fish.

FISH SPECIES	PYRETHROID PESTICIDE			
		1 (µg/g)	2 (µg/g)	3 (µg/g)
Nile Tilapia (*Oreochromis Niloticus*)	Allethrin Bifenthrin Fenpropathrin λ- cyhalothrin Cyfluthrin Cypermethrin Fenvalerate δ-methrin	0.6192 1.2622 3.2922 0.2869 2.4718 2.4442 0.7524 1.2542	0.6470 1.2592 3.1972 0.2798 2.1874 2.4714 0.7418 1.3210	0.6210 1.2574 3.3230 0.2866 2.4802 2.4878 0.7432 1.1874
African Catfish (*Clarias Gariepinus*)	Allethrin Bifenthrin Fenpropathrin λ- cyhalothrin Cyfluthrin Cypermethrin Fenvalerate δ- methrin Permethrin	BD 1.3974 BD BD 2.0002 BD 1.1890 1.7794 BD	BD 1.5182 BD BD 1.9714 BD 1.1874 1.8048 BD	BD 1.6366 BD BD 1.9498 BD 1.1906 1.8212 BD
Atlantic Horse Mackerel (*Trachurus Trachurus*)	Permethrin Allethrin Bifenthrin Fenpropathrin λ-cyhalothrin Cyfluthrin Cypermethrin δ- methrin Fenvalerate	1.8436 BD BD BD BD 5.1166 6.6804 0.2078 BD	1.8006 BD BD BD BD 5.3256 6.7944 0.2192 BD	1.8194 BD BD BD BD 5.3612 6.7614 0.2192 BD
Sardine (*Sardinella Maderensis*)	Permethrin Allethrin Bifenthrin Fenpropathrin λ-cyhalothrin Cyfluthrin Cypermethrin δ- methrin Fenvalerate	0.3682 BD BD BD 0.2318 1.3196 7.6802 BD BD	0.3902 BD BD BD 0.2938 1.4252 7.6370 BD BD	0.4398 BD BD BD 0.2418 1.4324 7.6340 BD BD
Chub Mackerel (*Scomber Japonicus*)	Permethrin Allethrin Bifenthrin Fenpropathrin λ-cyhalothrin Cyfluthrin Cypermethrin δ- methrin Fenvalerate	1.2136 BD BD BD BD 4.6388 6.0900 BD BD	1.2614 BD BD BD BD 4.5036 6.0966 BD BD	1.2546 BD BD BD BD 4.5118 6.1368 BD BD

BD: Below detection

Table A1.3: Concentrations (µg/g) of organochlorine pesticide residue in fish.

FISH SPECIES	ORGANOCHLORINE PESTICIDE		
		1 (µg/g)	2 (µg/g)

Nile Tilapia (*Oreochromis Niloticus*)	Gamma-HCH β-HCH δ- HCH Heptachlor Aldrin γ- chlordane α- endosulfan p,p'-DDE Dieldrin Endrin B-endosulfan p,p'- DDD Endosulfan-S p,p'-DDT	BD 0.3262 0.5752 3.2308 BD 0.1690 1.4188 0.1104 0.2588 0.1224 BD 0.1748 BD 0.6140	BD 0.2506 0.2704 3.1816 BD 0.1466 1.3992 0.0992 0.2404 0.1172 BD 0.1980 BD 0.5784
African Catfish (*Clarias Gariepinus*)	Gamma-HCH β-HCH δ- HCH heptachlor Aldrin γ-chlordane α- endosulfan p,p'- DDE Dieldrin Endrin B-endosulfan p,p'-DDD Endosulfan-S p,p'-DDT methoxychlor	BD 0.4112 BD 3.1850 BD BD 2.3746 0.2754 1.3102 BD BD BD BD BD BD	BD 0.4328 BD 3.1102 BD BD 2.2734 0.2638 1.3802 BD BD BD BD BD BD
Atlantic Horse Mackerel (*Trachurus Trachurus*)	Gamma-HCH β-HCH δ- HCH heptachlor Aldrin γ- chlordane α- endosulfan β – endosulfan p,p'-DDE Dieldrin Endrin B-endosulfan p,p'-DDD Endosulfan-S p,p'-DDT methoxychlor	BD BD 0.1840 2.7176 BD BD 1.4672 1.1118 BD BD BD BD BD BD BD BD	BD BD 0.1976 2.6676 BD BD 1.3068 1.0254 BD BD BD BD BD BD BD BD

Sardine (*Sardinella* *Maderensis*)	Gamma-HCH β-HCH δ- HCH heptachlor aldrin γ- chlordane α- endosulfan β – endosulfan p,p'-DDE Dieldrin Endrin B-endosulfan p,p'-DDD Endosulfan-S p,p'-DDT Methoxychlor	BD BD 0.4720 1.4342 0.3059 BD 2.5030 1.3380 BD BD BD BD BD BD BD BD	BD BD 0.4108 1.6306 0.2934 BD 2.1218 1.2846 BD BD BD BD BD BD BD BD
Chub Mackerel (*Scomber* *Japonicus*)	Gamma-HCH β-HCH δ- HCH Heptachlor aldrin γ- chlordane α- endosulfan Methoxychlor β –endosulfan p,p'-DDE Dieldrin Endrin B-endosulfan p,p'-DDD Endosulfan-S p,p'-DDT Methoxychlor	BD BD 0.1532 3.1442 BD BD 1.5556 1.0104 BD BD BD BD BD BD BD BD BD	BD BD 0.1416 3.0730 BD BD 1.2508 0.9092 BD BD BD BD BD BD BD BD BD

BD: Below detection

APPENDIX TWO

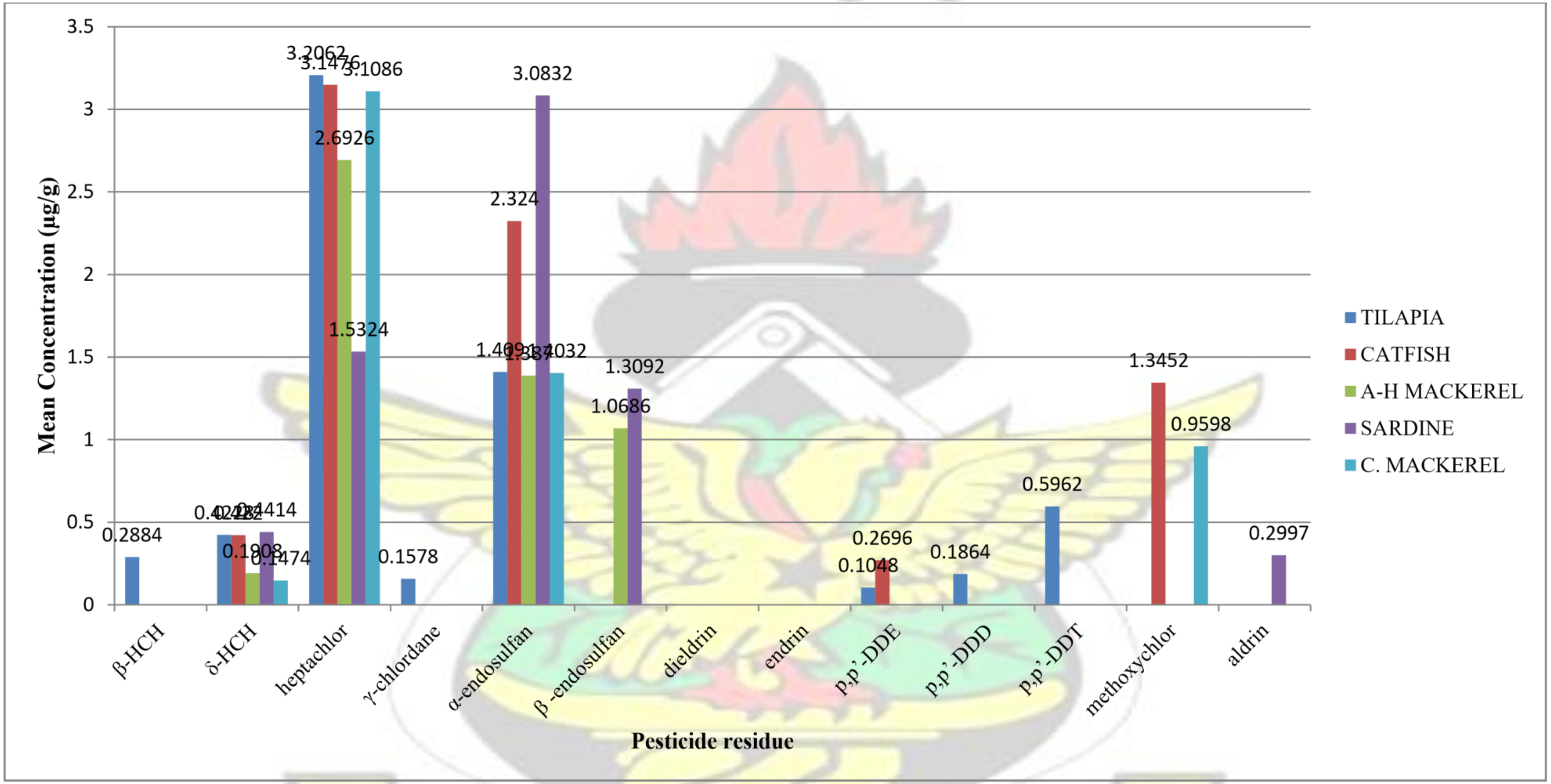
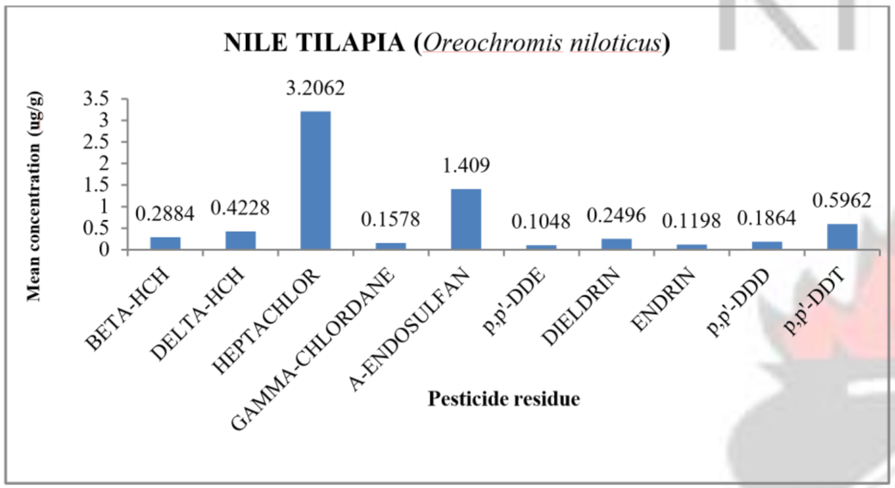


Figure A2.1: Graph of mean concentrations of Organochlorine pesticide residues detected in fish samples



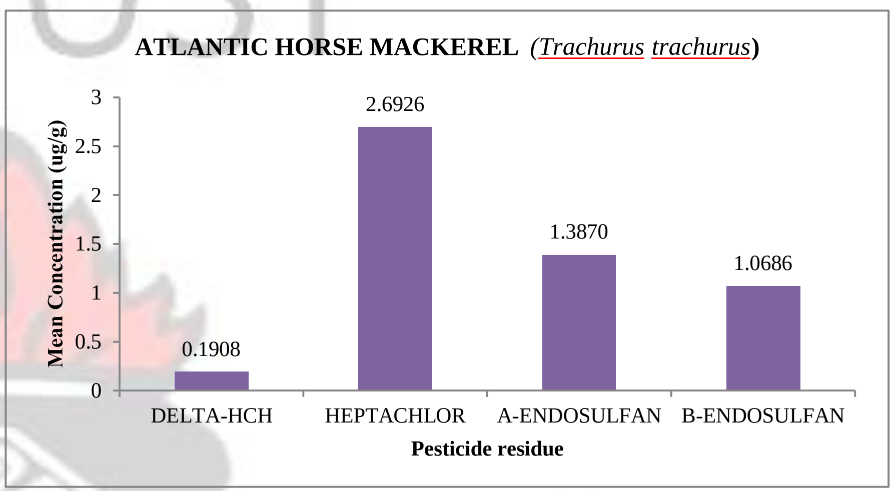


Figure A2.1a: Mean concentrations of organochlorine pesticides in Nile Tilapia Figure A2.1b: Mean concentrations of organochlorine pesticides in Atlantic horse mackerel

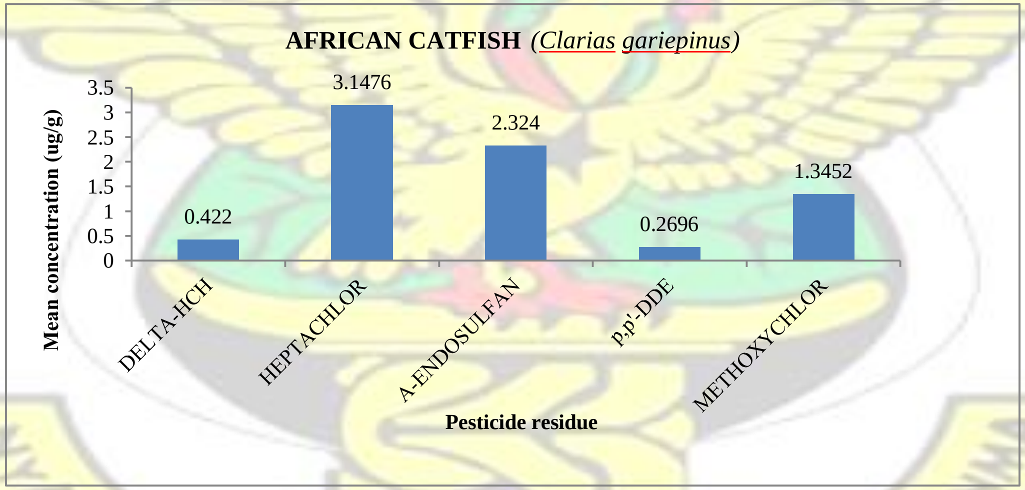
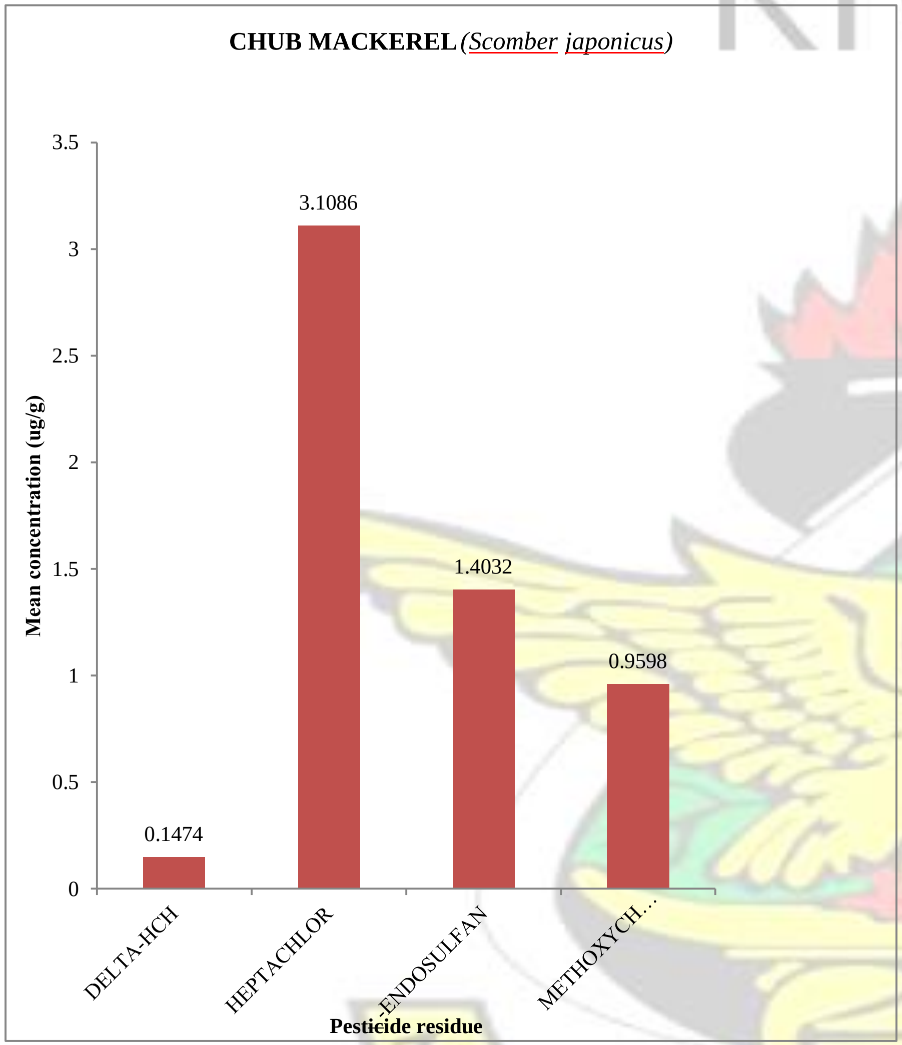


Figure A2.1c: Mean concentrations of organochlorine pesticides in African Catfish


CHUB MACKEREL (Scomber japonicus)
Mean concentration (ug/g)
3.5
3
2.5
2
1.5
1
0.5
0
0.1474
3.1086
1.4032
0.9598
DELTA-HCH
HEPTACHLOR
-ENDOSULFAN
METHOXYCH...
Pesticide residue

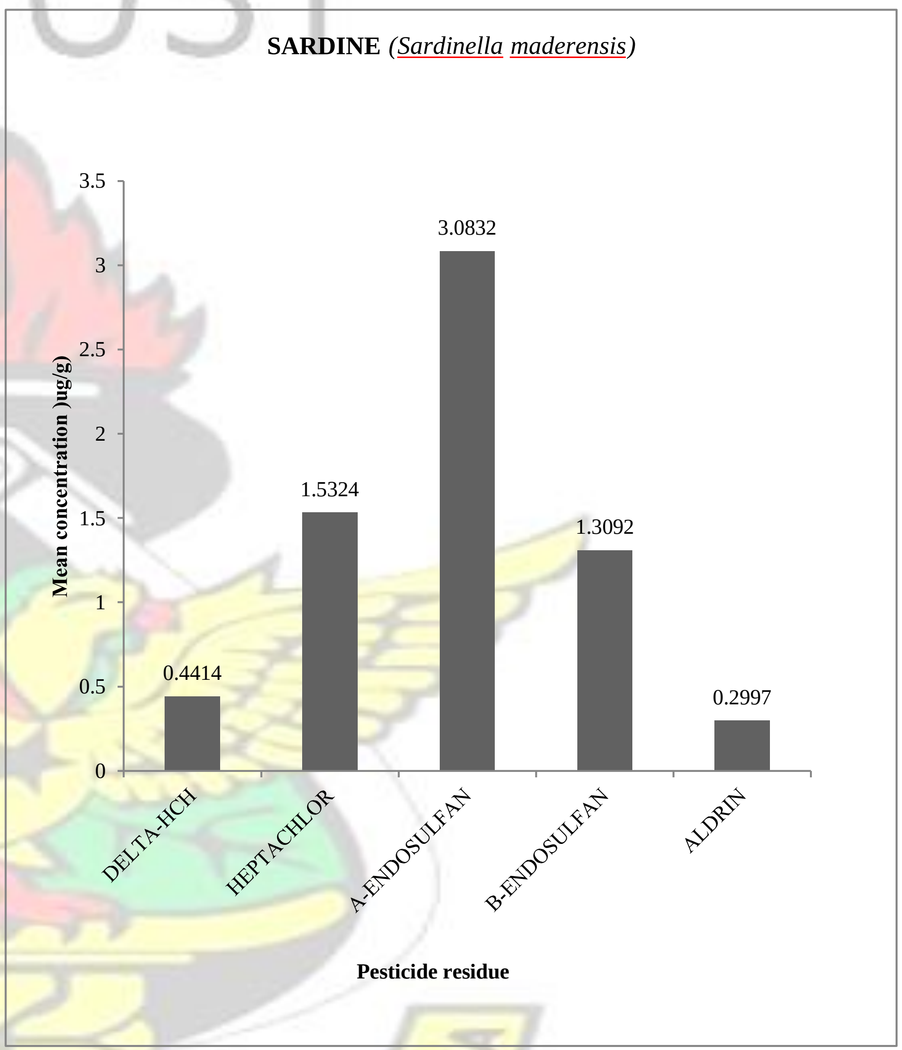

SARDINE (Sardinella maderensis)
Mean concentration)ug/g)
3.5
3
2.5
2
1.5
1
0.5
0
0.4414
1.5324
3.0832
1.3092
0.2997
DELTA-HCH
HEPTACHLOR
A-ENDOSULFAN
B-ENDOSULFAN
ALDRIN
Pesticide residue

Figure A2.1d: Mean concentrations of organochlorine Figure A2.1e: Mean concentrations of organochlorine pesticides in Chub mackerel pesticides in Sardine

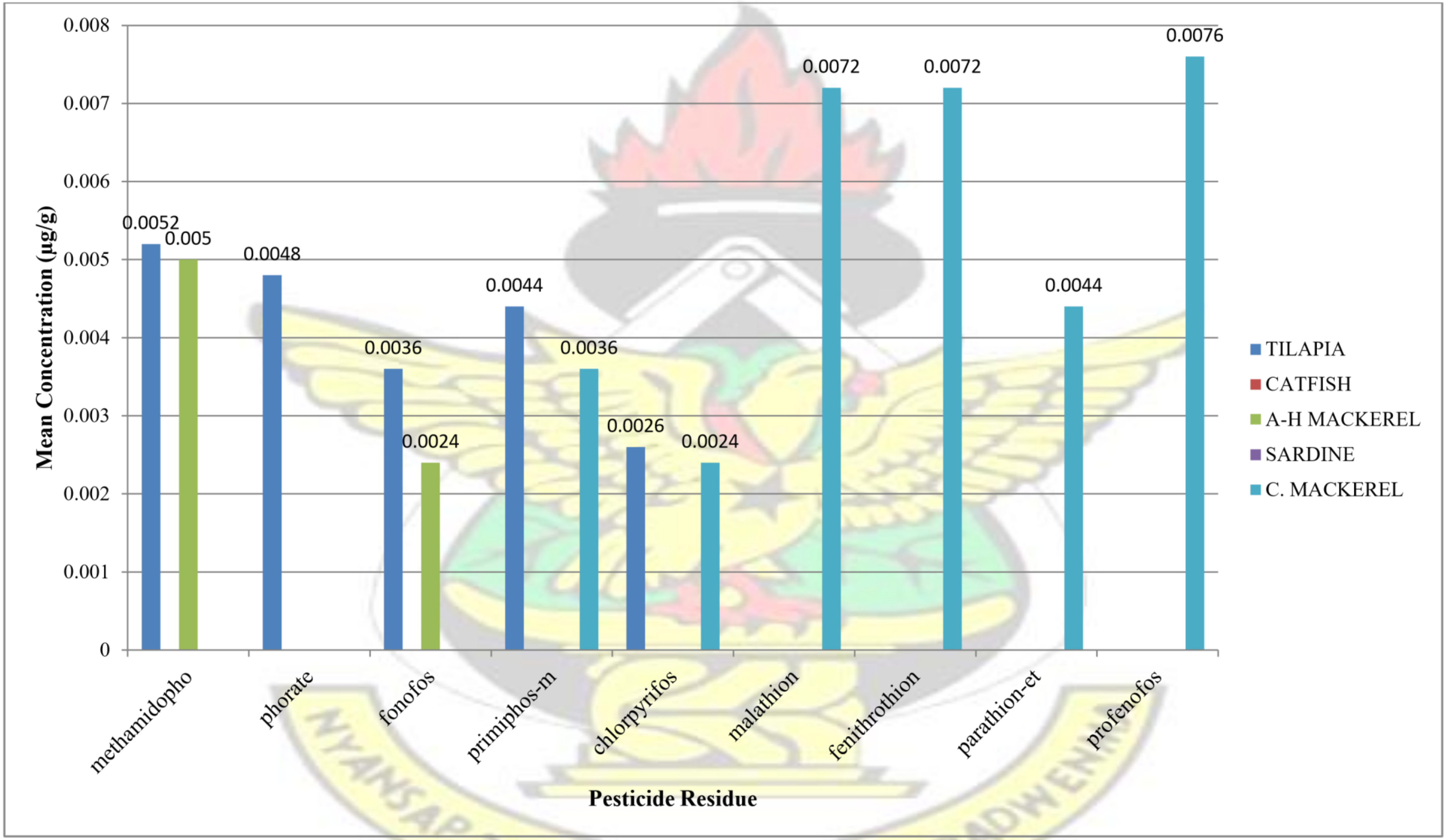
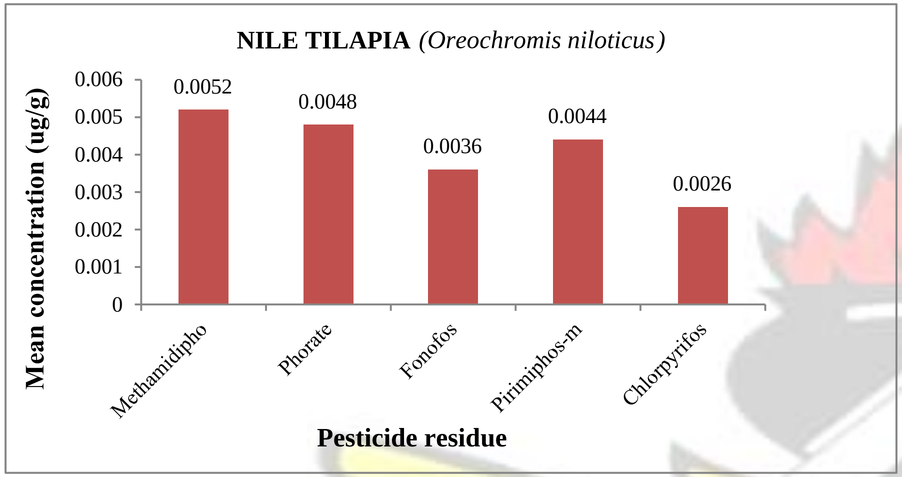


Figure A2.2: Graph of mean concentrations of Organophosphorus pesticide residues detected in fish samples



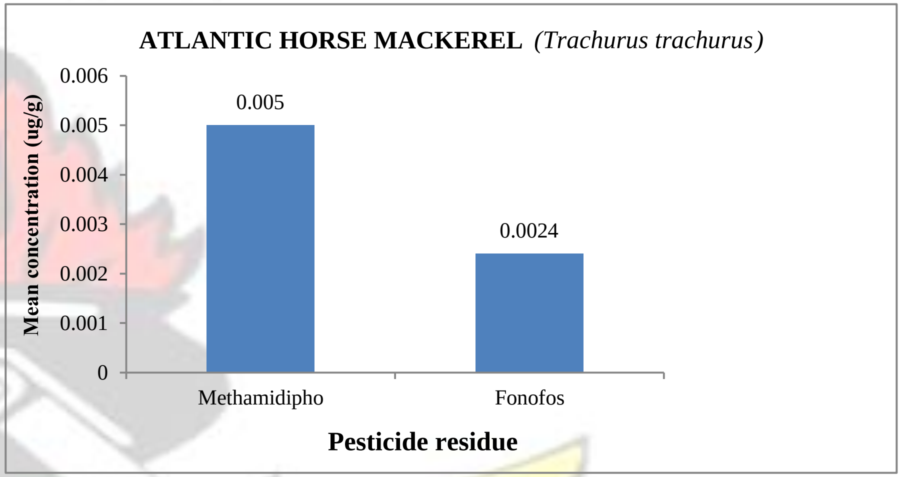


Figure A2.2a: Mean concentrations of organophosphorus Tilapia pesticides in Atlantic horse mackerel

Figure A2.2b: Mean concentrations of organophosphorus pesticides in

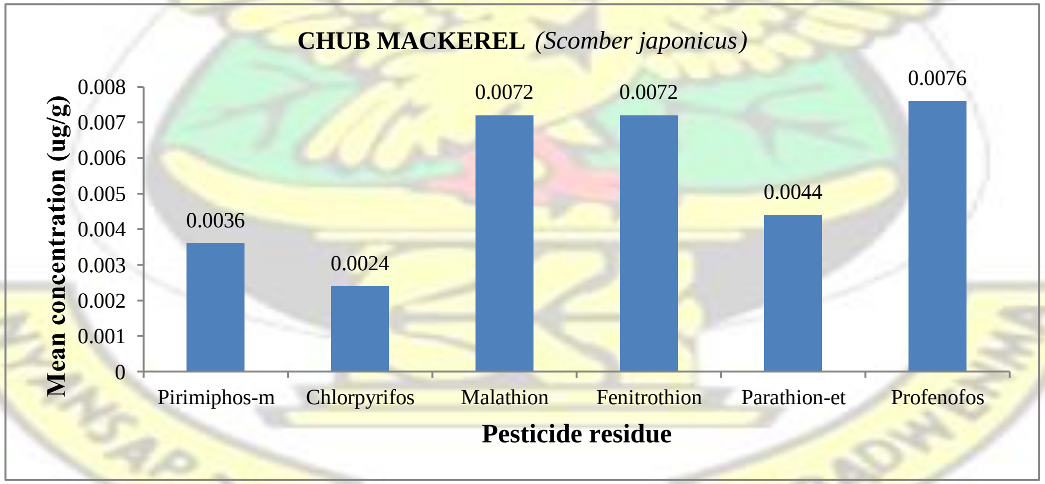


Figure A2.2c: Mean concentrations of organophosphorus pesticides in Chub Mackerel

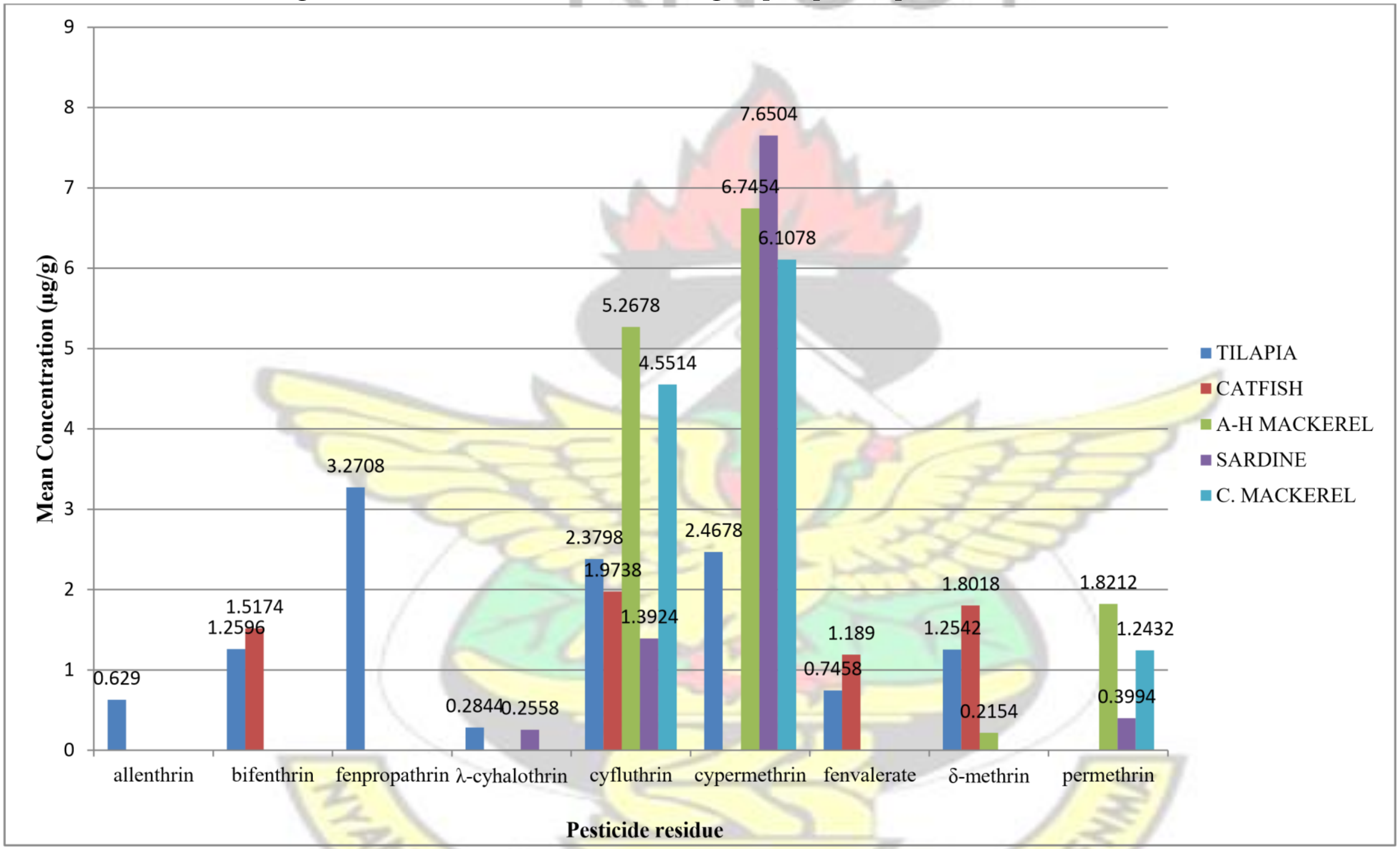
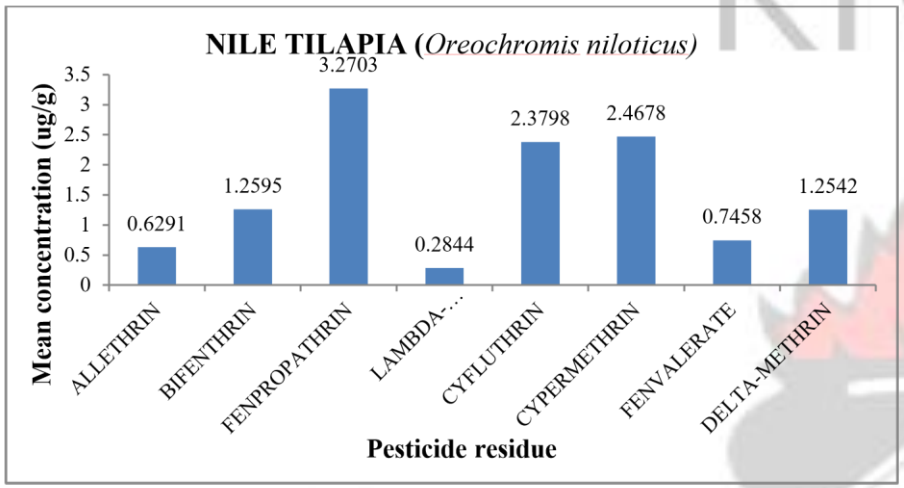


Figure A2.3: Graph of mean concentrations of Pyrethroid pesticide residues detected in fish samples.



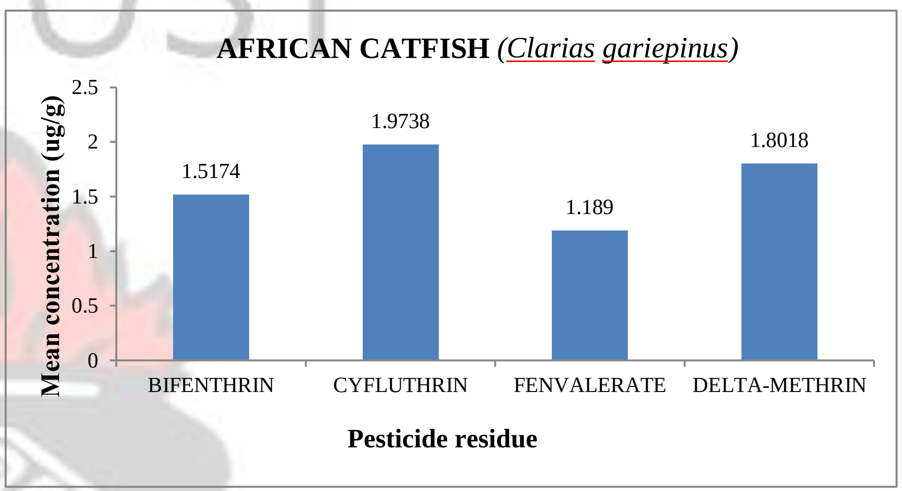


Figure A2.3a: Mean concentrations of pyrethroid pesticides Figure A2.3b: Mean concentrations of pyrethroid pesticides in Tilapia in African catfish

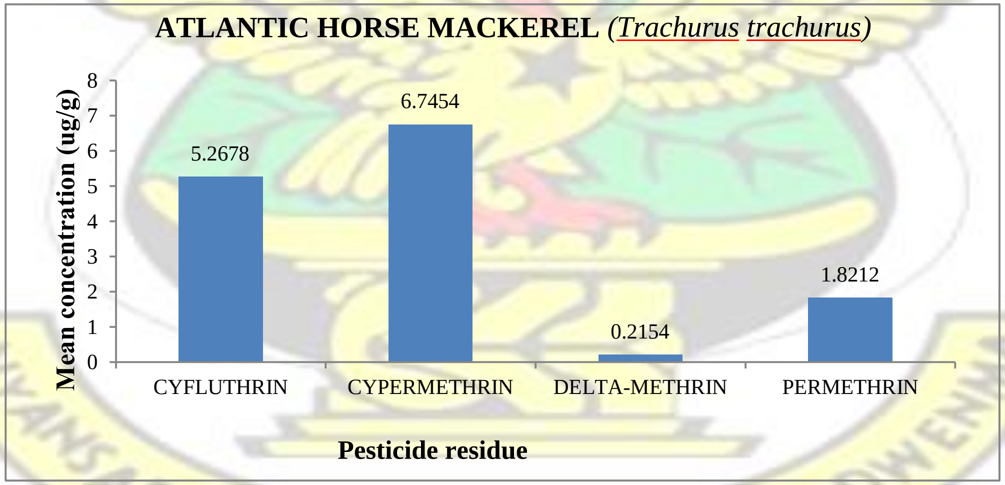
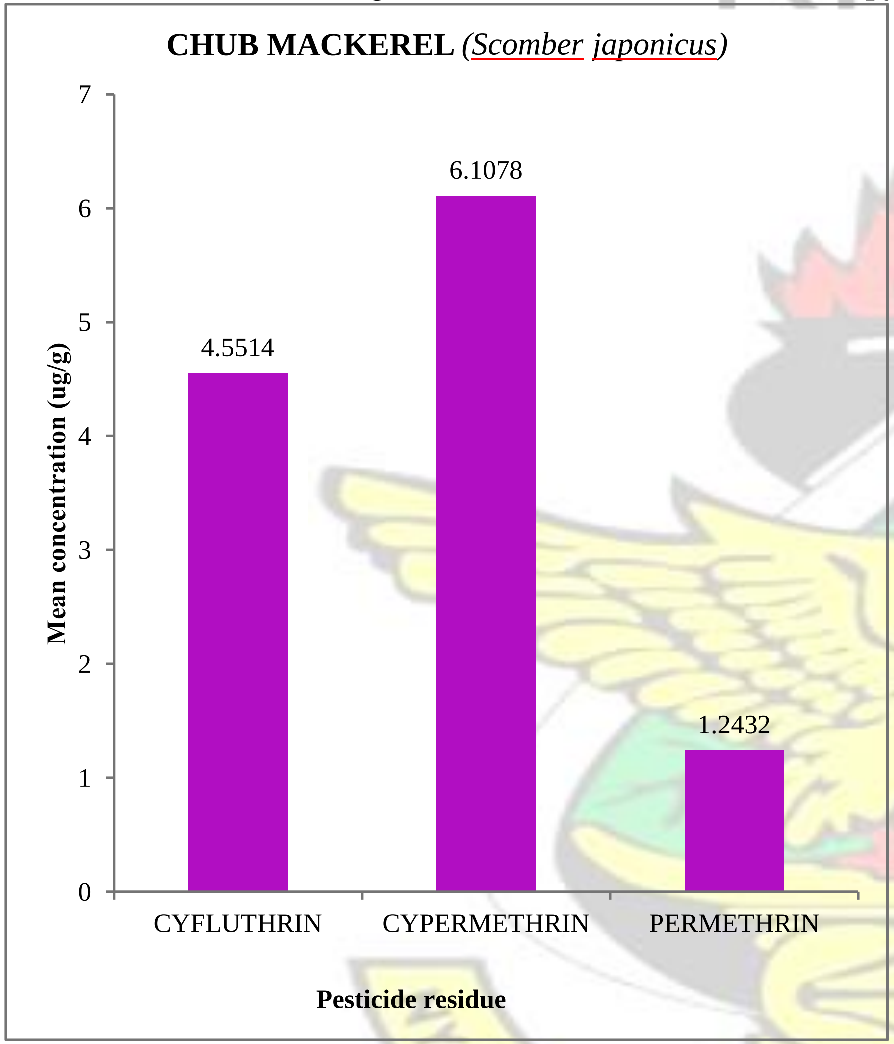


Figure A2.3c: Mean concentrations of pyrethroid pesticides in Atlantic horse mackerel



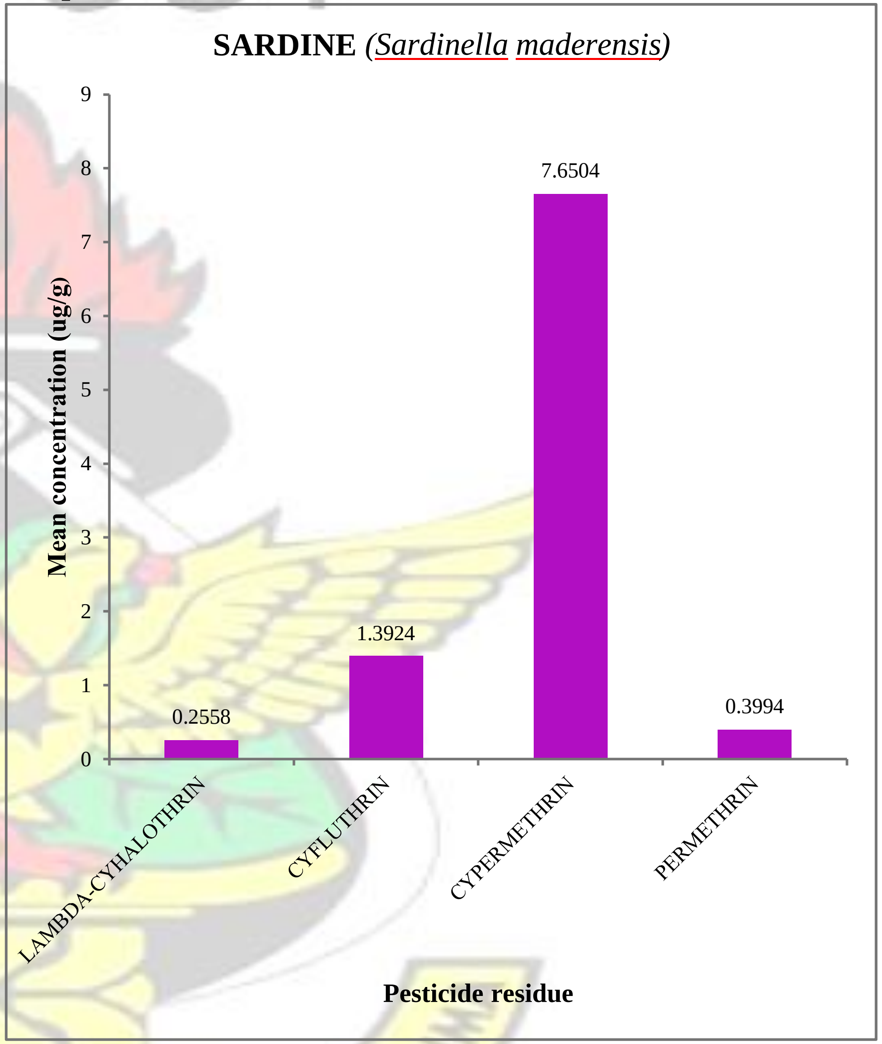


Figure A2.3d: Mean concentrations of pyrethroid pesticides Figure A2.3e: Mean concentrations of pyrethroid pesticides in in Chub mackerel Sardine