ASSESSMENT OF PESTICIDE RESIDUE LEVELS IN WATER, WASTEWATER LAGOONS, FISH PONDS AND FARMED FISH IN THE CATCHMENT OF RIVER KUJA, KENYA

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A THESIS SUBMITTED TO THE BOARD OF POSTGRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS OF THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY IN LIMNOLOGY IN THE SCHOOL OF AGRICULTURE AND NATURAL RESOURCE MANAGEMENT, DEPARTMENT OF AQUATIC AND FISHERY SCIENCES,

KISII UNIVERSITY

2023

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To my late father Stephen Nyaundi and mother Yusaliah who held my hand to school; my Spouse Dr. Rosemary Nyaundi and my children Dr. Patience Kiyuka, Faith Bitutu & Steve Nyaundi for their unwavering understanding and immense support.

ACKNOWLEDGEMENTS

Special thanks are extended to: Prof. Albert Getabu and Dr. James Onchieku for their mutual support to ensure the work is completed in time. Acknowledgements are made to Prof. James M. Njiru, Director General of Kenya Marine and Fisheries Research Institute (KMFRI), Drs. Christopher M. Aura, Director, Freshwater Systems and Chrispine S. Nyamweya, Assistant Director Limnology, all of KMFRI, without their inspiration, this study would have been in vain.

I wish to acknowledge Prof. Zachary M. Getenga of Machakos University-Kenya, and Drs. Edward M. Neyole of Masinde Muliro University of Science & Technology, Fredrick Kengara of Maseno University, and Prof. Nehemiah M. Nyaundi of University of Eastern Africa, whose immense mentorship and perseverance are highly recognized.

Further acknowledgements are accorded to Prof. Evans Basweti and Drs. Enock Obuba, Joash Kerongo, Reuben Omondi and Ogendi Mokua all of Kisii University for the many relevant lessons and focused guidance shared with them. I sincerely thank Dr. Enock Osoro at the Chiromo pesticides laboratory, University of Nairobi, for offering access to modern analytical equipment and sample analysis for pesticide concentrations. Special thanks are accorded to the National Research Fund of Kenya (NRF), for the offer of a partial scholarship that enabled research work on this thesis to be accomplished.

Special mention is given to my Wife Dr. Rosemary, my children Dr. Patience, Faith, and Steve by giving me moral support and allowing me to utilize the family resources for the completion of this study. Finally, I wish to express my sincere gratitude to all my brothers and sisters for their moral and motivational support they accorded me during the study.

ABSTRACT

Environmental contamination by pesticides is a matter of great concern worldwide. In Kenya, anthropogenic activities involving the use of pesticides in horticulture, cash crop farming and raising of livestock continue to contribute to the pollution load in Lake Victoria Basin. Whereas limited accounts concerning the pesticides distribution such as in the River Nyando catchment have been reported, there exist huge knowledge gaps on the subject in the highly populated areas of River Kuja watershed. Quantities of pesticide remains in cultured fish, wastewater lagoons, fish pond effluents, and river waters in the region have been scantly studied. This study investigated the distribution of organochlorine pesticide residues in water and sediment samples from fish ponds and their river waters as well as in fish from the fish ponds and wastewater lagoons in September 2016 to December 2017, in some selected parts of Kericho, Nyamira, Kisii and Homa Bay counties. Water quality parameters were obtained *In situ* and analysed. The study used a purposeful and multistage stratified sampling design with wards being the basic sampling units. Consequently, four wards were sampled in Kisii, three in Nyamira and one each in Kericho and Homabay counties. The former two counties were emphasized in the sampling because they are more densely populated than the latter two. Fish and sediment samples were obtained from the field and transported in cooler boxes packed in ice and later frozen to -20^0C. 2.5 L water samples were collected in amber bottles and preserved, transported and kept at 4°C in the laboratory. Pesticides in water samples were solvent-extracted using acetone-hexane, concentrated by rotary evaporation and cleaned up using liquid-liquid and solid-phase extraction method for water and solids. The SPE column were eluted with the appropriate solvent system followed by Gas Chromatography (GC) analysis and GC-Mass Spectroscopy (MS) for identification of pesticide chromatograms. Data sets were analyzed using Excel spreadsheet program 2013 and GraphPad Prism software version 5.03 with results presented in frequency tables and bar graphs. Determination of variations in organochlorine pesticides mean value concentration between sampling stations was performed using one-way ANOVA (Analysis of Variance) statistical method, at the 95% confidence level, while independent sample *T*-test was performed in determination of significant variation in OCPs mean values between wet and dry seasons. Tukey's *post hoc* test was applied when significant differences between means were observed to identify the specific stations that differed from one another ($p < 0.05$). Correlation analysis was done on levels of organochlorines and physico-chemical parameters to determine the associations among the variables. Pesticide contamination levels in fish and water samples were compared with those from NEMA, WHO, FAO, EU and US EPA water quality standards and mitigation measures suggested. Chromatographic analysis identified seventeen different organochlorine pesticides known to occur in three major groups namely, hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethanes (DDTs) and cyclodienes. HCHs constituted of four isomers: α-HCH, β-HCH, γ-HCH and δ-HCH. DDTs constituted of three metabolites: *p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDT while cyclodienes comprised of ten compounds: aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide, endosulfan I, endosulfan II, endrin aldehyde, endosulfan sulfate and methoxychlor. Mean (± SE) physico-chemical parameters results varied significantly viz; dissolved oxygen (DO) (6.96±0.897 mgL^{-1}), temperature (25.39±1.201 ^{0} C), conductivity (62.03±8.123 μScm^{-1}), pH (7.57±0.314), and TSS (193±5.462), TP (0.127±0.005) and TN (3.25±0.24) which contributed significantly to variations in organochlorine pesticide residue levels observed. Results of DDTs, cyclodienes and HCHs in fish ponds ranged below detection limit (BDL) to 0.27±0.03 μgL^{-1}, BDL to 0.11±0.00 μgL^{-1}, and 4.39±1.01 μgL^{-1} respectively; and BDL to 0.23±0.01 μgL^{-1}, 1.20±0.005 μgL^{-1}, and 1.71±0.02 μgL^{-1} in river water respectively. Mean OCPs sediment contents were significantly ($p < 0.05$) higher for dieldrin (3.043±0.43 μgKg^{-1}), endrin (2.56±0.460 μgKg^{-1}), heptachlor (3.61±0.02 μgKg^{-1}); DDT (2.97±1.32 μgKg^{-1}), endosulfan (6.31.27±1.051μgKg^{-1}),

methoxychlor (2.15±1.641 μgKg^{-1}) and lindane (2.96±1.32 μgKg^{-1}), respectively. Mean pesticides residue levels in fish ranged from 0.229 to 2.541 μgKg-1 for Nile tilapia (*Oreochromis niloticus*). Most dominant isomer in target species was lindane (γ-HCH) with (3.417 ± 0.983 μgKg^{-1}) and endosulfans. Mean endosulfan sulfate was 2.499 ± 0.071 μgKg^{-1} d.w. and frequently detected, and methoxychlor (2.235 ± 1.459 μgKg^{-1}), respectively. Mean aldrin and dieldrin was 2.028 and 0.574 μgKg^{-1} d.w. Concentration for DDT and its metabolites was 0.27-3.71 μgKg^{-1} for *p,p'*-DDE (dichlorodiphenyldichloroethene), BDL - 1.098 for *p,p'*-DDD (dichlorodiphenyldichloroethane), and 0.105-3.518 μgKg^{-1} for *p,p'*-DDT (dichlorodiphenyltrichloroethane) with significant differences in mean values ranges. The study revealed overall mean residue values for HCHs to be between BDL to 0.571 ±0.62 μgL^{-1} values that were below NEMA and WHO of 2.0 μgL^{-1} in water. Overall, the concentrations of all the DDT metabolites were below WHO maximum acceptable standards of 2.0 μgL^{-1} and below NEMA locally maximum acceptable thresholds in natural drinking water (1.5 mgL^{-1}). However, some sampling stations recorded scores above EPA (0.2 μgL^{-1}) and WHO maximum acceptable standards, with an implication of potential risk to public health and environment, as some sampled sediment and fish results showed higher residue values implying that prolonged exposure would be of public health concern. Available results indicate organochlorine pesticides (OCPs) exist in our environment, and their recent use in the sampled area. The study recommends regular aquatic monitoring in upstream catchment areas to detect persistency and changes in target environment for informed policy decisions and management in order to safeguard human and environmental health.

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ACRONYMNS

AAK	Agrochemical Association of Kenya
AU	African Union Commission
ANOVA	Analysis of variance
ATSDR	Agency for Toxic Substances and Disease Registry
BDL	Below Detection Limit
BHC	Benzene Hexachloride
CNS	Central Nervous System
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethene
DDT	Dichlorodiphenyltrichloroethane
DO	Dissolved Oxygen
d w	Dry Weight
EAC	East African Community
EMCA	Environmental Management and Coordination Act
ERA	Ecological risk Assessments
ERSE	Economic Recovery Strategy on Employment
EU	European Union
FAO	Food and Agriculture Organization of the United Nations
FDA	Food and Drug Administration
GC	Gas Chromatography
IARC	International Authority for Research on Cancer
ICRAF	International Centre for Research in Agroforestry
IPCC	Inter-governmental Panel on Climate Change
IPM	Integrated Pest Management
IUPAC	International Union of Pure and Applied Chemistry

JMPR	Joint FAO/WHO meeting on Pesticide Residue
KALRO	Kenya Agricultural Research Institute
KCBS	Kenya Central Bureau of Statistics
KGGCU	Kenya Grain Growers Association
LD	Lethal Dose
LVEMP	Lake Victoria Environmental Management Project
LVFO	Lake Victoria Fisheries Organization
LVFRP	Lake Victoria Fisheries Research project
LVWR	Lake Victoria Water Resources
MCL	Maximum Contamination Level
MDE	Methoxy Dichloro Ethane
MFO	Mixed Function Oxidate
MoALD & M	Ministry of Agriculture and Livestock Development
$\mu g\ L^{-1}$	Microgram per Liter
$\mu g\ Kg^{-1}$	Microgram per Kilogram
NAL	National Agricultural Laboratory
NEMA	National Environment Management Authority
NIP	National Implementation Plan
NLM	National Library of Medicine
OCPs	Organochlorine Pesticides
OSHA	Occupational Safety and Health Administration
PCB	Polychlorinated Biphenyl
PCPB	Pest Control Products Board
POPs	Persistent Organic Pollutants
PRA	Participatory Rural Appraisal
PRSP	Poverty Reduction Strategy Paper

SW	South West
TP	Total Phosphorous
TSS	Total Suspended Solids
UNESCO	United Nations Educational Scientific Cultural Organization
UNEP	United Nations Environmental Program
US-DHHS	United States Department of Health and Human Services
US EPA	United States Environmental Agency
WHO	World Health Organization

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CHAPTER ONE

INTRODUCTION

1.1 Background of the study

Pesticides are chemicals or biological substances meant for attracting, destroying or mitigating any pest (PCPB, 2012). Most known contaminants globally are pesticides (Wheelock et al., 2008). On the global scale, most commonly used pesticides are classified as herbicides, insecticides or fungicides and the same trend is captured on the local scale (Campbell et al., 2001; FAO, 2017; Max, 2020). Pesticides' leaching or run-offs from agricultural land by gravity flow pollute surface and ground water reservoirs downstream (Gavrilescu, 2005). Their residues are any substances in human foods or animal feeds resulting from the use of a pesticide and include any specified derivatives such as degradation and conversion products and impurities considered to be of toxicological significance (FAO and WHO, 2006). The global average pesticide application per hectare of cropland is depicted in Fig. 1.1

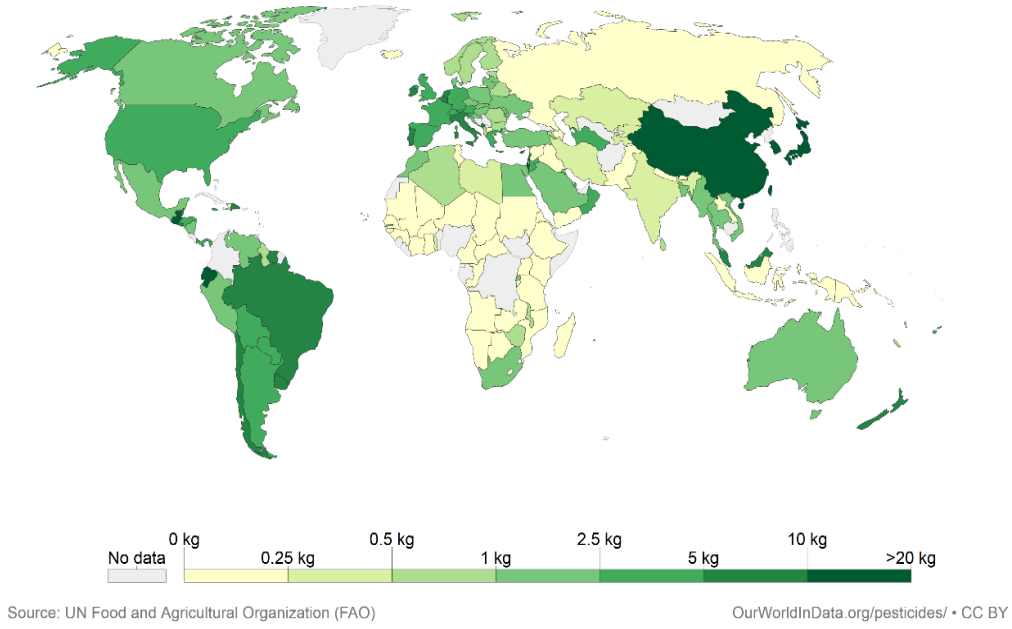

Figure 1.1: **Global average pesticide application per unit of cropland in Kgha^{-1} (FAO, 2020a)**.

Although pesticides have benefits, some have drawbacks, such as potential toxicity caused by organochlorine pesticides to humans and other desired organisms including fish including aquatic ecosystems (Saitoh et al., 2001; Megan et al., 2017) and are classified as the most dangerous and persistent organic chemicals known (Lamberth et al., 2013). Current global pesticide production is estimated at over 3 million tonnes with a monetary value of above 10 US $ billion worth of imports, indicating a steady rise in demand over the last four decades (Max, 2020). According to FAO (2017), pests are responsible for for the loss of 25-40% of potential global harvests and the demand for pesticides in Latin America in the last decade exceeded US $ 2 billion and this has been on the rise as the consumption was expected to rise by a factor of 7-12% (Wassaling et al., 2001; WDNR, 2006).

Many parts of the world have experienced negative environmental impacts as a result of agricultural intensification (Wilson and Tisdell, 2001). Over the years, economic development in the African continent, Kenya included, has relied heavily on agricultural production (UNCTAD, 2021). Due to rapid population expansion and need to produce enough food, there is tendency towards use of organic and inorganic chemicals for increased production, hence degrading the natural resource balance (Wandiga et al., 2003; Badeeb et al., 2016). In both the tropical savannah where intensive agriculture is practiced as well as in arid and semi-arid areas (ASALs) where cattle, sheep and goat rearing predominate, safe storage and disposal of pesticides remain a challenge (Walker, 2000; Tosi et al., 2018). In contrast to restrictions on the use of some chlorinated hydrocarbons, mainly insecticides in industrialised countries, production and application in developing countries has increased over the years (Asimeng, 2000). Recent studies commissioned by Food and Agriculture Organization of the African Union Commission (FAO, 2017) and the World Health Organization (WHO, 2008) showed the need for extended use of insecticides such as Dichlorodiphenyltrichloroethane (DDT), γ-HCH (lindane), aldrin, endosulfan and dieldrin. Reluctance to abandon DDT as a means of pest

control is evident in studies by Bouwman et al. (2011). The study aimed at increasing residual DDT activity and other chlorinated insecticides applied widely, in public health concerns such as tse-tse fly eradication campaigns. Main users of the latter chemicals are tropical countries where termites, ticks and mosquitoes are a public nuisance. Eexcessive use of such chemicals may create severe hazards to the environment (Wandiga et al., 2003).

Strict controls and proper use of pesticides and their derivatives cause low risk to the environment and human health (US EPA, 2002; WHO, 2006). However, studies in the Nyando catchment of Lake Victoria by Abong'o et al. (2014) and in India by Stadlinger et al. (2013) indicate that pesticides have intrinsic public health and environmental risks during their production, import, use, storage and disposal. Stored obsolete pesticides act as point sources of pollution to the local environment and yet few studies have been conducted on their effects on human health this aspect has known little studies in effects on human health (Kylin et al., 2005; Sereda et al., 2008). These organic pollutants are associated with toxicity to the aquatic environment and human health. Other similar pollutants are suspected to be carcinogenic, mutagenic and endocrine disruptors (Nevejan et al., 1996).

All types of land use in the Lake Victoria catchment involving application of pesticides affects the quality of its river waters (Nyaundi et al., 2019). Use of pesticides for agricultural and domestic use within the Lake Victoria Basin environment has been reported in previous studies (Getenga et al., 2004; Megan et al., 2017). Studies have shown that organochlorine pesticides (OCPs) are known to persist in the environment long after use and can be transported by air and water such that trace amounts can exist all over the world (Alle et al., 2009). The economy of Lake Victoria Basin is derived from fisheries (10%), agriculture (35%), industries and mining (15%) and the tertiary sector (40%) (Ntiba et al., 2004; World Bank, 2013). In East Africa, OCPs have been in use since the 1940s and have tended to accumulate in water (Madadi et al., 2005; Ssebugere et al., 2010) and in sediments (Ogwok et al., 2009; Ssebugere et al.,

2009; Werimo et al., 2009). Owing to ingestion of sediment during feeding, OCPs and their residues find their way into edible fish. Health risks associated with OCPs metabolites are well established (Engel et al., 2000).

In Kenya, available documented studies site gross contamination of most major river bodies across the country by discharge of industrial effluents, sewage, and agricultural waste among others (Nevejan et al., 1996; Getanga et al., 2004; Megan et al., 2017). Contamination of rivers due to pesticide use can constitute a significant environmental and health hazard (World Bank, 2013). Kenya's economy relies heavily on agriculture (60%), and contributes up to 26 percent of the Gross Domestic Product (GDP). Agriculture provides food security, and raw materials for agro-chemical industries, creates employment (18%) for income generation and more than 80 percent of informal employment in the rural areas (GoK, 2009), hence it earns foreign exchange for economic stability (NIP, 2006; KIPPRA, 2013). Most of Kenya's agricultural production consists of crops and livestock farming as studies show that more than 80 percent of its population live in rural areas (KIPPRA, 2013). An overview of the agricultural activities in the Lake Victoria Basin indicates that agriculture and fisheries are the major non-point sources of pollution with regard to fertilizer and pesticide loadings to the watercourses in the study area (Campbell et al., 2003; Musa et al., 2006; Osoro et al., 2016). In addition, the aquaculture sub sector has the potential of contributing significantly to the local and national economy as well as supporting food security challenges hence reducing poverty as is stipulated in Kenya's Vision 2030 Economic Blueprint (Ntiba et al., 2004; GoK, 2007) and the Big Four transformative Agenda comprising of Food Security, job creation in Manufacturing, Universal Health care and affordable Housing.

With the exception of OCPs, most of which were banned from use many years ago, for example DDT and persistent organochlorine pesticides (POPs), there are a few pesticides such as lindane, dieldrin and endosulfan that can cause pollution problems in the lake region (Nevejan

et al., 1996; Ssebugere et al., 2010). Pollution and increased eutrophication have been reported due to anthropogenic activities around the lake such as wetland encroachment and reclamations, increased water pollution from domestic and industrial wastes, fertilizer runoffs from agro-based farms and sediment loading through river discharges (Lung'ayia, 1998; Njogu et al., 2010). The Public health sector depends heavily on the use of pesticides in controlling disease vectors in breeding grounds such as mosquitoes and snails which are commonly found in stagnant waters and other terrestrial vectors such as the tsetse fly which cause sleeping sickness in humans (Kasozi, 2001). Pesticides use pose a great challenge to policy makers in Kenya in trying to develop a satisfactory balance at the same time encourage optimal agricultural productivity as well as observe environmental protection (Getenga et al., 2004). Studies by Getenga et al., 2004; Werimo et al., 2009; Stadlinger et al., 2013 indicate that current policy and registration locally is to ensure proper use of pesticides that minimizes risks to the environment and human health; but controls and enforcement of regulations in highly populated areas such as River Kuja watershed remains a challenge that calls for stringent measures to alleviate the potential risk now and in the future.

1.2 Statement of the problem

Organochlorine pesticides are stable, hydrophobic and contain lipophilic attributes that enables them to biomagnify along the trophic levels hence identified at the top of the food web either in food or in water and other aquatic organisms such as fish. These compounds are known to persist and have non biodegradable abilities once released to the environment. Therefore, pesticides offer potential poisonous agents to all forms of life and may present hazardous disease causing agents to workers, consumers, wildlife and to human public at large (Goldman, 2007; FAO/WHO, 2007). Anthropogenic activities involving pesticide use are rampant in the densely populated areas within the Kuja and Migori river basins of Lake Victoria (Rusongoza, 2003; Karani, 2005; LVBC, 2011).Whereas pesticides pollution has been documented in some

basins such as River Nyando (Getenga et al., 2004; Abong'o et al., 2014), Nzoia (Madadi et al., 2005; Musa et al., 2011), and River Sondu-Miriu (Wandiga et al., 2009), minimal documented information on their levels in fish ponds, wastewater lagoons and river waters in River Kuja watershed exist, hence the need to undertake studies on the pesticides environmental and human health challenges in River Kuja drainage basin. In addition, fish farming is becoming important in the region due to emphasis by the government on producing enough food to feed the public (GoK, 2007). In the target area, there is widespread use of pesticides in agriculture in controlling coffee, vegetable and animal pests (PCPB, 2012). When the pesticides are applied to farms and animals, they are likely to be washed down into fish ponds (Kellogg et al., 2002). This is because fish ponds are situated at the far end of the farm adjacent to the river, which makes it easy for pesticide residues to drain down into them. However, there is need to assess the impact of organic contaminant loading into this critical sector's environment as part of public health concerns (LVBC, 2007). In addition, pollution of the streams and rivers from organic contaminants such as organochlorine pesticides is increasing and the accumulation of these pollutants in water and fish to toxic levels is therefore inevitable, hence this study.

1.3 Significance of the study

Despite related studies which have been conducted in the region to show levels and exact quantities of pesticide residues in cultured and in fish grown in wastewater lagoons, as well as in fish pond effluent and their river waters downstream, gaps still exist in the study area that require further investigation. Therefore it is essential to determine the levels of pesticides in the water and fish from he study area that form part of man's food chain, with a view to establishing whether these fish are safe for human consumption. Moreover, there is need to monitor the effects, if any, of pesticide contamination on freshwater resources and naturally occurring foods such as fish.

1.4 Information gaps

The discovery of pesticides use in agriculture and its resultant improvement in food security issues globally was accepted and tossed as one of the best chemical discoveries. In addition, the recognition of organochlorine pesticides (OCPs) long term negative impact on the global environment and other non-target organisms has led to its use in agriculture largely being banned (Walker, 2000; Tao et al., 2013). Its negative impacts have slowly outweighed positive benefits, hence the need to eradicate their use both locally and internationally (Stockholm Convention, 2001). Some persistent organochlorine pesticides (POPs) such as endosulfan are found in the environment and can bioaccumulate in the organisms along the food chain (Sutherl et al., 2004).

According to studies done by Getenga et al. (2004) and Ndunda et al. (2018), minimal researchable evidence exist on OCPs pesticide residue levels in fish ponds, sediments and fish in River Kuja watershed to enable surveillance systems to be regular and be quantified locally within Kenya and in the Lake Victoria Basin. The levels of pesticide residues in each waterway or catchment and that of the immediate lacustrine ecosystem in the study area remain little known to date. Even as the debate about the quality of Lake Victoria waters rages in the media and the various researches done on the upstream catchments, there is little evidence that a well, targeted comprehensive analysis has been done on the lake or in all of its sub-drainage basins (Abong'o, et al., 2018). Monitoring of pesticide residue levels in water, sediment, and fish products within Lake Victoria Basin and its drainage system has recently attracted a lot of research interest. However, there is no conclusive evidence that a comprehensive analysis of organochlorine pesticide use, distribution and fate has been done in water, soil, sediments and fish in fish farming areas. Furthermore, data on River Kuja drainage system and any of its riverine systems in the heavily populated areas of South West Kenya calls for further assessment. This kind of data is necessary as it will be as a trigger and a boost to enhanced fish

farming practices as one of the policies currently being prioritized nationally in terms of improving human health and in harnessing food security under Kenya's Big Four transformative Agenda.

It is prudent to carry out and document these studies in order to control and manage total pesticide loading into our river waters be it riverine or lacustrine since total load could easily reach levels that are irreversibly damaging to the existing fragile ecosystems and their organisms, and this can result into chronic symptoms and death (PCPB, 2010). Previous studies by Mbabazi (1998), Kasozi (2001) and Wasswa et al. (2011) showed that ratios of lindane, endosulfan and that of DDT and its metabolites residues were significant in aquatic systems of Lake Victoria Basin. Their results indicated that previous use of these pesticides within the Lake Victoria Basin existed. The risks posed to the environment in general, human health and existing aquatic life by OCPs cause immediate or short-term occupational risks and reactions as well as toxicity from long-term exposure. Data from the study of organochlorine pesticide residue levels in fish farming areas as sources of human nutrition and relevant river waters such as River Kuja ecosystem which carry a fair share of sediments and nutrients deposition into Lake Victoria is therefore needed as a guide for future ecosystem policy formulation and management. Results from this study will form a baseline for related future investigations on organic contaminants in high altitude catchments within the Lake Victoria Basin. Minimal relevant scientific research study reports exist currently on the level of pesticides contamination in River Kuja watershed. The results of this study will form a basis for future reference and intervention with respect to impacts of pesticide residues on water, fish ponds, receiving river waters and cultured fish for human consumption.

1.5 Objectives of the study

1.5.1 Overall objective

To investigate the impact of organochlorine pesticide concentration levels in water, bottom sediments, farmed and wastewater lagoon fish in the watershed of River Kuja

1.5.2 Specific objectives

i. To identify and determine spatial and temporal variations of organochlorine pesticides in the target aquatic ecosystems in the watershed of River Kuja

ii. To identify and quantify spatial and temporal distributions of organochlorine pesticides residues in water, sediment and fish in River Kuja watershed

iii. To determine the relationship between physico-chemical parameters and concentration of various organochlorine pesticides in River Kuja watershed

1.5.3 Hypotheses

1. H_o: There are no spatial and temporal variations in organochlorine pesticides in River Kuja watershed

2. H_o: There are no spatial and temporal significant differences in the identity and quantified distributions of organochlorine pesticide (OCPs) residues in water, sediment and fish in River Kuja watershed

3. H_o: There exists no significant relationship between physico-chemical parameters and concentration of various organochlorine pesticides in River Kuja watershed

1.6 Expected outputs of the research

Overall, the project aims at achieving data on concentration of pesticides in farmed and wastewater lagoon fish, fish ponds water and their effluents in the target area. In addition, the project aims at achieving the following outputs:

(a) Identify organochlorine pesticides found in farmed and wastewater lagoon fish, fish ponds water, fish pond sediments as well as adjacent river waters, respectively

(b) Determine the concentrations of organochlorine pesticides in farmed fish, fish ponds water and fish pond sediments

The results from this study will enable the researcher to advice on whether cultured fish inhabiting River Kuja watershed are suitable for consumption by human beings and to disseminate the study results locally, regionally and internationally.

CHAPTER TWO

LITERATURE REVIEW

2.1 General overview

Pesticides are deterrents applied with an objective of attracting, preventing, stopping and destroying pests including weeds or animals (NIP, 2006). A huge amount of these chemicals are currently used in public health and other regions in order to do away with disease vectors and other pests. In addition, pesticides are compounds used in agricultural routine to help crops in farms and storage over destructive pests, and are known to be among the main constituents of basic laws of chemistry, for instance, involving combustion practices (Hassall, 1990). According to FAO (2006), pesticides are termed as any substance or mixtures aimed at eradicating animals, causing harm during, or otherwise changing yields, altering processing, storage, transport, or food marketing, agricultural commodities, wood and wood products or animal feedstuffs, or which can be given to animals for the eradication of insects, arachnids, or other pests in or on their bodies.

The first reaction to the use of pesticides was of applause as agricultural returns were happily received, although similarly threats and bad effects were quickly realized and documented (Elizabeth et al., 2011; Megan et al., 2017). This resulted into occupational risks to agricultural practitioners. Exposure to used pesticides led to environmental pollution as accumulation in the air, water and in the trophic levels posed a health risk to human existence including wild animals and associated wetlands (Musa et al., 2002; Kasozi et al., 2006). Other groups of pesticides contain destructive heavy metals such as mercury and arsenic attached to the carbon chain and this feature makes them to be biomagnified or be resistant and persistent for many years after use (Briggs, 1992; Jayaraj et al., 2016). In addition, chronic exposure of humans and other organisms to low pesticides doses or to those that are airborne do occur. Furthermore,

contaminated water and food may lead to serious toxicity due to residue accumulation in the body over a long period of time. Out of the huge number of pesticide chemicals manufactured or made for agricultural, horticultural and for veterinary and medical fields' purposes, a big proportion has been identified as being poisonous to fish and other aquatic life, though in normal use most are not likely to flow into freshwaters in biologically notable quantities. Possible health problems accompanied with chronic pesticide toxicity incorporate cancer, birth defects, neurological disorders, infertility, impotence, immunological disorders, liver and kidney damage; skin alterations and worsening of existing health problems (Jobling et al., 1995). Acute and sub-acute toxicity may also come from exposure to exceeding significant doses in people who are involved directly in the manufacture, formulation, mixing and in the use of pesticides or in suicide and homicide cases, in other words, during occupational practices. Exposure to humans may be through skin contact, breathing in or accidental swallowing. Acute toxicity symptoms differ with individual chemical used though this may incorporate symptoms such as numbness, sweating, headaches, fatigue, vomiting, central nervous system disorders, liver and kidney spoilage, coma or death (Turgut, 2007).

Many different chemicals that have been manufactured aim at controlling different pests. Botanic and inorganic chemicals have been applicable for years, but the 'pesticide problem' increased when organochlorine pesticides, growth hormone and herbicides became evident in the 1940s (Elizabeth et al., 2011), followed by other organic synthetic materials later. Some pesticides are grouped, depending on the availability or absence of the carbon atom changing them to be referred to as either living matter or non-living group (s). Non –living matter pesticides occur as a result of elements that occur in nature and have no carbon atom. While, organic pesticides are usually synthetic compounds like organochlorines which have hydrocarbon structures, differentiated from one another depending on the count of element (s), such as the chlorine molecule, joined to the carbon chain system (Wasswa, 2011). Pesticides

may get into water column by deliberate spraying or they may drift from general aerial spraying or be washed into rivers or lakes from land due to gravitational flow. Living organisms may channel pesticides into existing water bodies. Ultimately, fall-out from DDT known to be used well all over the world because of public health demand, makes every water body vulnerable to contamination. Despite their importance to man, pesticides are toxic and must be used well to minimize human exposure and retard health hazards. There are therefore governmental rules of pesticides in practice globally and analysis of pesticide residues in food is one way of evaluating effectiveness of the set control systems.

2.2 Organochlorine pesticide groups

As much as they are widely used as pesticides for agricultural or human health purposes, a known group of chlorinated compounds, such as organochlorines (OCPs) are classified as persistent organic pollutants (POPs) bringing adverse acute or chronic effects to humans, and which have high persistence once in contact with the environment (US EPA, 2002; Elisabeth et al., 2006). Some of the chlorine atoms get attached to the existing carbon chains of the organochlorines that exist in nature. Other atoms either from organic or chemicals existing in nature such as arsenic, mercury or manganese may get attached to the same carbon chain, hence changing the configuration and causing non-specific symptoms and effects to fish and other aquatic organisms in the environment (ATSDR, 2005; Abong'o et al., 2018).

Organochlorine synthetic compounds are classified into three main groups based on their chemical structure and this includes; hexachlorocyclohexanes (HCHs) and their isomers, the dichlorodiphenyltrichloroethane group (DDTs) and their metabolites: para-dichlorodiphenyldichloroethane (*p,p'*-DDD), para- dichlorodiphenyldichloroethylene (*p,p'*-DDE) and para-dichlorodiphenyltrichloroethane (*p,p'*-DDT) and finally, cyclodienes group of pesticides that includes aldrin, dieldrin, endrin aldehyde, heptachlor, endrin, endosulfan I and II, heptachlor epoxide, endosulfan sulfate and lastly, methoxychlor. These are the most studied

organic contaminants in Kenya (Getenga et al., 2004; Abong'o et al., 2014; Omwenga et al., 2016; Megan et al., 2017) as studies show that they have been extensively used in agriculture and for public health concerns and proven to have had effects on non-target to both aquatic and terrestrial organisms such as fish and humans.

2.2.1 The hexachlorocyclohexanes (HCHs) group

Previously before the IUPAC (2003) code naming was adopted, hexachlorocyclohexanes (HCHs) and group of isomers were formally known as the benzene ring compounds. These Hexachlorobenzene pesticides are known to be prepared through the chlorination of benzene whereby the analyte and the product both reach a state of equilibrium level like before the reaction was triggered, for instance, presence of aluminium bromide ($AlBr_3$). A benzene molecule consists of only two types of atoms, that is, only hydrogen and carbon in a circular shape, an example of such a stable compound is presented in Figure 2.1

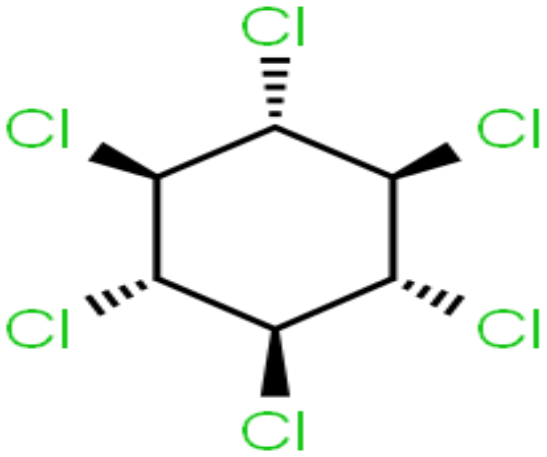

Figure 2.1: **A hexachlorocyclohexane compound, HCH (Guangping, 2014)**.

In nature, these organic compounds existed in the form of eight isomers normally formed either from human-initiated fires, forest fires intentionally initiated by cut and burn, or from volcanic eruptions but the most common occurring ones are the four isomers - alpha (α), beta (β), delta (δ) and gamma (γ) (HCH) isomers. Locally, γ-HCH is sold under the name lindane as the common name, and is mainly for the purpose of spraying to deter insects that attack green

vegetables, other edible nuts and grains, livestock, and in other domestic organism habitats (Osoro et al., 2016). In commercial set-ups, several forms of the technical-grade HCH as a combination of many isomers of HCH exist with naming of these different compounds coined following hydrogen atom position of the chemical benzene ring structure. Furthermore, other types of similar molecules can be detected in vapour form attached to smaller quantities of nature such as dust particles free in the air. γ-HCH exists in the market as an insecticide, powder or in liquid form, at times it is sold labelled as prescribed medicine or as beauty products like creams and lotion in treating, including controlling those tiny animals that live in between animal hair and the skin, and are known to attack humans as well (ATSDR, 2005), as essentially all the prescribed treatment strength is due to exposure to γ-HCH properties (lindane). Vaporization of HCH isomers that have been released into the environment, especially the atmosphere, could disintegrate due to contact or other factors in the free air.

Contamination of the environment by organochlorine pesticides is found in many places due to the fact these elements are highly lipophilic and do not readily decompose in the environment, hence, they stay in the environment and in the food web long after being applied, hence become chronic in the trophic level either in plants or in animal development patterns (Omwenga et al., 2016). They can also be transferred in great distance by air and water such that trace amounts are exist in samples studied globally (Alle et al., 2009). For instance, harzadous wastes in aquatic areas have been found to exist in quantifiable amounts, especially the United States sampled area of Cincinati, Ohio (US EPA, 2000). Studies in the past by the US Department of Health and Human Services (DHHS) (2005) have shown that persistence in exposure to most of these pesticides, especially the isomers of HCH may reasonably be known to cause carcinogenic reactions to human beings (cancer) as well as causing endocrine disorders, especially to mothers and their unborn infants.

Though the human cancer causing potential of lindane (γ-HCH) has not been proven conclusively, the United States Environmental Protection Agency (US EPA, 2004) has established suggestive evidence that lindane (γ-HCH) has cancer causing pathogens. US EPA went further to identify mixed HCH in use currently and α-HCβH to contain possible cancer causing pathogens while β-HCH could also contain cancer inducing products. This is then magnified during trophic level staging. The process of HCH isomer breakdown by fungi, algae, and bacteria in water, soil and sediments, though taking a long time, has been proven to bring forth less toxic substances to human foods such as fish and other aquatic organisms and edible animals that thrive in water and in terrestrial plants (ATSDR, 2005).

Generally, HCH pesticide isomers and its bioaccumulated products in the food web, in fish and in human bodies may be stored in a short time within the fat tissue due to its lipophlic properties. At the same time, their by-products can be expelled from human body faster in the form of urine of through sweat. Endocrine disorders is also known to occur in humans when air containing HCH isomers (α-, β-, γ- and δ-HCH) is inhaled in toxic quantities (Aktar et al., 2009). Other effects include haematological disorders, headaches, dizziness and causing mutations in the endocrine system and blood involving birth formations. Past studies have shown that occupational health hazards and related risks globally and locally have been reported in workers who come into contact with these HCH pesticide reactants and their by-products with detrimental results.

It has been reported previously that some workers who have ingested huge quantities either by accident or unknowingly, may have gone through seizures and even died (Abong'o et al., 2014). A few people who have been in contact with *γ*-HCH on a higher scale have reported blood group changes and uncontrolled disruptions of coordination in the brain, although a clear cut explanation of its cause has not yet been clearly known. In addition, a direct correlation linking exposure to *γ*-HCH and disorder of the blood in human beings is yet to be fully

established. Animals that consumed α-HCH or γ-HCH were observed to become unconscious or developed convulsions while others have developed insensible uncoordinated actions. Generally, available date show that HCH pesticide and their dissipated products produce internal organ illnesses in fish and humans when either of these gets exposed over a measurable period of time (WHO, 2008; Aktar et al., 2009). Recommendations and regulations on acceptable thresholds of how much of these HCH pesticides and their dissipated products are actually tolerable in natural drinking water for a given period without producing health hazards concerns were investigated and presented (Appendix 4).

Additionally, US EPA has given acceptable limits of 1.2 mgL^{-1} of HCH pesticides of drinking water for 10 days in a given period, especially to children, in order to deter negative impact to their health. To human adults, the agency recommends that they should not be exposed to 20^{-4} mgL^{-1} of HCHs in naturally occuring drinking water throughout their adult life (ATSDR, 2005).

2.2.2 Dichlorodiphenyltrichloroethane (DDTs) group

DDTs contain two aromatic (benzene) rings and in particular is colourless, has no smell and is a tasteless crystalline chemical compound which represent the main group in the organochlorine pesticide group (OCPs) compounds. The compound was originally manufactured and developed as a pesticide. DDT is one of the most well-known synthetic compound which was widely used, after the Second World War, to control insects in agriculture and disease vectors such as ticks in livestock as well as Public health concerns such as controlling disease causing vectors in humans, such as the tse-tse fly. An example of DDTs is presented in Figure 2.2 with colouration indicating the two carbon, benzene, rings (blue) having double (green) and triple (red) chlorine atoms attached to them.

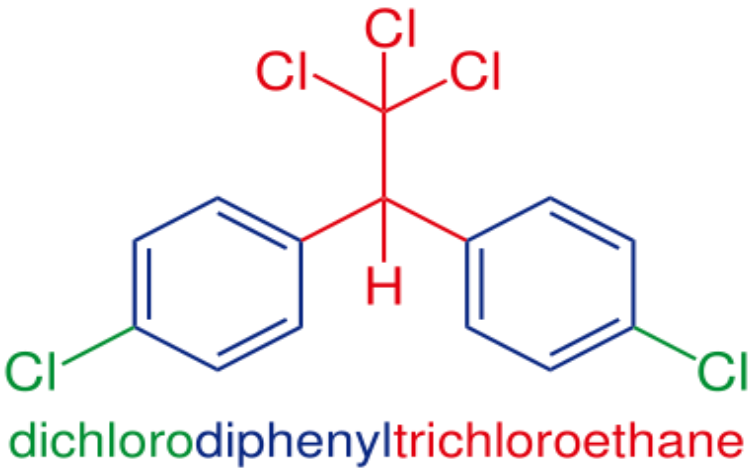

Figure 2.2: **Molecular structure of a dichlorodiphenyltrichloroethane, DDT (Gallistl, 2017)**.

Environmental conditions convert DDT, the parent compound, into *p,p'*-DDD and *p,p'*-DDE as well into *p,p'*-DDT metabolites and which are more toxic than the parent compound itself (Murty, 1986). Past studies by Aktar et al. (2009) have shown that DDT was widely used by the military as a deterrent against typhoid, malaria and other vector-bone diseases such as sleeping sickness, caused by the tsetse fly and in livestock keeping, this practice was maintained even after the war ended, the pesticide was widely used on multiple agricultural practises and in controlling diseases brought about by other infectious vectors in local and global enterprises. DDT is the most important compound among the organochlorine pesticides (OCPs) groups, and its accompanying metabolites *p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDT, which enter the environment as environmental pollutants or breakdown products of DDT (Figure 2.2). These metabolites are more persistent and bioaccumulate more easily in tissues than the parent compound and are also equally virtually everywhere in the environment. Availability of organic factors such as microorganisms in the air assist in breaking down DDT slowly into more soluble compounds, *p,p'*-DDE and *p,p'*-DDD (ATSDR, 2002) and these metabolites may be observed or recovered in water or in edible aquatic organisms such as fish occurring as contaminant residues many years after use. Exposure to these chemicals can be direct, for

instance, occupational exposure or can be indirect through ingestion of these foods exposed to the residues of these pesticides' chemicals (Ndunda et al., 2018). In other instances, bio magnification may occur under natural conditions and this process normally leads to accumulation along the food chain or along the trophic level, as has been researched on and documented to cause deaths to humans, in case exposure to these chemicals occurs over a long given period of time. Studies carried out in the north, for instance in the European areas indicate that OCPs, especially DDT and its main metabolite *p,p'*-DDE, persist in the air and water mediums and are regarded as main environmental pollutants (Aktar et al., 2009).

Based on the bio magnification strengths of DDT pesticide and resultant metabolites in aquatic foods including fish, sediments and other marine organisms, researchers in the past have most often targeted the compound in order to find out if contamination actually exist in the areas sampled as it is regarded as the main pollutant whenever they conduct pollution monitoring surveys (Aktar et al., 2009; Omwenga et al., 2016; Nyaundi et al., 2023). However, DDT is known to vaporize faster than other pesticides sprayed or released into the environment and acts effectively in disease vector control, such as malaria (Omwenga et al., 2016). Past studies show that DDT was detected in various food commodities, for instance, fish, poultry, milk, animal products and human fat (Kanja, 1989). In addition, available data show that DDT is linked to neuro-behavioural changes, endocrine disorder and is associated with premature births in humans and other mammals (Aktar et al., 2009).

In Kenya, there was great use of DDT in the 1950s and up to 1970s in controlling especially mosquito, malaria causing vector and the tsetse fly which causes sleeping sickness, especially in the infested areas within the low and highland regions of the Lake Victoria Basin (Kanja, 1989; Rao et al., 2007). According to documentaries presented by PCPB (2010), DDT was banned from being used in Kenya in the year 1987, much later than in developed countries such as Western Europe, whereby use of this compound was stopped in 1972. After its use was

banned, a recommendation was put forward to replace it with organophosphate pesticides which, though more toxic, are known to loose their energy content from the environment much faster (IUPAC, 2003). It is worthwhile to note that factory production of DDT pesticide compound is still being recorded for vector disease control in some countries globally, including Kenya, as previous studies within the Lake Victoria Basin and along its coastal waters indicate (Getenga et al., 2004; Omwenga et al., 2016; Megan et al., 2017; Abong'o et al., 2018). This compound has a high affinity to fats, whereby it dissolves much faster in it and other non-polar solvents such as carbon dioxide and hexane, and partitions readily into the lipid content of all living organisms and has been demonstrated to bioaccumulate (build-up of pesticide toxins in the tissues of an organism) and biomagnify, the building up of toxins at different trophic levels in a food chain. The concern about DDT's persistence and negative health effects has had a significant impact on agriculture and vector control (Nyaundi et al., 2023). DDT has ability to cause alterations such as inducing microsomal enzymes, homeostasis of biochemical processes and as well as to naturally occurring substances in the body in an organism's body such as fish in water and in humans exposed to it (US EPA, 2002). Although DDT is highly hydrophobic, hence insoluble in water, it can dissolve in most organic solvents. Studies show that it can progressively alter an organism's response to various drugs and other toxic compounds in the body. Furthermore, it can vaporize easily and faster under natural conditions,

hence, lost from air and aquatic environment. Large amounts of DDT pesticides use in the United States was for agricultural purposes, especially in herbicides control in cotton farming and this amounted to over 80% of total use before it was banned (Ndunda et al. 2018). Though DDT is banned in Kenya, it is restricted to be used only for public health purposes, such as in homes for the eradication of mosquitoes which cause malaria (Getenga et al., 2004).

2.2.3 Cyclodienes family of pesticides

Cyclodienes depicts several other pesticides compounds such as aldrin with a chemical formula ($C_{10}H_6Cl_8$) whose main use has been in the construction industry whereby it is applied to control infestation of insects such as ants which are known to destroy posts. Other examples include dieldrin, endosulphan and heptachlor pesticide compounds, whose function is majorly to destroy and control occurrence of harmful insects in domestic, agricultural and industrial set-ups. An example of a cyclodiene pesticide is presented in Figure 2.3

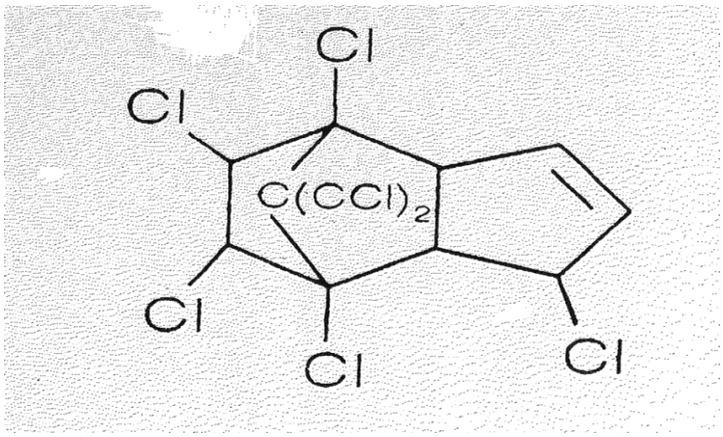

Figure 2.3: **An example of a cyclodiene (Endosulfan). Source: (US EPA, 2002)**.

Chlorinated insecticides that were banned nearly 40 years ago and contain chemical properties similar to DDT include endosulfans and are known to cause changes in the normal functions of the central nervous system (CNS). Human adults that have come into contact with high amounts of endosulfan in their lives or from toxic levels of this pesticide result in either death and actually suffer from headache, nausea, diarrhoea, vomiting, convulsions and other related symptoms (ATSDR, 2005).

Agricultural activities around the world are using endosulfan pesticide to control insect pests that affect cabbage, potatoes and other pests. Endosulfan, a highly toxic and an endocrine disruptor to both insects and to mammals including humans, is known to cause chronic and acute toxicity at a given period of exposure and is easily absorbed by humans through the

dermal tissue, the stomach during digestion and even the lung cavity during respiration processes. The International Union of Pure & Applied Chemistry (IUPAC, 2003) have reported low doses, of levels such as 30 μgKg^{-1} wet weight, causing loss of lives and instances of general body fluid toxicity have also been known to cause lethal neurological injuries (ATSDR, 2002). Although endosulfan remain banned in most European countries including Norway and France, and even far-east countries such as the Philippines, available data show that it is heavily in use in the United States and India in the control of sleeping sickness, preserving wood products, and used in urban farming. Endosulfan cyclodiene pesticide is banned and declared to be unsafe in the United States (Rao et al., 2007).

Documented laboratory experiments, US EPA (2004), have indicated that endosulfan toxicity is mainly recorded in the central nervous system (CNS) and the brain with more damage being recorded in human females who are more susceptible to its effects than in males. According to studies by United States Environmental Protection Agency (US EPA, 2004), endosulfan parent pesticide gets broken down into endosulfan sulfate which has molecular structures that is similar to the parent compound and its product is of pathological concerns, with estimated time it takes to be broken into two recorded to be approximately five years. Research by Food and Drug Administration (FDA) body allows not more than 24 μgKg^{-1} of endosulfan cyclodiene pesticide on commercial tea products (US EPA, 2002).

Endosulfan pesticide is critical to human health and the environment as its apparent persistence and toxicity to many non-target organisms such as fish and plant tissue is known (Tomkin & Merriweather, 1992; Shetty et al., 2000). It is known to break down within a few weeks of application especially on crops, may take years to completely breakdown or disintegrate. Additionally, because of its lipophilic properties, endosulfan does not easily dissolve in water but is known to stick to sediment material undissolved in water surface and attaches itself to rock and soil particles at the river or other aquatic habitats.

Laboratory assays have indicated that this toxic pesticide can encourage growth of human female breast cancer cells, however, there is little available data to show that endosulfan is carcinogenic to human beings' mammalian glands (Grunfeld et al., 2004). The other organochlorine synthetic compound known for its toxic effects to humans is aldrin, known to be very resistant to leaching into groundwater but which easily bio concentrates in food in its simpler form. Its toxicity to an adult human being is estimated at about 5 g, equivalent to 3 $mgKg^{-1}$ wet weight for a sixty kilogram body weight of an adult person. Aldrin, which is rapidly metabolized by both plants and animals into dieldrin during dissipation, easily concentrates in animal meats and the primary sources are in dairy products, with symptoms of aldrin intoxication including vomiting, general malaise, nausea, dizziness, headaches, and followed by muscle twitching and convulsion and may bind strongly to soil particles.

As aldrin dissipates into dieldrin in its simpler form, its residues hardly exist in large quantities but only in small amounts and is rarely found in foods and animals. Although aldrin stands banned in Kenya, it has previously been used in protection of wood and wood products from termites in the building industry and in controlling soil insects affecting potatoes, corn, protecting rice weevils in water and against grasshoppers that affect fodder (Getenga et al., 2004; Saoke, 2005).

Furthermore, another important way that pesticides are lost into the atmosphere is through vaporization, whereby the contaminants escape from the aquatic environment. Other studies have shown that human immunity to disease is also affected by exposure to cyclodienes (Gangemi, 2016). Due to their persistent nature and their strength to repel water molecules, limited information exist to show that aldrin pesticide can alter the human immune coordination ability. In addition, research by the International Authority for Research on Cancer (IARC, 2011) show that currently limited data exist that shows that aldrin can trigger cancer in humans and that available data only show limited evidence in experimental samples (ATSDR, 2005).

Although endrin, as another organochlorine synthetic compound, is known for its pathogenic strength, the same research by IARC also show that there is limited evidence for endrin pesticide to harbour significant amount of cancer causing cells to humans and to the animals accessed for use for experimental purposes (Fisher, 1999). However, when in significant quantities, it can be highly toxic to fish. Previously it has been used in controlling mice and moles infestation that destroy crops in farms and in storage. Studies show that it can contaminate surface waters through run-off during wet seasons and can enter the atmosphere through vaporization of its compound and is mainly used as an insecticide on stored crops such as cotton and grains.

Limited data exist to show that endrin has significant carcinogenicity strength, level of cancer-causing cells in humans hence, due to this, it cannot be classified at same level as dieldrin. It is also known not to accumulate in animal fat tissue in high quantities such as that of dieldrin cyclodiene pesticide as is easily metabolized by animals during respiration processes; limited experimental evidence exist to show that endrin may also depress an organism's immune ability to fight disease (ATSDR, 2005). Local conditions such as weather pattern variations, seasonality, level of adipose tissue and water chemistry especially in cold regions may affect the half-life of this compound to last up to twelve years, providing humble time for it to bio-concentrate in organisms although it does not last long due to high level of vaporization. Globally, endrin cyclodiene pesticide has seen its use severely minimized in many countries and even banned altogether (MacDonald et al., 2000).

A study by Fisher (1999) on aldrin, dieldrin and endrin pesticides effect on factory employees mainly to find out if occupational contamination did occur, results showed that endrin was not recorded in their body tissues, but in cases of accidental and acute over-exposure. However, the study found a significant amount in the bile tract and in liver cancers of the sampled factory employees. Studies have shown that it can be detected as far as in the arctic freshwater, mainly

due to its properties such as high stability in environment, hydrophobicity and does not evaporate easily. Consumption of food contaminated with endrin pesticide is the main source of contamination to humans and fish. However, studies by WHO recommend for contemporary intake to be below acceptable daily threshold of 0.0002 $mgKg^{-1}$ of adult body weight. Previous surveys involving edible foods have not included endrin, therefore, recent experimental results is not readily documented (ATSDR, 2005).

Dieldrin is an organochlorine pesticide which, due to its strong affinity to soil, therefore highly resistant to percolation into below ground aquifers, gets heavily relied upon by agriculturalists to principally control insect pests such as the wood borers, textile pests and termites whose habit is mainly is in the soil and several other similar vectors whose life history include growth in the open and tilled land (WHO, 2008). Major primary contaminant sources to humans include consumption of animal meat, butter and milk as well as ingestion of other dairy products.

Recent cancer research carried out by the World Cancer Research Fund International (IARC, 2011) whose major duty is to carry out experimental and laboratory research with authority on cancer prevention research which is related to weight, nutrition and physical works has drawn conclusions that negligible data, hence inadequate evidence is available to show that dieldrin pesticide exposure contain carcinogen pathogens on humans and that minimal evidence exist for use of experimental animals to show that it can affect human and other aquatic organisms' immune response. Similarly, from these results, IARC which estimates global incidences of infant mortality and deaths occasioned by cancer cases concluded that dieldrin as an organochlorine pesticide can be classified into group three cancer causing pesticides.

Fish exposed to dieldrin, especially for experimental purposes has been found to die within a given time when exposed for longer to values ranging from one point one to forty one (1.l – 41 μgL^{-1}) in natural water. Locally, Kenya is one of the countries that has declared dieldrin

pesticide banned and its use severely restricted. It is known to cause negative impacts to public health as well as to the environment. The short-term damage caused by dieldrin, whose half life in an organism, is approximately 5 years, has been proved to be quite various to insects that inhabit the aquatic media as well. It is classified as one of the persistent organic pesticides (POPs) as it may persist in nature and harbours hydrophobia properties. This cyclodiene pesticide, though it can vaporize from the soil, is known to bio concentrate under natural conditions and in foods such that it can be detected along the trophic level, hence detectable along the food web. Due to its persistent nature and high lipophilicity, dieldrin provides the necessary conditions of bio-concentration and bio-magnification in fish and human tissues. Past studies have shown that dieldrin has been detectable in arctic water, air, and in other aquatic organisms including fish (Montgomery, 2000). This is due to the fact that it has low volatility, capacity for long-range transport in air and water, is highly soluble in fats and can persist in the environment for long periods.

Aldrin and its dissipated compound dieldrin contaminants have been detected in water, human breast milk, fish, air, soil, birds and in mammals, including human samples. The public normally gets exposed to these harmful organochlorine pesticides through diet as the main source. A study by FAO and WHO (2006) jointly recommend a daily intake dose to be 6.0 μgKg^{-1} of body weight per person but available data from studies carried out in India show that this was surpassed to be as high as 19 μgKg^{-1} of body weight.

Heptachlor is another cyclodiene pesticide which is used as an insecticide to control cotton pests, crop pests, and even in combating malaria; it evaporates easily, and hence its loss into the atmosphere is faster after use (Roberts et al. 2009). In nature, heptachlor is dissipated into its simpler form known as heptachlor epoxide whose power to damage an organism is comparable to its parent compound heptachlor and studies have shown that it is easily stored in the adipose tissue of an organism (Ndunda et al., 2018). Contamination is through contact

and is used basically against termites and soil insects. It gets attached readily to bottom sediments, and bio concentrates in adipose tissue of both terrestrial and aquatic organisms (US EPA, 2004). Although limited evidence is currently available to show that cyclodienes such as Heptachlor may create low immunity response in humans, several developed and developing countries have banned the use of heptachlor cyclodiene pesticide, Kenya included (NIP, 2006). Heptachlor has high hydrophobicity properties, but can dissolve in other organic solvents including ethanol and methanol as well as in available animal adipose tissue. Occupational pesticides contamination involving workers who were in the industrial production of heptachlor showed a high amount of cancer of the bladder in their bodies, indicating that prolonged exposure is harmful to human health, proved so by the fact that there was no previous recorded bladder cancer causing ingredients had been in use at the sampled factory.

Furthermore, it became difficult to interpret the results due to a smaller number of the deaths recorded. Even if deaths from narrowing of veins and arteries were observed, especially those leading to the brain, no loss of lives from the liver or the organs that produce and store bile, essential for production of insulin, were recorded (NLM, 2010). The toxicity dose of heptachlor in experimental organisms range between 4 $mgKg^{-1}$ wet weight in mice to 116 $mgKg^{-1}$ in hare and indications of attack include seizures and jerks and lack of coordination.

An additional organochlorine pesticide of significant interest is methoxychlor, which previously has been in use in place of DDT as its molecular structure and properties are similar to DDT pesticide. Although a possibility of a few metabolites of methoxychlor of some significance may exist, studies show that it does not bioaccumulate in nature but it gets metabolized easily and faster; bio degrades and vaporizes easily (ATSDR, 2002). After methoxychlor cyclodiene pesticide has been ingested and absorbed by living organisms, it is quickly released and does not biomagnify in the trophic tree. Methoxychlor's presence in air or in water is dependent on agricultural farming seasons as it is an insecticide applied mainly

in livestock and crop farming and for public health purposes to guard against malaria incidences. In addition, it can be sprayed against cockroaches and fleas in domestic pets (Smith et al., 2001).

Aquatic organisms such as fish metabolize it and change it into less poisonous substances and therefore it does not build up to high poisonous residue levels as regards to bioaccumulation effects. Documented literature has shown that methoxychlor biodegrades into 2 halves in distilled water in 37 to 46 days but in natural waters of the USA, the division moment can be in 2 to 5 hours (Smith et al., 2001). Experimental mice fed on methoxychlor diet at measured quantity of 500 μgKg^{-1} day^{-1} for two years; showed practically no weight gain, with a conclusion given that it may not have had appetite other than poisonous symptoms of the pesticide in the sampled food (ATSDR, 2002). For drinking water, the European Protection Agency (EPA) has put forward acceptable threshold limits of 40 μgL^{-1} as the maximum contamination level (US EPA, 2004).

Once methoxychlor has been applied especially in open ground, it settles there as it does not readily dissolve in water even with run-offs. Additionally, presence of optimum oxygen quantities in the ground encourage methoxychlor pesticide to vaporize and biodegrade faster than in grounds with low oxygen distribution, as de-oxygenated sediments found in aquatic environment do not encourage biodegradation of the pesticide (Smith et al., 2001). High underground water aquifers together with higher application frequency may present a greater risk to groundwater and to human health (Wasswa, 1997; 2011).

Methoxychlor, commonly available as a General Use Pesticide (GUP) vaporizes at a slower pace, but the rate of evaporation contributes to the product cycling in the air or water. Studies have shown that greater quantities of commercial methoxychlor, of approximately 90% purity, could have estrogenic or reproductive effects (Madadi et al., 2005). The European Protection

Agency (EPA) has classified methoxychlor pesticide acute oral lethal toxicity risk to be in the toxicity level four matrix (EPA, 2004; Kayla et al., 2022).

2.2.4 Organochlorine pesticides' toxic effects on aquatic organisms and their fate in the environment

Organochlorines (OCPs) are a class of carbon chains having a chlorine atom attached to them and are classified as persistent organic pollutants (POPs) that are used as pesticides and which stay for a long time in the environment long after use, with negative implications on human health. Aktar et al. (2009) argues that even though organochlorine insecticides stand prohibited from use in almost all the European countries and in the United States in the last almost 4 decades, most of these compounds were used successfully before the ban in eradicating malaria and typhus, an infectious disease which was common during periods of low food supply or during war time. Typhus bacterial disease mode of transmission is through chiggers, ticks or by fleas. Furthermore, past studies by Food and Agriculture Organization of the United Nations (FAO, 2005) have shown data on use of different pesticides for various purposes. Therefore, this results indicate that over 40% of all pesticides currently in use belong to the OCPs group of chemicals.

Currently, most of those extensively preferred organochlorine pesticides for example DDT, hexachlorocyclohexane (HCH), aldrin and dieldrin and other cyclodiene pesticides used for different pests in Third World countries of Africa and Asia (FAO, 2020; Kayla et al., 2022) are those belonging to chlorinated compounds, this is partly due to the fact they are usually sold cheaply and circulated in various common names in the market hence are easily accessible and affordable by most users. Many of these commercially available pesticides are made to alter normal growth pattern of both plant and animals including fish leading to dysfunction and reduced vitality (Lallas, 2001). The environment, mostly composed of water, air and soil is the backbone of most contamination by pesticides as it bears the blunt of the negative effects of

these contaminants and threatens the inter-dependence of plant and animal in both terrestrial and aquatic ecosystems (Kayla et al., 2022). Even though global estimates indicate consumption of pesticide is approximately over 2.5 million tons annually, losses and negative implications brought about by pests result into approximately a third of the global agricultural food and other commercial productions each year (Hoving, 2007). For instance, in India, annual food losses are estimated to over 6,000 Rupees from contributing factors that include diseases (26%), birds (10%), weeds (33%), insects (20%), rodents, and others (11%).

Previous studies on the pest problem in India is compounded by emergence of newer pests and diseases due to, probably climate change and other related human factors (Rajendran et al., 2003). Every year, the magnitude of the problem increases by the appearance of newer pests and diseases as greater use of OCPs in achieving higher agricultural production itself leads to increased pollution of environmental compartments such as the aquatic system, bottom sediments, and air. Documented data, Pimentel (1995), have put forward facts that due to the ability of most organochlorine pesticides to dissolve in non-polar solvents such as fats and other chemical compounds including hexane, affinity to bioaccumulate in edible foods such as fish, in addition to having ability of long range transport, enables these contaminants to pollute soil, water and air, occurring long seasons after application.

Furthermore, results from this study indicated that a little percentage (0.3%) of sprayed pesticides goes into specified pest while 90% go elsewhere into non-target organisms. According to a study by WHO (2006), approximately 80% of applied organochlorine pesticides are in use in developing nations which, unfortunately, occur in hot and humid climatical conditions that favour pest multiplication. Various types of pesticides are encouraged by the users in these areas for commercial purposes and to increase food production in Third World countries where crop loss is high because of extreme temperatures and increased humidity, and which encourage fast growth of harmful pests (Kannan et al., 1993; Lakshmi, 1993).

Due to lack of conducive rules and regulations, improper market policy uptake and lack of knowledge by the existing general population, agricultural workers from Third World countries get exposed to high levels of agricultural pesticide contamination, including other non-target aquatic and terrestrial organisms (Smith et al., 2001; Rutaisire et al., 2009). The most common method of exposure hence the primary form of contamination, especially to most users such as farmers in developing countries, is predicted to be through occupational hazard (Konradsen et al., 2006) in one way or the other may lead to human health concerns and environmental pollution linked to pesticide use (Rajendran et al., 2003). Similarly, other risk groups include factory workers involved in laboratory formulation of the relevant compounds, mixers, as well as other relevant production employees, all classified as occupational hazard groups. Further down the chain are those affected by the already contaminated ecosystem or habitat such as aquatic foods including fish and those who consume them such as predators in the upper trophic level including humans whereby an estimate from previous data indicate that loss of lives and other terminal ailments because of pesticide contamination lead to approximately a million in a year globally (Mwevura et al., 2002).

Over exposure and continuous use or wrong application of pesticides encourage the risk and hazard to both human and environmental health as it interferes with other ecosystem services such as water quality aspects, as over 90% of applied pesticides are documented to alter the normal health functions of many aquatic and terrestrial species such as fish and humans. Pesticides affect the life of many aquatic ecosystems where a large number of microorganisms, invertebrates, plants and fish live (FAO, 2005; Stadlinger et al., 2013). Studies in India where large quantities of pesticides started since the 1960s when the 'Green Revolution' was initiated and maximum agricultural based pesticides were used to achieve more food production due to increasing population have produced detrimental and far reaching effects to human health and aquatic ecosystems (Babu, 2005).

2.3 Organochlorine pesticides residues in fish in the world

A large number of developed countries, especially in Europe and the United States, have taken it upon themselves to investigate and document the status and effects of OCPs exposure to water, humans and the environment. This is due to the fact that these contaminants' persistence, biomagnification in food chains and their detrimental effects on non-target organisms contain far reaching negative results (Chau and Afghan, 2002). For instance, investigations on six different fish species that had been collected from Lake Michigan between 1929 and 1966 and preserved using ethyl alcohol in a local Museum were carried out in order to find out the probable time that these sampled fish may have started to get exposed to organochlorine pesticide contaminants (Grob and Barry, 2004).

The results from this study showed that DDT pesticides appeared in 1949, four years after the first time that the area had been sprayed or exposed to these pollutants for industrial and agricultural purposes, while dieldrin was recognized in that studied environment in 1955 (Torres et al., 2002). Furthermore, other related studies carried out in subsequent decades, up to the year 1985 on organochlorine pesticide residue levels in aquatic organisms such as fish in the sampled area, showed that DDT concentrations ranged from undetectable to 92.2 μgKg^{-1} on wet weight basis (Sereda et al., 2008). In addition, DDT pesticide concentrations exhibited far much higher residue levels than other pesticide groups such as HCH and its isomers as well as those of cyclodienes, for instance, heptachlor, heptachlor epoxide, aldrin and dieldrin (US EPA, 2004).

The Great Lakes of North America viz; Superior, Michigan, Huron Erie and Ontario presents a unique environment and contain geographical features in that they are all connected and drain a large catchment area into the Atlantic sea. However, investigations carried out in 1970 that involved coho fish samples from Lake Michigan indicated a concentration on residue levels that was 5 times more than that was recorded from fish sampled in other Great Lakes of North

America. (Wassaling, 2001; Torres et al., 2002). The decision to use coho salmon samples obtained from Lake Michigan aquatic system offered a unique scientific opportunity to create major public awareness on the negative impact and environmental risks brought about by use and exposure of DDT and its metabolites after dissipation. The results from the study indicated that coho fish from Lake Michigan was highly contaminated and presented major public health and environmental hazard concerns to those who consumed them at that time (Sadasivaiah, 2007). Studies that have presented status and OCPs contaminant levels in aquatic organisms and the environment in Europe is majorly from those samples obtained in the Baltic Sea and its drainage basin.

For instance, investigations on the biota and on the cod fish obtained from the littoral zone South west Dasfjordan coastal area of the Baltic Sea in 1969 showed total DDT of 0.57 to 2.15 μgKg^{-1} (wet weight) contrary to those sampled in Sonef area, adjacent to an intensive horticultural fruit production area, which contained a concentration level of 1.98 to 33 μgKg^{-1} wet weight of DDT (Sadasivaiah, 2007). Similarly, samples of cod studied in 1971, contained 90 to 135 μgKg^{-1} (wet weight) of DDT pesticides in liver tissue and the concentration obtained from liver fat content was noted to be highest concentration level, at 576 μgKg^{-1} (WHO, 2008). A preliminary study carried out in fish ponds in North Eastern France to find out how management can affect pesticide profiling in cultured fish indicated that high amounts of pesticides used in farms coupled with shorter durations of crop rotations and bare soil practices led to high contamination levels of sediments and fish (Sereda et al., 2008; Lazartigues et al., 2013). The authors reported that reducing amounts of pesticide used by adopting policy changes with favourable public participation, carrying out long-term crop rotations and adapting pond creation in tandem with fish farming practices and watershed management, all could reduce pesticide levels in edible fish and contribute to a better sustainability of extensive fish farming.

A study on the potential of barrage fish ponds for the mitigation of pesticide pollution in streams as knowledge on their effect on water resources was deemed necessary for the development of appropriate water quality management plans at a regional scale. Therefore, a 1-year field monitoring of pesticide concentrations and water flows measured upstream and downstream from a fishpond in North East France was done to evaluate its capacity in reducing pesticide loads. The highest concentration in the inflow to the pond was 26.5 μgL^{-1}, while the highest concentration in pond outflow was 0.54 μgL^{-1} (Gaillard et al., 2015).

Other regions have published investigative results of organochlorine pesticide content in fish and in the environment as well. For instance, studies involving levels and patterns of PCBs, DDT and HCH organochlorine pesticide groups obtained from bottom sediments and Tilapias (*Tilapia mossambica*) freshwater fish collected from Hong Kong inland drainage and other water bodies upstream. Similar samples were obtained from newly constructed fish pond areas within Hong Kong for comparison purposes and produced the following results: DDT, HCH, and PCB groups in river sediments were in the concentration range thus; 2.82 to 8.63 μgg^{-1}, 0.05 to 2.07 μgg^{-1}, and 43 to 46 μgg^{-1} respectively. These concentration residue levels indicated a statistically significant ($p<0.05$) higher level than values obtained from fish pond sediments, $p<0.05$ (Torres et al., 2002).

Hepatic levels of organochlorines were observed in deep-sea fish from the Nord Fjord in Norway. Benthic fish from sampled bays in Norwegian waters were investigated to show PCB and other OCP pesticide residue levels. Results from this study indicated that the levels exceed acceptable thresholds by a factor of 1.5 to 50 μgL^{-1}, and DDT metabolites by 1 to 2 magnitude level and this was attributed to DDT pesticide use in nearby fruit growing farms which resulted in fish getting exposed to the contaminant measured. In addition, the study tried to relate these results to DDT concentration decline levels measured in 2005 in Nord Fjord fish to that of deep-sea fish in Norwegian waters and tried to evaluate those elevated levels towards land,

especially as PCB sources had not been recorded being in use since the studied period. Although HCH group of compounds were also not recorded in the study, the conclusion was that littoral zones and estuaries efficiently stored atmospheric pollutants. Chlordanes and HCB were less important, and were not detected (Torres et al., 2002).

Similarly, an investigation was carried out in 1974 involving total DDT from fat content in sampled Barbus *spp*. fish from two targeted rivers in Iran. The results showed the sum DDT in fat content to be in a range of 60.6 μgKg^{-1} body weight to 196 μgKg^{-1} body weight. Other OCPs residues recorded from fish in nearby dams, catchment and reservoirs was < 25 μgKg^{-1} body weight (Sadasivaiah, 2007). OCP patterns and their residue levels such as DDT group, HCH and its isomers as well as selected PCBs were studied from bottom sediments and in *Tilapia mossambica* fish obtained from other sampled water bodies in Hong Kong waters including from fish ponds with results showing a range of DDT, HCH, and PCBs in river sediments were 2.82 to 8.63 μgg^{-1} body weight, 0.05 to 2.07 μgg^{-1}, and 43 to 46 μgg^{-1} body weight, respectively (Torres et al., 2002).

Furthermore, DDT obtained from sampled areas of the Amazon drainage basin of Brazil was investigated to detect main metabolites, and other organochlorines in sediments (n=10). The samples were synthesized by capillary column of the Gas Chromatography coupled by Electron Capture Detection (GC-ECD) and residues obtained mostly in the sampled bottom sediments in concentrations of the range from 10 to 100 μgKg^{-1} (ppm, dry weight). The presence of *p,p´*-DDT in most of the samples reflected the use of this insecticide against vectors of malaria between 1946 and 1993 which led to its ubiquitous presence in the environment of the Brazilian Amazon (Torres et al., 2002).

Another study was carried out involving 50 fish species in the Pearl River mouth towards the ocean and in Daya Bay of the South China Sea, to document DDT metabolites and HCH organochlorine pesticides (OCPs). The results from this study were that DDT pesticides

observed in the sampled fish were higher than the other OCPs in the same area, this is when the results were compared with those from other regions of the same country (Klumpp et al., 2002) indicating a similar trend in contamination of existing aquatic systems, hence the available aquatic fauna and flora. The presence of organochlorine insecticides in the aquatic fauna and flora has not been clearly understood and can even be found in far lying regions from where the pesticides were sprayed. For instance, studies by Mwevura et al. (2002) documented occurrence of DDT and γ-HCH in two freshwater fish species thus; in the Putitor mahseer (*Tor putitora*) sampled tissues and in the Snow trout (*Schizorhorax richardsonii*) fish organs that thrive in the temperate zones of the Himalaya Mountain ranges.

Similar studies involving different fish species were also carried out from different geographical areas along Queme river in the Republic of Benin, mainly to find out if the aquatic fauna and flora could be contaminated and is in danger of exposure from toxic OCPs remnants resulting from human domestic and industrial activities along the river, such as use of these contaminants to carry out illegal fishing and if cotton growing and farming along the low lying areas nearby could contaminate the fish in Queme river, increasing the probability of pesticides' exposure from gravitational run-offs during wet seasons.

Metabolites of DDT and HCH isomers had highest frequency of occurrence and identified pesticides in fish muscle tissue, α-endosulfan, β-endosulfan, dieldrin, and lindane (γ-HCH) were also detected with results indicating pesticides residue levels in sampled fish having a range between undetectable to 1,364 ngg^{-1} lipid weight. Based on results recorded, the conclusion obtained from this study was that the daily intake of chlorinated pesticides pesticide residue levels in natural water of Benin river and fish were within FAO and WHO (2006) acceptable standards, hence public health risk resulting from consumption of the sampled fish from Queme river was not harzadous and therefore did not pose an immediate health risk (Elisabeth et al., 2006).

2.4 Organochlorine pesticide residue levels in fish from Kenya

Lake Victoria Basin region experienced an upsurge of the use of organochlorine pesticides since the 1940's, mainly in controlling the tsetse flies and mosquitoes, but implementation of policy changes of 1986 involving Pest Control Products Board (PCPB) parastatal body in Kenya restricted and banned these pesticides from use. Past documented data (Wasswa et al., 2011) from Sub-Saharan African countries indicate that these countries import approximately 50 billion Kenya Shillings worth of annual pesticides purchases, which approximately account for about 3% of global pesticides import and export trade (PCBP, 2009).

Furthermore, studies by Ndunda et al. (2018) show that due to a growing population and the need to feed the ever increasing human population, pesticides use in the Lake Victoria Basin between 1990 and 2000 increased by almost 200% compared to about 20% in the developed countries. There is therefore urgent need for regular checks and balances of pesticides residue loads in the Third World countries, especially Africa, including those in the Lake Victoria Basin aquatic ecosystems (MDG, 2000; Omwenga et al., 2016). Previous studies on pesticide concentrations in fish and bottom sediments in Kenya indicated significant levels in sampled water and in terrestrial environment. However, there is need for consistent and regular monitoring of these contaminants as fish form a major protein source (Ndunda et al., 2018) for sustained environmental and human health purposes.

In a study conducted to investigate organochlorine pesticide residue levels in Kenya's Rift Valley Lakes, Pullin et al. (2004) documented undetectable to insignificant DDE residues in sampled fish from Lake Naivasha. Similarly, initial pilot survey on possible contamination by some metals and chlorinated hydrocarbons on fish in Lake Nakuru in Kenya by World Bank (2013) indicated insignificant dieldrin, *p,p´*-DDE and DDT contaminant levels. On a wet weight basis, concentration levels documented involving the three pesticides were below 0.007 μgKg^{-1} in Lake Nakuru fish samples. In the same survey by World Bank (2013), analysis

involving an African catfish from Lake Baringo, reported high levels of 2.13 μgKg^{-1} body weight of DDE organochlorine pesticide contamination.

Other organochlorine pesticides contamination studies was carried out by Kanja (1989) who analysed residue levels in Kenyan mother's milk while he also analysed sampled fish collected in the littoral zones of Rusinga Island in Lake Victoria, Kenya, in which the targeted samples were treated to four different categories and labelled as cooked, dried, fresh or smoked fish samples. Results showed that pesticide residues was detected in only 3 treated categories of fish as the cooked sample did not record any OCPs contaminant residues. Overall, total DDT residue concentration levels were recorded to be in the range of 0.031 to 0.367 μgKg^{-1} fish body weight while that of the smoked fish sampled showed the highest mean of 0.149 μgKg^{-1} body weight of DDT metabolite pesticides.

Organochlorine pesticides contamination of Lake Nakuru *Tilapia grahami* (Boulenger) fish studies by Elizabeth et al. (2011) indicated that residue levels were low to non-detectable. Other related investigation by Mitema and Gitau, (1990) showed that organochlorine residues in fish from Lake Victoria were below the maximum residue limit. Furthermore, an elaborated organochlorine pesticide residues study by Mugachia et al. (1992) on fish obtained from Tana River at Masinga dam site, and Athi River at Sabaki point at Malindi and lastly in Lake Naivasha, indicated OCPs concentration range was within levels obtained and reported from other investigated areas earlier in the Lake Victoria Basin.

However, values obtained of the isomer lindane (γ-HCH) levels in the analysed fish samples in three stations exceeded the maximum residue threshold set by the World Health Organization (WHO) and Food and Agriculture Organization (FAO) of the United Nations. As reported earlier in this study and also due to documented persistent negative effects of organochlorine pesticide use in the region, heptachlor and endrin cyclodiene pesticides, the Pest Control and Products Board (PCPB) in Kenya banned them from use as insecticides in

1986 (PCPB, 2012). In 2004, other cyclodienes (dieldrin and aldrin) faced the same fate as they were allowed only for termite control in the construction sector. In the same year (1986), DDT was also banned for use in agriculture and related Public Health activities in Kenya such as spraying for control of mosquitoes that cause malaria (Pest Control Products Board, 2010).

2.5 Pesticides and associated health effects

The most common pathways of exposure to organochlorine pesticides contaminants includes consumption of treated food sources, or at times being in close contact to areas glaced with pesticides such as farms or lawns within human settled areas which may expose the general population to these residues. Many international or local regulatory bodies such as World Health Organization (WHO), Food and Agriculture Organization (FAO) or National Environment Management Authority (NEMA) often indicate pesticides residues maximum acceptable standards in foods in the local market. Other independent studies have indicated that humans are often exposed to pesticides through ingestion, consuming contaminated food such as fish (Rutaisire et al. 2009; Kinaro et al., 2015) or by direct inhalation of contaminated air and in addition, through water or dermal absorption. Past studies by Kanja (1989) and similarly by Bouwman et al. (2012) showed that OCP pesticides were detected in human breast milk, adipose tissues, semen, blood, faeces, umbilical cord blood, urine, amniotic fluids and infant meconium. Existing government, regional and international governments have played a major role in the control of many of these harmful chemical residues, especially derivatives of the chlorinated pesticides, building up to toxic levels in the aquatic environment. If not closely regulated, many of these residues exhibit bioaccumulation which build up to harmful levels in the body as well as in water and in other aquatic organisms (Kinaro et al., 2015; Ndunda et al., 2018).

Furthermore, children born to mothers whose diet had been formally been exposed to hexachlorocyloxane (HCH) isomers, for example lindane (y-HCH) or cereals that had been

treated by alpha HCH pesticides developed a condition named as pink sore (hormonal imbalance or infection) and experienced high infant mortality of ratio (IMR) of 9:1 (Engel et al., 2000; Jurewicz et al., 2008). In other words, consuming foods that are exposed to dieldrin, aldrin and hexachlorocyclohexane (HCH) isomer residues are linked to illnesses and death but this depends on the magnitude and duration of exposure. Severe weakness, hyper pigmentation and photosensitive skin lesion form some of the illnesses and acute effects caused by consumption or direct exposure of OCP pesticides (Stober, 2000; FAO, 2020a). For example, research has shown that breast feeding mothers who consume cereals which are treated with HCH isomers pass on this contamination to their sucking children.

In humans, OCPs concentrations have been linked to birth of premature births and children whose weight is below the WHO/FAO global acceptable standard measure and whose mothers have a blood concentration above 10 μgKg^{-1} of DDE and 9.8 μgKg^{-1} of β-HCH. Exposure to these pesticides also alter levels of maternal thyroid hormones during human gestation period. Metabolic activities, natural secretion or storage in the fatty tissues are symptoms indicating occurrence of pesticide residues in the human body. As most OCPs are lipophilic (Wandiga et al., 2009), those pesticides that are not ingested or expelled are often stored in the fatty tissue, especially in fish (Engel et al., 2000). Adverse human health failure such as birth defects or reproductive defects have been documented to occur due to exposure to the OCPs (Stober, 2000). For example, employees who work at pesticides production industries and those who spray crops in farms face greater risk of occupational hazards (Engel et al., 2000). Already, OCPs are implicated in abroad range of adverse human health and environmental effects including immune system dysfunction, endocrine disruption and cancer related diseases (Garabrant et al., 1992; WWF, 1999).

Available data (IUPAC, 2003) show that egg shell reduction in the Baltic Seal's development to maturity is known to be affected by exposure to DDE quantities in water. Abnormal

behaviour in rats has also been known to occur when these organisms have ingested endosulfan pesiticide. Similarly, egg size development defects in frogs, its larvae and tadpole development has been studied and noted to have occurred due to effects of persistent known quantities of endosulfan in the aquatic environment (IUPAC, 2003). Research suggests that the development of abnormal growth of the testicular germ cells during earlier life development that could be linked to contaminated foods or environment with POPs, especially during pregnancy or via mothers sucking their young ones (Katherine et al., 2008) occured. Furthermore, contaminated water or food to *p,p'*-DDE metabolite can cause abnormal testicular germ cell development. Additionally, contamination from other cyclodiene pesticides can affect reproduction of different experimental animals used in laboratories as guinea pigs, frogs, rats and mice (Elizabeth et al., 2011).

2.6 Public health concerns

Documented data on water quality challenges in the Lake Victoria Basin (World Bank, 2013) have shown that water-borne diseases are on the increase. Although this may be true to some level, past studies by Mitema and Gitau (1990) indicated that threshold levels of the OCPs in fish and water had not been above the WHO and FAO (2008). However, their study showed presence of the banned pesticides and that they were observed to occur in the sampled environment. Other studies show that water-borne disease risks are reported to have increased as a result of declining water quality in the Lake Victoria wetlands (World Bank, 2013). Although studies by Mitema and Gitau (1990) sought to investigate impact of organochlorine pesticide residues on fish sampled from selected stations in Lake Victoria, Kenyan portion, and results showed residue levels to be below specified maximum contamination limit, these results were comparable with those obtained in other studies within the region. However, the study concluded that lindane (γ-HCH) levels in some samples exceeded the maximum residue limits set by WHO and FAO. As earlier indicated, Mugachia et al. (1992) sought to undertake an

extensive study on organochlorine pesticide contaminants of fish sampled from selected stations in Lake Naivasha, in the Tana River stations and at Masinga dam including stations at the estuary of Athi (Sabaki) river at Malindi, and the results of this study is expressed as within recommended standards. Whereas levels of some pesticides have been documented in some basins such as Nyando (Getenga et al., 2004), sparce recent data exist on pesticide levels in the drainage basin in highly populated areas of River Kuja watershed. Therefore, there is need to monitor the effects, if any, of pesticide contamination on freshwater resources and naturally occurring foods such as fish, which form part of human food requirements.

2.7 Studies conducted in Kenya on water contamination by pesticides

Studies carried out by investigative scientists on the status of contamination by pesticides in Kenya has shown that these contaminants still exist in our environment. For instance, Njogu et al. (2010) carried out a scientific survey on OCPs contaminant levels such as DDT and its metabolites in Mirror carp (*Cyprinus spectacularius*), Common carp (*Cyprinus carpio*) and in (*Oreochromis leucostictus*) sampled in Lake Naivasha, and the results indicated contaminant levels of cyclodienes and the metabolites to range from BDL to greator than 28.0 μgKg^{-1} body weight showing that pesticide residue levels obtained was of different mean levels in each species, hence, the variations were sample specific.

These results on the variations was indicative of the fact that various stages in fish life, its level within the food web affected the organochlorine pesticides retention capacity, and probably an indication that different cyclodiene pesticides had been in use before within the Lake Victoria region area, prior to the period under study.

Similarly, Madadi et al. (2005) carried investigations on organochlorine pesticides residue levels on fish, sediments, water, and aquatic plants which were obtained from Rivers Nzoia (0.01 to 0.41 μgL^{-1}), Sio (0.01 to 0.31 μgL^{-1}) and Lake Victoria, Kenya (0.01 to 0.26 μgL^{-1}) at

Sio Port landing site (Mulukoba) and detected different pesticides residue levels. In addition, the study also targeted probable changes in the two wet seasons (short and long rainy season) within the same study area. The data obtained from the water samples indicated that organochlorine pesticides, DDTs and HCHs residue level concentrations in river water samples from Nzoia were higher in than those obtained from Sio River.

There was a disparity in that the short rain season river samples indicated higher concentrations than those collected in the wet season with variations attributed to probably previous use of detected pesticides and lake water mixing. In the dry season, DDTs and HCHs pesticides residue levels were lower than the WHO maximum acceptable limits. Recorded pesticide concentration variations was attributed to differences between one sampling station and the other, seasonality, type of sample and and effect from the relevant environmental attributes during the study period.

Studies by Getenga et al., (2004) and by Abon'go et al. (2014) on natural water and soil analytes obtained along River Nyando showed that isomers of HCH, and cyclodienes such as aldrin, dieldrin, endosulfan, lindane, heptachlor, methoxychlor, endrin and heptachlor epoxide existed and contained significant residue levels in the sampled stations. The studies reported high contamination measurements of γ-HCH and α-HCH with α-HCH indicating 0.22 μgL^{-1} levels along the target river, except at other sampled stations that produced higher residue level of 0.69 μgL^{-1}. In addition, the study reported residue levels of lindane in water of 1.24 μgL^{-1}. Megan et al., (2017) and Wandiga et al. (2002) study report showed that aldrin, endosulfan, dieldrin, endrin, DDT and its metabolites and γ-HCH in marine water, bottom sediment and water plants including fish from the Kenyan coast in the range 0.503 to 9.025 μgL^{-1} of sea water recorded varied residue level concentrations (Addison et al., 2008) Table 2.1 illustrates thresholds by National Environment Management Authority (NEMA) Regulations on Waste Management, Toxic and Hazardous Chemicals of Environmental Management and

Cordination Act (EMCA) of 1999 regulations. The regulation provides that hazardous waste and substances and chemicals shall not be imported into Kenya or exported from Kenya as well as transported through Kenya without a valid permit issued by the authority (NEMA), and under whose docket is to coordinate environmental issues in Kenya.

Table 2.1: **NEMA (K) maximum permissible quality standards/concentrations in natural water**

No.	Name of OCPs pesticide	Maximum permissible thresholds (concentration)	unit of measurement (mgL^{-1})
1.	Dichlorodiphenyltrichloroethane (DDTs)	1.6	
2.	Endosulfan	0.01	
3.	Hexachlorocyclohexanes (HCHs)	2.0	
4.	Lindane (γ-HCH)	0.01	
5.	Endosulfan	0.01	
10.	Dieldrin	NC	

Source: IUPAC, 2003; Water quality Regulations, 2006 (Legal notice No. 121). Kenya Gazette Supplement No. 68.

In general, the study by Madadi et al. (2005) on the OCPs total contamination levels of DDT, HCH, methoxychlor and endrin in water, fish, sediments, and aquatic plants indicated that values were within the World Health Organization (WHO) and Food and Agriculture Organization (FAO) of the United Nations maximum acceptable standards of tap water, but heptachlor epoxide, dieldrin, endosulfan, aldrin and heptachlor, exceeded the allowable acceptable standard values for natural water for domestic use such as drinking.

In addition, the detected residue levels of DDT, lindane, heptachlor and endosulfan were above the United States Environmental Protection Agency (US EPA) and Australian acceptable standards for drinking water. Overall, results by Madadi et al. (2005) on the concentrations of pesticides in Kenya's northern part of Lake Victoria show that total organochlorine pesticide

concentrations obtained were higher than those of organochlorine residue levels in River Kuja watershed samples.

Anthropogenic activities involving normal spraying of pesticides use on land surfaces are more often associated with risk of ground as well as underground water aquifers' contamination. There are four main ways that enable various water bodies get exposed to pesticides. One of the main ways involves drifting of the contaminants away from the intended target area or site after the spray, others can spill during occupational activities, and other residues reach the soils through leaching, percolation during soil erosion as runoff. For instance, they may be introduced accidentally or by neglect (Barlaz, 2002). Oerke and Denhe (2004) carried out a study on water contamination by pesticides and concluded that in general, only about 10 to 40% of the pesticides applied for pests or weeds reach their intended purpose or site that is targeted and he attributed this to the fact that a significant proportion of the pesticides applied remain in the soil to the benefit of the pesticides whose intended purpose is to treat, for instance the roots and not the leaves that are above the ground.

Other pesticides that often because of higher risk are those, for instance, herbicides that are intended to eradicate unwanted weeds as they emerge from the soil leaving a higher chance of them being swept away during heavy rains as run-offs, ending up in water bodies downstream, even before the actual effect is felt (Megan et al., 2017). Furthermore, 'point source of pollution' is another way that allows pesticide contamination to occur at particular stations either continuously or consistently over time. This often involves pesticides storage points, direct spraying into water courses or through leaky warehouses or poor disposal of the contaminants' containers (Oerke and Denhe, 2004).

This often leads to poor understanding or conclusions involving their sources as it becomes nearly impossible to assign the contaminant source to one particular farmer as the culprit. In contrast, diffuse pollution tends to originate from normal agricultural practice as pesticides

make their way from their target to surface and ground water over long periods of time and it is difficult, if not impossible to assign this type of contamination specific sources as well (MEA, 1993). Past studies have shown that most pesticides are hydrophobic and persistent over a long period after application therefore this may affect its ability to dissolve and contaminate the aquatic medium that has been exposed to it; the geographical area from a water body, how far the water body is located from the point of exposure, vicinity to crops nearby, soil texture, various weather patterns, and finally the procedure used to apply the chemical (Barlaz, 2002). The Environmental Protection Agency (US EPA, 2002) of the United States of America is the body that sets maximum acceptable standards of individual pesticides limits of allowable concentrations for individual pesticides in public water bodies of water either in public or private enterprises (Hecky and Bugenyi, 1992). Similarly, the British government or the United Kingdom (UK) sets Environmental Quality Standards (EQS), or maximum allowable thresholds of some pesticides in natural water bodies beyond which toxic levels for domestic use is achieved (Barlaz, 2002; WDNR, 2006). Current rules and regulations set by the European Union (EU) regulates maximum acceptable standards for pesticides in water required for industrial or agricultural purposes, for instance, water used for drinking, fisheries and water used for manufacture of soft drinks. In Kenya, National Environment Management Authority (NEMA) sets the maximum acceptable standards of organochlorines or other pesticides in natural river waters (NEMA, 2006).

2.8 Bottom sediment contamination by pesticides residues

Hecky (1993) and Wheelock et al. (2008) in their previous research work on organochlorine pesticides level of contamination on different organisms living in the same aquatic media proved that these organisms tend to accumulate different quantities of pesticides residue levels. This was attributed to the amount of time of exposure, different metabolic processes in each organism as well as age of these organisms. In addition, Njogu et al. (2010) was of the opinion

that aquatic micro-organisms that dwell within bottom sediment material in the tropical climate accumulate higher amounts of OCPs and other related contaminants absorbed from sediment matter (Stephens & Sreenivasan, 2004).

UNEP (2013) carried out a study on pollution of streams and rivers by human activities such as the dumping of agricultural wastes and chemicals and concluded that these activities have contributed to ecosystem contamination of fish and other organisms in the littoral zones of tropical Mauritius Island. Recent data has reported pesticides residue occurrence in sediment samples from the Kenyan coast sampled areas. These studies include the investigation by Megan et al. (2017) in which presence of endosulfan, dieldrin, aldrin, γ-HCH, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD and endrin organochlorine pesticides residues were in detectable to undetectable concentrations while others were absent in target samples. Their sediment residue levels were in the range from 0.584 to 59.00 nanograms per gram.

The study further noted that contamination by alpha hexachlorocyclohexane was detected proportionally along the Kenyan continental shelf at different depth strata. Furthermore, lindane was recorded in six sampled stations at a residue level range from 7.3 to 53.2 nano grams per gram of organic carbon. River Sabaki bottom sediment contained higher levels of DDT metabolites and dieldrin at 37 nano grams per gram concentration levels and 510 nano grams per gram of organic carbon, respectively.

Additionally, Wandiga et al. (2009) investigated presence of organochlorine pesticides residues in macro-invertebrates organisms and in bottom sediments at sampled stations in the Kenyan coastal region. Sediment samples collected from the littoral zone at the mouth of River Sabaki were contaminated with PCB organophosphates in the residue level range from 7.1 to 62.2 nano grams per gram of organic carbon. Similarly, the study noted that DDT metabolite residue levels, especially that of *p,p'*-DDE concentration occurred at levels ranging from a mean value of 32.1 to 508.8 nano grams per gram of the target contaminant residue.

2.9 Pesticides contamination in fish

Studies have shown a strong relationship between fatty tissue content and DDT metabolites as well as those of endosulfan in fish tissues residues as was demonstrated by Munga (1985) who conducted his research in the Hola irrigation scheme. Eggs, liver tissue and the lateral muscle were measured to find out if DDT metabolite and endosultan organochlorine pesticide residue levels from four fish species that included *Labeo gregorii* (Gunther, 1894), *Oreochromis mossambicus* (Peters, 1852), Redbelly tilapia, *Tilapia zilli* (Gervais, 1848) as well as *Clarias gariepinus* (Rurchell, 1822) existed. Results obtained in the study showed the liver tissue contained highest average concentration of endosulfan and total DDT (wet weight), in the order (liver tissue >eggs > muscle tissue) in a 7.1:2.4 ratio. In other words, average residue level of DDT metabolite in the liver tissue was 7.1 and 2.4 times above that observed in muscle and eggs, while overall, endosulfan concentration in fish liver tissue was 12.5 and 5 times higher as compared to that observed in fish muscle tissue and in eggs proportionally in a (12.5:5.0) comparison ratio.

In studies carried out by Mitema and Gitau (1990), insignificant quantities of α-HCH, dieldrin, α-HCH, aldrin, and *p'p'*-DDT pesticides were recorded in Nile perch (*Lates niloticus*) fish from Lake Victoria. Results indicated DDT metabolites (*p,p'*-DDE, *p,p'*-DDT, *p,p'*-DDD), produced larger quantities of OCPs in fish samples analysed during the study. The conclusion achieved from the results was that it was inevitable that pesticide residue levels was recorded in the sampled Lake Victoria Basin environment sites due to previous public health concerns and need to produce more yields from the agricultural farms. Mugachia et al. (1992), carried out investigation on detecting organochlorine pesticides contaminants in six fish species obtained from the point at which river Athi enters the Indian Ocean.

Results indicated the presence of higher pesticides residues in the liver tissue as well as in egg samples than in fish muscle tissue. Target pesticides concentration levels decreased in the

order: *p,p'*-DDE, *p,p'*-DDT, *p,p'*-DDD, β-HCH, α-HCH and heptachlor. From the data obtained, it was concluded that since sharks were at the tertiary level of the trophic pyramid (highest point of food web structure) they in turn contained the largest contaminant availability in their body organs implying that sharks therefore had a significantly higher average occurrence of DDT in comparison to marine crustaceans and the saltwater catfish at the base of the trophic tree.

Studies by US EPA (2002) indicated a relatively different concentration pattern of endosulfan and DDT pesticides in their tissues in the sense that relative concentrations in the egg, liver and the fillet of *Clarias gariepinus* (Burchell, 1822) had a different concentration pattern of total DDT than the matrix that existed in *Labeo gregorii* (Gunther, 1894) fish. Furthermore, their investigation indicated that *p,p'*-DDE concentration was higher compared to that of either *p,p'*-DDD and *p,p'*-DDT and bioaccumulates in the adipose body organ of more aquatic organisms including fish. Available data on OCPs concentration by Elizabeth et al. (2011) documented the benthic dwelling freshwater fish, *Labeo cylindricus* (Peters, 1852) (Cypriniformes: Cyprinidae), sampled in Lake Baringo. Results from the study showed that fish had a residue concentration quantity of 0.4 μgKg^{-1} body weight for *p,p'*-DDE in the fillet sample. DDT pesticide residue level in *Labeo cylindricus* (Peters, 1852) fish were above those of similar fish samples obtained from Hola Irrigated farms as investigated by Munga (1985) which showed that contaminant levels obtained from other Kenyan rivers investigated during the study were lower.

In comparison, investigation by Elizabeth et al. (2011) indicated that DDT concentration ratio in fish was in the order of one to seven μgKg^{-1} wet weight, while the latter results of DDE contamination in fish showed 7.4 to 10 μgKg^{-1} wet weight and DDE levels in biota of 4 times 10 μgKg^{-1} wet weight from Lake Nakuru, although these results when placed in comparison,

those obtained from the marine coastal waters along the coast of Kenya were fairly higher (Megan, 2017) in residue concentrations.

Anthropogenic activities in the upper catchment areas drained by the rivers studied could be a contributing factor attributed to the observed pesticide concentration presence and their variations. For example, the Sabaki river catchment sweeps a large basin composed of various agro-chemical industries whose liquid and solid waste is drained into the Indian Ocean as run-offs or as effluent from point sources. In summary, they found very low levels of DDT (<0.001-0.064 μgKg^{-1}), especially in samples collected from Lake Nakuru littoral zones (Elizabeth et al., 2011).

2.10 Fisheries and aquaculture sub-sector

In general, fisheries sector plays an important role in Kenya for socio-economic development of the country's food needs as it contributes a significant role to Gross Domestic Product (GDP) by generating income, livelihoods and employment (KeFS, 2020). In Kenya, capture freshwater fisheries contribute about 85% of the total fisheries production while coastal and marine waters contribute only 6%, with aquaculture producing about 7% of the national fish production. In their report, Roberts et al. (2009) points out that aquaculture sub sector involves culturing aquatic organisms (animals and plants) in a controlled environment. In addition, aquaculture sub sector has the potential to contribute in a significant level to Kenya's local and national economy and supporting food security challenges hence reducing poverty as is stipulated in Kenya's Vision 2030 Economic Blueprint (GoK, 2007; KeFS, 2020), due to a variety of water sources in the inland and marine environment aquatic resources of Kenya.

Demand for fish from this sector is growing owing to the growing population and the changing eating habits of most Kenyans. Fish production from natural stocks has already reached its limits and is declining while aquaculture production is increasing. In East Africa the contribution of aquaculture to the total fish production is still insignificant although it has been

practiced in the region since the 1920s (Osoro et al., 2016). The predominant aquaculture production system in East Africa at present is small-scale earthen ponds, characterised by low inputs and low yields (Roberts et al., 2009). Pesticides may enter fish ponds by deliberate spraying of surrounding farmlands or they may drift from general aerial spraying or be washed into rivers or lakes from the land. Living organisms such as humans and fish eating birds may bring pesticides into existing water bodies. Ultimately fall-out from DDT now believed to cover the world makes every water body vulnerable to contamination or uniformly distributed throughout the existing ponds or streams (Murphy, 2007).

A large number of halogenated organic compounds, often referred to as organochlorines (OCPs) such as DDT, hexachlorocyclohexanes (HCH), and cyclodienes compounds have been synthesized and distributed for use as pesticides since 1941 but they have been documented as being of great concern, due to their ability to become toxic and poisonous once released to the environment. More specific studies involving these bioaccumulative organochlorine pesticides started in the early 1960's and the results obtained enabled the countries affected in both developed and to the developing countries to ban their use altogether (Cooke and Stringer, 2007; EPA, 2002).

Due to this, the Kenya Government using authority given by pest control products Act of 1982, formed the Pest Control Products Board mandated to control these hazardous pesticides during production, distribution and when used for various purposes. In summary, these persistent organochlorine pesticide compounds were banned or restricted by the Government of Kenya from use in the environment as from 1986 (PCPB, 2009). In 1998, a provision was made for lindane to be strictly used only as a seed dressing fungicide, especially in the construction industry whereby it was allowed to act as an anti-termite agent. However, sadly this compound is still detected in the environment as it is still distributed and sprayed as an insecticide in cotton growing farms within low lying areas of Lake Victoria.

2.11 Absorption, accumulation and excretion of organochlorine pesticides in fish

Existing literature (US EPA, 2002; Wandiga, 2009) has shown that fish are able to absorb and store substances that are not naturally produced in their bodies but are found to exist in water as the medium of existence. These substances may exist as undigested foods or chemicals out of weak or incomplete metabolic activities and exist freely in their environment (Abong'o et al., 2018). One of the major ways through which these substances are obtained is either through water as fish obtain oxygen by passing huge quantities of water through their gills as they breathe. Additionally, water is a medium through which fish survive and are bound to come into contact with these chemicals as they swim and move within water (Wandiga, 2002; US EPA, 2002). Several factors influence the processes through which organochlorine pesticides are passed into aquatic organisms in water such as fish and these may include physiological activity, medium conductivity, lipid content and stage of body development. Other influencing contaminant absorption means may include, (Ezemonye et al., 2015; Ndunda et al., 2018) the chemistry of the pesticides molecule, the fish physical condition and water temperature as the main medium of survival. DDT is known to be have a higher affinity to lipid material hence it is easily taken up during metabolic activities or during feeding. It is then taken and digested slowly, and bioaccumulates in the fish body or other aquatic organisms and then stored for a long time as it biomagnifies itself within the trophic levels (Sadasivaiah, 2007).

Studies by Werimo et al. (2009) on marine and freshwater fish samples such as bluegills, gold fish and tissues from the rainbow trout showed that DDT pesticides and its metabolites is rapidly absorbed by the sampled fish after being exposed within a specific period (Madadi et al., 2005) . In addition, HCH and its isomers were observed to be absorbed faster into these organism's body tissues than the rate at which others are, such as endosulfans. Dieldrin is absorbed into fish intestinal tissue even in lower concentration of exposure, than into other body organs even when exposed to higher concentrations (WHO, 2006).

Investigations carried out by the European Protection Agency (EPA) in 2002 indicated that degradation of DDT and mirex, the pesticide previously used specifically to control fire ants in the United States by fish was very slow (Metcalf et al., 2002). This was observed to be case after 48 hrs, even after administering DDT to dogfish via the stomach tube, artery or the caudal vein, the uptake was observed to be very low. The study also observed that little conversion or metabolic excretion of the pesticide and its metabolites through gills or urine was evidently very low (EPA, 2002). Fish are known to contain enzymes that facilitate metabolism of fats in a process termed as Mixed Function Oxidate (MFO) and has been documented to cause the metabolism or digestion of organochlorine pesticides (OCPs) in fish. This process takes place mainly in the liver. Similarly, other mammals that thrive in the aquatic medium undergo the mixed function oxidate (MFO) process although for this process to function at the optimum, their body temperature must be higher than that for fish which occurs at an average of 25 °C (Gangemi et al., 2016). In other words, MFO takes place faster and conductively in fish whenever the temperatures are at optimum of 25 °C and this process confined to liver and occurs rarely in other body tissues. Other enzymatic processes trigger these processes as well as these chemicals that are found in the liver but not produced in an aquatic organism's body are excreted by mechanisms comprised not only MFO's but certain changes in the body chemical formulation during digestion, mediated by MFO's during excretion and respiration processes (FAO, 2020).

Detoxification process in fish caused by other factors such as hydrolysis, reductions or methylation represent only the first indication in the reduction of toxic compounds in the body for fish survival (Aktar et al., 2009). The second step comprises the temporary joining of two or three bacterial cells as the first step with an amino acid molecule or other acids derived from glucose during breakdown of food and the increase of the body's polarity uptake and eventually elimination of the contaminant (Damalash et al., 2008). However, despite these active body

and organism's survival tactics to detoxicate through employment of these biochemical pathways, this may sometimes result into the activation of other relatively non-toxic compounds (Werimo et al., 2009; Njogu et al., 2010).

After fish has come into contact with DDT pesticide in water either through food consumption or through aspiration by passing huge quantities of water through its gills, it has been observed that the major metabolic product of DDT contaminant is DDE and to some notable level, DDD. These two metabolites are retained for a long time due to their low non-polar strengths (Bonner et al., 2007). Dieldrin is a simpler form of aldrin as it results from breakdown of aldrin, but is more toxic to fish than the parent compound (EPA, 2004). Endosulfan sulfate is as a result of the breakdown of Endosulfan but is poorly metabolized by fish. In addition, endrin is metabolized through a process by which an hydroxyl group or groups are added into an organic compound, followed by other present or past enzymes in the liver. Other studies have shown that the adipose tissue facilitated the process of maximum residue accumulation (MRA), an international index allowable for a pesticide contaminant to occur or stay in an organism's body without necessarily becoming toxic(FAO, 2020). In fish, this half-life was found to be about 130 days. Furthermore, after 16 months of investigation using uniformly labelled Mirex C^{14} compound which is a chlorine box, the study resulted in digestion and detection of virtually any type of degradation product but hundreds of analyses showed no indication of a mirex digestion (Bonner et al., 2007).

Other previous studies involving fish metabolic activities have shown that hepatobiliary path, the process by which bile is produced in the liver and transported into the stomach, was observed to be the main route of excreted OCP contaminants (FAO, 2017) in fish, although the renal path way and gills as well contribute and perform a crucial role as shown in the studies by Litchfield (2005). In other studies involving OCPs, results have indicated that compounds with lower polarity, such as HCH isomers, and this includes α, β and γ-HCH are eliminated at

a slower pace from the fish body than those with higher polarity such as aldrin and other cyclodienes.

Research by EPA (2002) on organochlorine pesticides indicated that dieldrin got excreted at a slower pace than lindane, but dieldrin became detoxicated faster than DDT pesticide and its metabolites (Katsuram et al., 1979). Furthermore, studies conducted by WHO (2006) found out that the reproductive pathway serves the purpose of excretion for fish to get rid of organochlorine pesticide contaminants from the body after results showed that a large proportion of DDT absorbed by Killi fish got deposited in the male reproductive testes and ovaries in females, respectively. Further, the study showed the residues were incorporated in the fish female eggs and a significant amount shed during spawning by the females. In addition, the study indicated that sampled male fish shed higher amounts of measured DDT pesticides contaminants when releasing milt (male reproductive substance) than did females in eggs (Aktar et al., 2009; Ezemonye et al., 2015).

In research carried out by Osoro et al. (2016) and Nyaundi et al. (2020) concluded that generally, the potential impact of pesticides is more on the aquatic organisms than on the terrestrial ones because in the aquatic environment, (Njogu et al., 2010) the body of the organism is washed constantly by the pesticide's residues in water, although at very small quantities but over a given period, it results into higher concentrations and frequency on the sampled organism. Alternatively, in the terrestrial environment, persistence and hydrophobic nature of pesticides enable their chemical remnants to be transported to greater distances by other environmental factors such as wind and water and thus affecting aquatic organisms even when detectable in low concentrations (LVBC, 2011).

In comparison between organophosphorus and organochlorine compounds, it is evident that the latter produce symptoms that are both acute and chronic effects to fish for a long time in the environment and show high levels of toxicity (Gangemi et al., 2016) than the former

pesticide compounds. Even though this is the case, previous results have indicated that some given organophosphorus contaminants may provide high toxicity incidences in the aquatic mediums, comparable to organochlorines (Lu, 2006). Laboratory investigation by Jureiz et al. (2008) on preserved samples indicated that fish are more vulnerable to DDT than humans and that this toxicity occurred as early as 1944. Persistent poisonous attributes of OCPs play major concern to environmental managers and conservationists to date since chronic impact may be insignificant or result in various nonspecific symptoms (Ndunda et al., 2018) and to non-target victims overall. Some of these may include symptoms such as small muscle contractions in the body due to disruptions of the nerves that serve them, fatigue (like chronic feeling of weakness and tiredness with no given reason), visual disturbances, nausea and headaches (Lu, 2006).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study area

River Kuja forms part of a larger Lake Victoria drainage basin water resource, situated between latitudes 1°16' N and 1°54' S and longitudes 33° 55' E and 35°51' E. Gucha River, at times referred to as River Kuja downstream, starts from the highlands of Kiabonyoru in Nyamira County passing through the heart of former Gucha District, running west through Migori Town where it is joined by River Migori and other smaller rivers downstream and thereafter flows into Lake Victoria at Aneko point (Figure 3.1). The Kuja or Gucha which traverses Nyamira, Kisii and Migori Counties dominates the eastern half of the Lake Victoria Basin with 24 sub basins (Werimo et al., 2009; LBDA, 2011), covering a catchment/basin of about 6,900 km^2. River Kuja traverses a distance of about 149 km downstream, with a discharge of approximately 58 m^3 per second of water. On the basis of the watercourse of the Kenyan affluent rivers that flow into Lake Victoria, River Kuja forms part of that as it flows within the former Nyanza Province, and whose wetland area of 6,600 km^2 form part of its inflow into the lake. From its Kenyan catchment area, the river rises within the Kisii highlands and discharges into Lake Victoria (Figure 3.1). Its tributaries namely, Mogonga, Nyakomisaro, Iyabe, Kemera and Chirichiro, and other seasonal streams dominate the northern part of the Gucha river catchment (GoK, 2009). Nationally, the river system supports major farming activities as well as being important as a source of water for domestic and industrial use.

However, population increase and agricultural, industrial and urban development, soil erosion, and subsequent alterations in the communities in River Kuja catchment, contributes to changes in its water quality and functioning of the ecosystem of the lacustrine environment (LVEMP, 2003; Abong'o et al., 2014). Nationally, the river system is of major significance because it

supports major farming activities as well as being important as a source of water for domestic and industrial use and due to the catchment based development activities such as horticultural farming, cattle dips, coffee pulberies and development of waste water treatment systems or lagoons in urban areas. Other activities include mining operations, urban development and agro-processing factories leading to the catchment system experiencing pollution from both non-point and point sources, therefore the river ends up as an agent for carrying pollutants into the lacustrine environment (Abuodha, 2005).

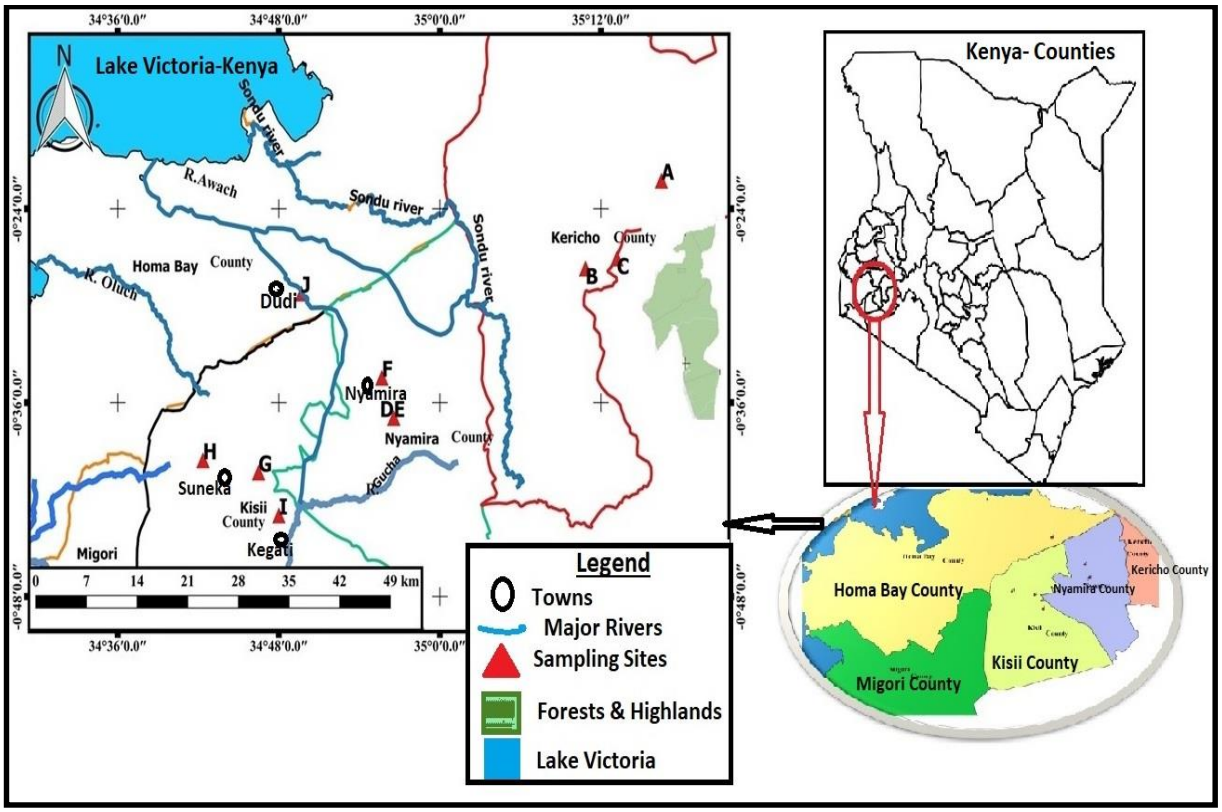

Figure 3.1: **Map of River Kuja watershed indicating areas sampled, September 2016 to December 2017.**

The study was conducted in heavily populated areas of Kisii and Nyamira Counties whose current population density is about 1, 200 persons per square kilometre (KNBS, 2015), and some randomly selected stations of Kericho and South Nyanza (Table 3.1). The areas were selected as suitable sampling stations for the study because of the large human settlements, agro-based industries and related agricultural activities within their immediate vicinities

(Nevejan et al., 1996; LBDA, 2011). This area has undergone rapid ecological changes resulting from agricultural practices such as catchment encroachment and degradation, leading to massive deforestation and water pollution (Mbabazi, 1998; LVBC, 2007) within River Kuja drainage basin contributing to changes in its water quality and the functioning of the ecosystem of its lacustrine environment and calling for continuous assessment and monitoring (Rusongoza, 2003).

Table 3.1: **Names and locations (Global Positioning Coordinates) of sampling stations.**

Station	Station Name	GPS Position
A.	Kericho waste water lagoons, and adjacent stations	00° 22’ 16.14” S 034° 16’ 30.38″ E
B.	Kisii, Omogonga and Nyakomisaro rivers, fish ponds and adjacent stations	00° 27’ 42.24” S 035° 10’ 50.99″ E
C.	Kericho fish ponds next to tea estate and adjacent stations	00° 27’ 05.02” S 035° 13’ 11.15″ E
D.	Nyamira horticulture fish ponds area and adjacent stations	00° 36’ 57.20” S 034° 56’ 33.75″ E
E.	Nyamira fish culture ponds, Gachuba and adjacent stations	00° 36’ 57.20” S 034° 56’ 33.75″ E
F.	Nyamira, Eaka and Nyambiri rivers and adjacent stations	00° 34’ 27.99” S 034° 55’ 40.68″ E
G.	Kisii coffee research & Municipal fish multiplication centre and adjacent stations	00° 40’ 19.93” S 034° 46’ 29.33″ E
H.	Kisii wastewater lagoons, Nyakomisaro, Riyabe river waters	00° 39’ 34.26” S 034° 42’ 21.14″ E
I.	Kisii Kegati aquaculture centre and adjacent river waters	00° 42’ 59.16″ S 034° 48’ 01.36″ E
J.	Dudi awach coffee factory site and adjacent river waters	00° 29’ 14.99″ S 034° 49’ 41.22″ E

3.1.1 Research design

Water, sediment and fish samples for pesticides data were taken from eight pre-selected sampling stations within River Kuja watershed, on a quarterly basis, between September 2016 and December 2017 in the catchment of River Kuja, in order to cover spatial and temporal pesticide distributions (Figure 3.1). The research design covered field sampling stations, distributed over the study area. However, due to logistical challenges, only 8 stations (A-H) were consistently accessed and sampled. In addition, other sampling areas did not contain fish ponds. Sampling was carried out in January and July (dry season) including Aprl, October and November (wet) seasons of 2016 to 2017, respectively. The type of effluent targeted in this study came from horticultural farms, cattle dips (livestock dipping tank), coffee pulberies, fish ponds and wastewater lagoons. The research design also involved laboratory Gas Chromatographic identification and quantification of the organochlorine pesticides (Thurman and Mills, 1998; US EPA, 2004).

Approximate locations of selected sampling stations were recorded using Global Positioning System (GPS) navigation unit (Garmin II model). The stations were named alphabetically, and are shown in Figure 3.1 and their related locations on the world map is presented in Table 3.1. Purposeful and multistage sampling method was used in collecting the required data along River Kuja watershed. Specific streams and river systems sampled, and along which fish farms were located included; Nyakomisaro, Omogonga, Gucha, Eaka and Nyambiri. The stations were selected objectively, in the upstream reaches, mid reaches and those targeting areas after major agricultural farms, agro-based industries and urban influence to represent the target area. Some sampling stations, for instance, stations that were within vicinity of cattle dips (livestock dipping tank) activities did not contain fish or ponds, hence were not sampled (Table 3.1). On site, random sampling method was employed in picking the sample. Samples were picked from stratified and randomly selected fish ponds, the wastewater lagoons of Kisii and Kericho

Municipal Towns (station A & H) and at specific purposively selected points along streams and rivers within the study area, respectively. Individual fish were sampled by net from fish ponds. Sample size determination was done using the Fisher (1999) formula: $N = Z^2pq/d^2$ whereby, N-Desired Sample size; p-Proportion in the large population estimated to contain pesticides and heavy metal residues (probability); q-Expected contaminated proportion (1-p) (1-0.5) =0.5; The standard normal deviation set at 1.96 of the 95% confidence interval; d-The degree of accuracy desire set at 0.05 significance. Therefore: $N = 1.96^2 (0.5 \times 0.5)/ (0.05)^2 = 384$.

3.2 Sample collection

3.2.1 Physico-chemical parameters measurements

Portable electronic water quality meters were used to collect data on the physical and chemical parameters in the sampling stations. Surface water *In situ* measurements of physico-chemical variables were conducted using Yellow Spring Instrument (YSI) multi-parameter water monitoring equipment (Model: 650). Physico-chemical parameters measured *In situ* on site were: temperature, dissolved oxygen, conductivity, pH and turbidity. Water sample collection bottles were pre-cleaned, filled, and stored in cooler boxes at temperatures of about 4^0C, for collecting samples for further laboratory analysis of dissolved nutrients, according to APHA (2005) standard methods.

General environmental conditions about sampling stations, for instance, time of sampling, human activities, weather conditions and physical features, were noted. Water samples for total nitrogen (TN) and total phosphorus (TP) were carefully kept without controlled preservation and were processed immediately following APHA (2005) standard methods.

3.2.2 Water sample collection for pesticides analysis

Samples were collected in triplicate both in the dry and wet seasons. Composite water samples, were obtained using the Van Dorn Sampler (APHA, 2005) equipment and transferred into 2.5 L amber glass bottles, one per sampling station, which had been pre-washed with triple ^{0} ^{0} distilled water and dried. Prior to pesticides extraction, all the water samples were temporarily stored in a Coleman cooler box with wet ice, transported to the laboratory and kept in a standard fridge at 4 ^{0}C in the dark before liquid-liquid extraction (LLE), cleaning and GC analysis (Thurman and Mills, 1998). Samples stored at 4 °C were used within 2 days after collection in order to avoid pesticides degradation by microorganisms.

3.2.3 Sediment and fish sample collection for pesticides analysis

From the same stations where water samples were obtained, an Ekman Grab bottom grab was used to scoop the sediment in triplicate, which was thoroughly mixed on a clean piece of aluminium foil then a representative sample of 500 g was then packed in zip lock plastic bags, kept in ice-boxes with ice, later transported to the laboratory, and stored in a - 20 ^{0}C deep freezer before extraction, clean-up and analysis. Solvent-phase extraction (SPE) method was used (Thurman et al., 1998) in extraction of both fish and sediment samples. Fish samples were obtained by use of an Electro Fisher Machine (Samus, 1000 model) having a scoop net attached to its electrode (Appendix XIII). Length measurements for the fish sample were taken using a one-man graduated ruler and specific biometrics kept in the data book, whereas related fish muscles tissues of about 100 g were carefully extracted along the lateral line, preserved, and later dried in Salvis Model oven at a temperature of 110 °C for at least 48 hours as described in APHA (2005). Fish (*O. niloticus*) sample was carefully obtained from muscle tissue, due to high lipid content per volume ratio in the selected fish. The mass of the sample was obtained using a digital analytical balance series (SHIMADZU AUW 320) with an accuracy of 0.001 g.

Fish specimen analysed in this study were Nile tilapia (*Oreochromis niloticus*), as it has been proven to be a capital fish, a delicacy to a larger population in the study area and can withstand low dissolved oxygen (DO) levels & has a faster growth rate with optimum economic gains to fish farmers. Sampling consisted of collecting two fish composites per station. Each composite contained 5 adult fish of the same species and of similar size (so that the smallest individual within the composite is no less than 75% of the total length of the largest individual) as described by EPA (2000, 2002). The samples were collected and stored in a Coleman cooler box containing ice and transported to the Chemistry Department, Chiromo Campus, University of Nairobi, Kenya, for analysis.

3.3 Sample analysis

3.3.1 Nutrients

Sub-surface water samples for nutrient chemical fractions such as total suspended solids (TSS), total nitrogen (TN) and total phosphorus (TP) were collected using a Van Dorn water sampler using pre-treated 1 litre polyethylene sample bottles and thereafter stored in cooler boxes at temperatures of 4^0C, for further dissolved nutrient analyses in the laboratory. Preserved samples were analysed for dissolved nutrients by spectro-photometric method. In addition, total nitrates (μgL^{-1}) and total phosphates (μgL^{-1}) analysis was by autoclave digestion using methods described by Sasaki et al., and APHA (2005). TP concentrations were analysed by hydrolysing the unfiltered samples with potassium persulphate, under heat and pressure, to orthophosphate, which was subsequently analysed using the ascorbic acid method. TSS was determined by filtration of a volume of water sample through pre-weighed GF/C, which was then oven dried and final weights taken to determine the difference as the TSS (μgL^{-1}) weight per unit volume of sample.

3.3.2 Organochlorine pesticides (OCPs)

3.3.2.1 Liquid-liquid extraction (LLE) and clean-up for OCPs in water

Liquid-liquid extraction (LLE) of HPLC grade device (Heildoph Nimax 1010 DT Model) method was used in extraction of water samples for estimation of organochlorine pesticides concentrations (Thurman and Mills, 1998; APHA, 2005; Osoro et al., 2016). Once in the laboratory, the samples were later extracted into an organic solvent (Dichloromethane) and stored appropriately, for analysis. 50 ml of 0.2M Dipotasium hydrogen phosphate buffer were added to a water sample of 2.0 litres, transferred into a separatory funnel and its pH adjusted to 7.0 by adding drops of 0.1 N Sodium hydroxide and 0.1M HCl solutions to neutralize the sample. 100 g Sodium chloride were then added to salt out the pesticides from the aqueous phase. While slowly releasing pressure from the separatory funnel, 60 ml triple distilled dichloromethane (DCM) were added to this solution and shaken for two minutes. Separation of the phases was achieved after allowing the sample to settle for 30 minutes. A 250 ml Erlenmeyer flask was then used to collect the organic layer and extraction twice repeated using 60 ml portions of dichloromethane (DCM). After storage in the refrigerator at 4 ºC, the extracts were combined into a mixture and then cleaned by passing it through Al_2O_3 chromatographic column (glass packed with the alumina, then topped with anhydrous sodium sulphate). Pesticide residues were sequentially eluted with 175 ml of n-hexane. The elutes were then concentrated to 1 ml each using a rotary evaporator at 40 °C, and reconstituted them with 0.5 ml HPLC grade isooctane for GC analyses.

3.3.2.2 Solid-phase extraction (SPE) and clean-up for OCPs in sediment sample

Prior to mixing, the wet sediment samples were allowed to thaw for 4 hours in the laboratory then EPA 3540 Soxhlet extraction method of sediments applied (Grob and Barry, 2004). Soxhlet extraction method has been recommended for obtaining extracts from sediment samples and fish matrices, whereby the analytes are continuously heated to boiling point, re-

condensed and boiled again with the target sample collected in a hot solvent within the GC apparatus. Before transferring the sediment sample to the Soxhlet thimble, triplicates of 20 g samples were dried overnight with activated anhydrous sodium sulphate (Na_2SO_4) then extracted with 200 ml of hexane to acetone (3:1v/v) in a 250 ml round bottomed flasks for a minimum of 16 hours. After storage in refrigerator at 4 ºC, the extracts were combined and cleaned by passing them through Al_2O_3 chromatographic column topped with anhydrous sodium sulphate. The elutes were concentrated to 1ml using a rotary evaporator at 40 °C, and reconstituted in 0.5 ml HPLC grade isooctane for GC analyses (US EPA, 2004). The final samples were analysed by a Varian Chrompack CP-3800 GC equipped with electron capture detector (GC-ECD).

3.3.2.3 Solid-phase extraction (SPE) and clean-up for OCPs in fish sample

The muscle tissue was obtained from the fish samples, crushed 10 to 20 g and homogenized, followed by extraction of the total lipids in each fish tissue based on the method described by Randall et al. (1998) and lipid normalized concentrations were obtained using the ratio between pesticide concentrations in tissue and lipid fraction in the tissue (Grob and Barry, 2004). The fat was weighed and extracted for pesticide residues, according to method described by Wedad et al. (2017). 25 g of the sample were inserted into a homogenizer for 20 minutes at 100 revolutions per minute (rpm). The extracts concentrated for lipids were extracted and cleaned up for water or sediments above, followed by GC analysis (US EPA, 2004). Sample concentrations were done using a Rotary evaporator, Buchi Rotavapor GR-200 Series by evaporating in a water bath at a temperature of 40 °C as described by APHA (2005). They were then shaken using an orbital shaker (Thurman and Mills, 1998), with organic solvents during extraction as described by APHA (2005) Heildoph Nimax 1010 DT Model.

3.3.2.4 Determination of lipid content in fish

The moisture content in fish specimens were determined using the methods described by EPA (2000, 2002), Ssebugere et al. (2010) and by APHA (2005). Three 10 g portions of the homogenate fish samples were weighed out in pre-weighed beakers and extracted thrice with 50 ml chloroform. A 20 g portion of anhydrous sodium sulfate was added to each sample and shaken in an orbital shaker for 30 minutes to remove moisture. The extracts were then stored in the fume-hood to allow the solvents to volatilize. The extracts were combined and left until only the lipid portion was left by decanting. The moisture content was obtained by subtracting the final weight from the initial weight of the sample. The mean percentage moisture content was then calculated and standard deviations from the mean obtained.

3.4 Quality assurance

Sampling, extraction and analysis were done in triplicate to allow verification of the detected pesticide residues (Osoro et al., 2016). Recovery tests were carried out using the reference pesticide standards to determine performance of the methodology. Quantification of pesticide residues was carried out using high purity pesticide reference standards. Field blanks and method blanks were also incorporated to check contamination during sampling, transportation and laboratory preparation procedures (UNEP, 2013). OCPs analysis was carried out on a GC-ECD system equipped with a DB-5 capillary column (30.0 m length, 0.32 mm ID and 0.25 μm film thickness). Detector temperature was set to 290 ^{o}C, base temperature of 280 ^{o}C, reference current of 1 nano amperes (nA), pulse amplitude of 50.0 V and pulse width of 1μs. Helium was used as carrier gas (70 kPa in constant pressure flow mode) with a flow rate of 20.0 mLmin^{-1} and nitrogen as make-up gas (30 mL min^{-1}). The OCPs were identified by comparing their retention times with reference standards and quantified by external standard calibration. GC-MS was used for confirmation of peaks.

3.4.1 Cleaning of glassware and sample containers for GC analyses

Sample containers and glassware used in the study were soaked with a dilute nitric acid (conc) solution overnight then cleaned with regular soap and double rinsed with distilled water and finally with acetone (APHA, 2005). Apparatus for pesticide analysis were cleaned by washing with soap and water, rinsing with hot water, distilled water, twice with analytical grade acetone, twice with pesticide grade ethyl acetate and finally with pesticide grade hexane. Used glassware were soaked in detergent for 24 hours, washed and rinsed in distilled water before drying in an oven at 100 ^{0}C for 24 hours. The containers were then baked at 150 ºC for 45 min. in an oven to remove traces of organic solvents. These were then stored in a closed cupboard to avoid dust deposits.

3.4.2 Materials and chemicals used in pesticides extraction and analysis

All chemicals and reagents used in the study were of analytical grade while the organic solvents used were triple distilled as described in APHA (2005) and Thurman and Mills (1998). Identification and quantification of pesticide residues in the samples obtained was done by use of high quality pesticide standards mixture of over 99% purity (anal). The pesticide standards were obtained from Dr EHRENSTORFER GmbH, (Ausburg, Germany). Solvents such as Dichloromethane (DCM), acetone, isooctane and hexane were sourced from Fisher Scientific (USA). Other consumable chemicals such as hydrochloric acid (HCL), methanol, sodium chloride (NaCl), aluminium oxide (AlO), sodium hydroxide (NaOH), copper and anhydrous sodium sulphate ($NaSO_4$), all of analytical grade, were also obtained from Fisher Scientific (USA). General purpose reagents (GPR) were triple distilled in all-glass fractional distillation apparatus glassware, before use. Distilled water for pesticide analysis was purified by extraction twice with pesticide grade hexane in an Erlenmeyer flask. Before use, the purified water was heated to boiling point, for ten minutes, to remove traces of hexane.

3.4.3 Separation and detection methods for organochlorine pesticides

Gas chromatography (GC) is adapted as the highly preferred method for separating and quantifying different pesticides solvents in various matrices or arrangement (APHA, 2005; FAO, 2020). Gas chromatography laboratory protocol allows analyte separation of organochlorine pesticides by sorting and dividing analytes between a moving gas phase and constant phase in which case that can be a liquid or an inert gas such as helium held onto a solid adsorbent support (US EPA, 2004). Those compounds that react faster are normally eluted faster within the column than the slower ones. The sample containing the pesticide is injected into a heating block containing a precision instrument for preservation according to protocol (APHA, 2005; Ndunda et al., 2018), where it is volatilized as vapour by carrier gas stream into the GC apparatus. Each compound moves forward at its own pace, depending on differences in their concentration ratio between the liquid immobile section of the sample and the running gas section. Retention time of a sample in a GC column is the time taken for a solvent to be observed or recorded between injection and detection and this is a characteristic and classification of each compound as per experimental protocol (Wedad et al., 2017). The portion of each pesticide compound that passes through the detector is what is known as the peak area of the chromatogram. In conclusion therefore, a good Gas Chromatography (GC) detector should therefore be highly sensitive and be able to detect very low amount of the sample being produced (Wheelock et al., 2008; Wedad et al., 2017). Detectors that are recommended in Gas Chromatography protocol are various but the preferred one in this study was the Electron capture detector (ECD) with mass spectrometry for compound identification purposes and is the most commonly used detector for routine laboratory assays.

3.5 Data analysis

Data was recorded and stored in Excel spreadsheet program for Windows 2013. Processed data values were summarized according to sampled stations and seasons (wet and dry) for the study into frequency tables and bar graphs as mean (± SE) readings for each sampling station. Descriptive and inferential statistics were used to analyse the data collected using a level of significance of 0.05. Statistical analyses were performed using GraphPad Prism version 5.03 (GraphPad Software Inc., California, USA). Data normality was confirmed using D'Agostino and Pearson omnibus K2 test. Determination of the variations in organochlorine pesticides mean concentrations values between sampling stations was performed using one-way ANOVA (Analysis of variance) statistical method, at the 95% confidence level, while independent sample *T*-test was performed in determination of variations in mean values of OCPs between wet and dry seasons. Significant differences were determined at $p < 0.05$. Tukey's *post hoc* pairwise comparison test was applied when significant differences between means were observed, to identify the specific sampling stations that differed from one another. Correlation coefficients between the levels of organochlorines and physico-chemical parameters was assessed using a dimensionless index, Pearson product moment correlation test (r) whereby a p-value of ≤ 0.05 was considered statistically significant.

3.6 Test of hypotheses

The hypotheses were tested by comparing the means of the measured concentrations with those of the acceptable limits. The null hypotheses was used in the analysis, with the hypotheses rejected if the calculated S values were less than the threshold values ($S_{calculated} > S_{threshold}$) at the 95% confidence level.

CHAPTER FOUR

RESULTS

4.1 Introduction

The results on the spatial and temporal concentrations of organochlorine pesticide residues classified as hexachlorocyclohexanes, dichlorodiphenyltrichloroethanes and cyclodienes in water, sediments and fish samples obtained from fish ponds, waste water lagoons and rivers receiving run-off from farms in River Kuja watershed are presented in this chapter. The type of effluent targeted in this study originated from horticultural farms, cattle dips (cattle dipping tanks), coffee pulpberries and wastewater lagoons. The following organochlorine pesticide residues were identified and quantified: α-HCH, β-HCH, γ-HCH, δ-HCH, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, aldrin, endrin, dieldrin, endrin aldehyde, endosulfan I, endosulfan II, endosulfan sulfate, heptachlor, heptachlor epoxide, and methoxychlor. Determination of variations in organochlorine pesticides mean concentrations value between sampling stations was performed using one-way ANOVA (Analysis of variance) statistical method, at the 95% confidence levels, while independent sample *T*-test was performed in determination of variations in mean values of OCPs between wet and dry seasons. Significant differences were determined at $p < 0.05$. Tukey's *post hoc* pair-wise comparison test was applied when significant differences between means were observed, to identify the specific sampling stations that differed from one another.

4.2 Concentration of the organochlorine pesticides (OCPs) in earthen fish ponds water

4.2.1 Concentrations of the HCH isomers in the earthen fish ponds water

The mean (± SE) spatial concentrations of hexachlorocyclohexanes (HCH) pesticides and its isomers (α-HCH, β-HCH, δ-HCH and γ-HCH) in fish ponds water samples from sampling stations B to G depicted a fluctuating trend in concentrations. The mean γ-HCH (gamma) pesticide compound concentration recorded for sampling station D, F and G was 0.572 ±0.032 μgL^{-1}, 0.194 ±0.003 μgL^{-1} and 0.454 ±0.007 μgL^{-1}, respectively. The observed HCH isomer residue level range was from below detection limit (BDL) to the highest mean γ-HCH concentration of 0.585±0.002 μgL^{-1} (Figure 4.1). A one-way analysis of variance (ANOVA) test showed that mean γ-HCH concentration was not significantly different among the sampling stations ($p > 0.05$; F = 1.613; $p = 0.426$).

Stations B, C, D and E showed moderate variations in mean residue levels of β-HCH (beta) and δ-HCH which were mostly below the detection limit (BDL) during the sampling period. In addition, α-HCH (alpha) isomer also recorded mean residue value of below detection limit (BDL) in station C and E to 0.17 ±0.008 μgL^{-1} in station D. In addition, the distribution of β-HCH and δ-HCH (delta) isomers in station E and F recorded BDL concentrations during the sampling period. Overall, HCH pesticides concentration results in stations B to E stations in River Kuja watershed exhibited significant mean (± SE) variations among the sampling stations, with values ranging between BDL to 0.572 ±0.002 μgL^{-1}, respectively. A one-way analysis of variance (ANOVA) test of results obtained from sampled stations indicated that the mean α-HCH isomer concentrations was not statistically significant among sampling stations ($p > 0.05$; F = 2.415; $p = 0.349$), at the 95% confidence level, Figure 4.1.

In station B, only α-HCH (alpha) pesticide indicated a significantly low mean residue level of 0.109 ±0.072 μgL^{-1} but in station C and E it recorded BDL residue levels. (Figure 4.1).

However, in sampling station F results showed isomer α-HCH, β-HCH and δ-HCH (delta) indicated below detection limit (BDL) pesticides values, as nil values were recorded during the study. Further, observations made on the analysed data sets (Figure 4.1), indicated mean δ-HCH isomer residue concentrations of 0.006 ±0.0001 μgL^{-1} as the lowest overall in all the stations from B to G sampled. However, in station B, C and D residue levels shown by α-HCH, β-HCH and δ-HCH was that of below detection limit (BDL) as no reading was recorded during the sampling period but stations D and G indicated presence of γ-HCH pesticides. ANOVA results showed that mean δ-HCH concentration was not statistically significant among sampling stations ($p > 0.05$; F = 1.746; $p = 0.163$) at the 95% confidence level.

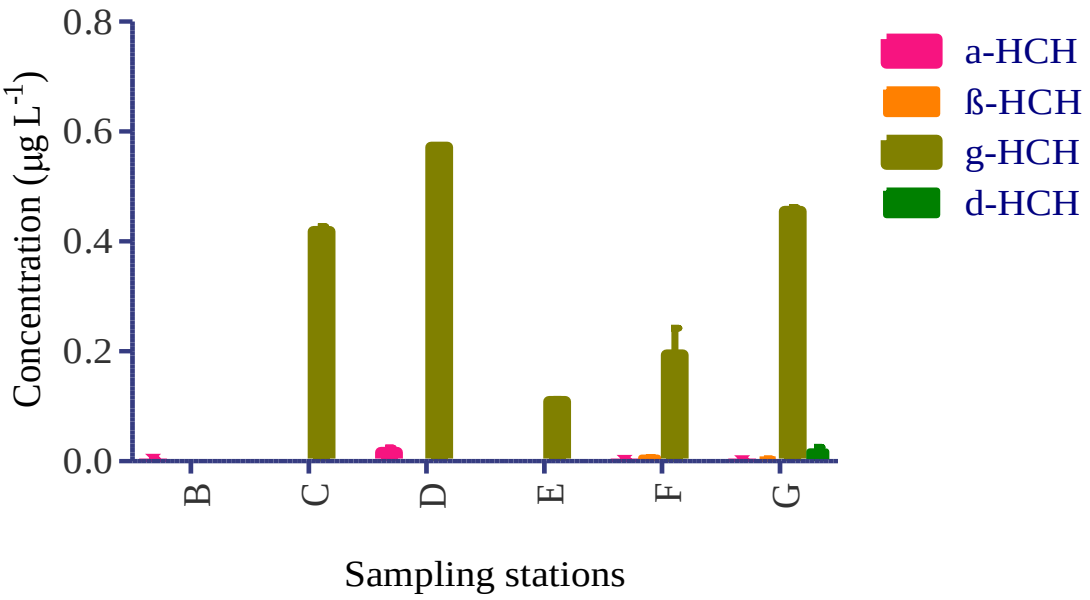

Figure 4.1: **Spatial mean (± SE) variations of the HCH isomers in the earthen fish ponds water**.

Mean (± SE) temporal distribution results of HCH isomers during wet and dry seasons is shown in Figure 4.2. Overall trend of the results indicated that mean residue levels obtained in the wet season were higher than levels recorded in the dry season. Analysis of the target pesticides indicated that mean α–HCH (alpha) isomer residue level was below detection limit (BDL) in

target fish ponds during the wet season, while γ-HCH had the highest mean concentration in sampled fish ponds water (0.392 ±0.081 μgL^{-1}). Additionally, the temporal distributions showed moderate variations in mean concentrations of γ-HCH (0.392 ±0.081 μgL^{-1}) and β-HCH (0.194 ±0.036 μgL^{-1}) residue levels during the wet season (Figure 4.2). In the entire data sets observed in the wet season, highest mean concentration level recorded was by γ-HCH (0.392 ±0.081 μgL^{-1}) in fish ponds water samples while the lowest recorded was by α-HCH (BDL) within the study period. The independent sample *T*-test showed that the mean β-HCH concentration was significantly different among wet and dry seasons ($p < 0.05$; t = 1.959; $p = 0.005$).

In addition, independent sample *T*-test on temporal α-HCH mean level concentrations showed no significant differences between wet and dry seasons ($p > 0.05$; t = 1.401; $p = 0.162$) at the 95% confidence level. Furthermore, average temporal concentrations of HCH isomers in fish ponds water samples are shown (Figure 4.2) and the pesticides residue levels ranged from below detection limit (BDL) to 0.032 μgL^{-1}. Isomer γ-HCH recorded the highest mean value of 0.0291 ±0.002 μgL^{-1} and the lowest residue value was recorded by δ-HCH (0.009 ±0.0001 μgL^{-1}) during the dry season. Furthermore, *T*-test statistical analysis on γ-HCH mean concentration values indicated that means differences were significantly different among sampling seasons ($p < 0.05$; t = 1.689; $p = 0.001$).

Comparison of HCH isomer concentrations in fish ponds between wet and dry seasons as illustrated in Figure 4.2 indicate that isomer mean concentrations during wet and dry seasons showed modest fluctuations. Mean residue level for lindane in the dry season (γ-HCH) was shown to be in the range from 0.009 ±0.0003 μgL^{-1} to 0.029 ±0.003 μgL^{-1} whereby lowest mean concentration level was exhibited by β-HCH (0.009 ±0.0003 μgL^{-1}). The isomer with the highest mean concentration in fish ponds water in the dry season was α-HCH (0.025 ±0.0003 μgL^{-1}). Overall mean (± SE) results indicated HCHs residue variations in fish ponds during the

in wet and dry seasons (temporal) contained lower mean residue concentrations between seasons, as compared to mean values obtained between different stations (spatial) distributions. This is especially shown by α-HCH and δ-HCH pesticides in sampled water column (Figure 4.2) in the dry season. A statistical *T*-test run on mean α-HCH concentration indicated that the differences between wet and dry seasons were not statistically different ($p > 0.05$; t = 1.203; $p = 0.081$) at the 95% confidence level. Overall, mean temporal value for lindane (γ-HCH) in wet and dry seasons was observed to be higher among the four HCH isomers, at 0.332 ±0.073 μgL^{-1} (wet) and 0.022 ±0.006 μgL^{-1} (dry) season, respectively. However, *T*-test results on δ-HCH temporal variations showed no statistical significant difference between sampling seasons ($p > 0.05$; t = 2.030; $p = 0.634$), at the 95% confidence level.

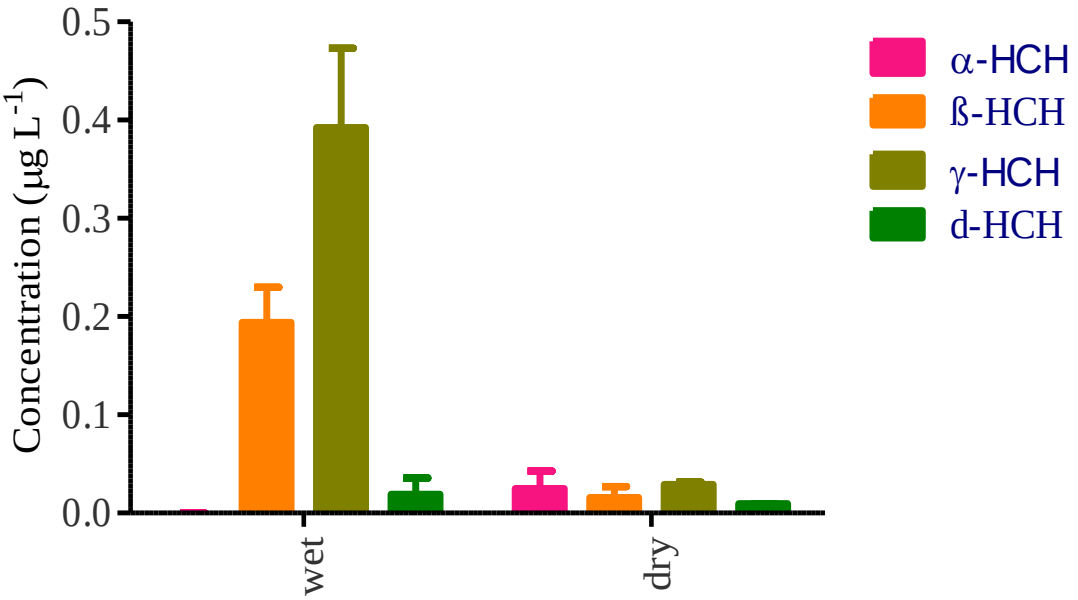

Figure 4.2: **Temporal mean (± SE) variations of the HCH isomers in the earthen fish ponds water**.

Table 4.1 shows correlations between pesticide residue concentrations and water quality parameters in water samples from fish ponds during wet and dry seasons. Negative and positive correlation with ($p < 0.05$ significant level), were calculated during the study. Strong positive

correlations were in the range of 0.745 to 0.957 (Table 4.1) and they were observed for α-HCH isomer against pH (r = 0.957; p = 0.0002) in the wet season, and whose relationship was significantly different ($p < 0.05$) between wet and dry season. The highest positive correlation of 0.988 was obtained for the parameters δ-HCH against total phosphorus, and the relationship was observed to be statistically significant (p = 0.020; $p < 0.05$) between the wet and dry season. The highest negative correlation of -0.889 was obtained between δ-HCH against temperature levels, and observed to be significantly different among wet and dry season. Similarly, a strong negative correlation of -0.889 (p = 0.03) was observed between δ-HCH and temperature during the wet season, α-HCH and DO, δ-HCH and conductivity; δ-HCH with DO as well as between δ-HCH and TN concentrations respectively, in water samples from fish ponds during the wet season.

Positive correlations in the dry season were in the range of 0.359 to 0.526 (Table 4.1). Physico-chemical parameters were therefore less strongly correlated in the dry season than in the wet season. The highest positive correlation in the dry season was (r = 0.526; p = 0.181) between δ-HCH and pH, though not statistically significant ($p > 0.05$), while the lowest was between α-HCH isomer concentration and conductivity (r = 0.359; p = 0.38). Both correlation relationships of δ-HCH with pH and α-HCH against conductivity were not significantly different ($p > 0.05$) among sampling seasons.

Table 4.1: **Pearson correlation coefficients between the HCH isomer concentrations and the levels of water quality measurements in earthen fish ponds during the wet and dry seasons.**

Wet season	**Temp** (°C)	**Cond** (μScm^{-1})	**TSS** (μgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (μgL^{-1})	**TN** (μgL^{-1})
α-HCH	r =-.381	r =-0.234	r =0.394	r=0.025	r =0.957	r =0.235	r =0.593	r =-.081
	p=0.352	p =0.578	p=0.334	p =.953	p=**0.0002**	p=0.575	p =0.121	p=0.848
β-HCH	r =-.661	r =-0.144	r =0.636	r =-.173	r =0.144	r =0.812	r =0.567	r =-.510
	p=0.075	p =0.733	p=0.089	p=0.682	p =0.733	p=**0.014**	p =0.143	p=0.196
γ-HCH	r =-.592	r =0.339	r =0.480	r =0.650	r =0.380	r =0.261	r =0.678	r =0.193
	p=0.123	p =0.412	p=0.229	p=0.081	p =0.353	p=0.533	p =0.065	p=0.647
d-HCH	r =-.889	r =0.082	r =0.745	r =-.025	r =0.233	r =0.905	r =0.988	r =-.250
	p=**0.003**	p =0.847	p=**0.034**	p=0.953	p =0.579	p=**0.002**	p =**0.020**	p=0.550
Dry season								
α-HCH	r =-.032	r =0.359	r =-.849	r =0.497	r =-0.572	r =-.854	r =-.927	r =-.701
	p=0.941	p =0.387	p=**0.008**	p=0.210	p =0.139	p=**0.007**	p =**0.001**	p=0.053
β-HCH	r =-.454	r =-0.474	r =-.118	r =-.106	r =0.033	r =0.014	r =-.257	r =-.239
	p=0.259	p =0.235	p=0.781	p=0.802	p =0.938	p=0.974	p=0.538	p=0.569
γ-HCH	r =-.738	r =-0.439	r =-.805	r =-.167	r =-0.410	r =-.531	r =-.675	r =-.413
	p=**0.037**	p =0.275	p=**0.016**	p=0.692	p =0.313	p=0.176	p =0.066	p=0.309
d-HCH	r =0.087	r =0.163	r =0.035	r =-.525	r =0.526	r =-.161	r =0.160	r =-.269
	p=0.838	p =0.699	p=0.934	p=0.182	p =0.181	p=0.704	p =0.705	p=0.519

Note: Boldface represent statistically significant *p*-values of the correlation coefficients as determined by Pearson's correlation test. *r* represents Pearson's moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

The strongest negative correlation (r = - 0.927, p = 0.001) during the dry season was obtained for the α-HCH and total phosphorus (TP) contents, while the levels of α-HCH and total suspended solids (TSS), α-HCH and turbidity, δ-HCH concentrations and pH in water samples

from fish ponds showed weak or no correlation. The spatial variat ion of physico-chemical parameters is presented in Appendix IX. Temperature, pH, DO, and TN did not show any significant spatial variation ($p > 0.05$), while the parameters: conductivity, total suspended solids (TSS), turbidity and total phosphorus (TP) depicted a significant spatial variation ($p < 0.05$) between wet and dry season.

4.2.2 Concentration of the DDT metabolites in the earthen fish ponds water

Dichlorodiphenyltrichloroethane (DDT) metabolites concentrations analysed between different sampling stations in this section were: *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT. Figure 4.3 shows mean (± SE) concentrations of DDT metabolite residues detected in fish ponds (µg L^{-1}) water samples between different stations. The mean DDT and its metabolites recorded at different study stations was 0.112 μgL^{-1} in sampled fish ponds water. Spatial residue concentrations ranged between BDL to 0.197 ±0.063 for *p,p'*-DDE; BDL to 0.090 ±0.021 for *p,p'*-DDD (at sampling station C & F) and BDL to 0.072 ±0.007 for *p,p'*-DDT (at sampling station B and D) for the three DDT metabolites (Figure 4.3). However, the overall mean results of the three DDT metabolites obtained during the study period were 0.239 ±0.076 μgL^{-1}; 0.038 ±0.011 μgL^{-1} and 0.059 ±0.023 μgL^{-1} for *p,p'*-DDE, *p,p'*-DDT and *p,p'*-DDD in stations C, D and F, respectively. All the DDT metabolites were in concentrations below the detection level (BDL) in station B. A one-way analysis of variance (ANOVA) test in mean *p,p'*-DDE concentrations between sampled stations over the two year period indicated a statistically significant difference ($p < 0.05$; $F = 65.258$; $p = 0.007$) in fish ponds water samples (Figure 4.3). Tukey's *post hoc* test for separation of means revealed that mean *p,p'*-DDE concentration for station F varied significantly from mean *p,p'*-DDE concentration observed at sampling stations C and D.

Additionally, DDT metabolites' spatial distributions in fish ponds water samples in sampled stations indicated concentrations ranging from BDL to 0.052 μgL^{-1} in station C. In station F,

metabolite *p,p'*-DDD exhibited widest concentration range, while *p,p'*-DDE had the narrowest spatial distribution, and stations D and G showed concentrations ranging from BDL to 0.008 μgL^{-1}. Hence, the spatial distribution of the metabolites exhibited a wide variation during the sampling period. However, the distribution of both alpha and beta DDT metabolites exhibited a similar range, that is, from BDL to 0.05 μgL^{-1}. Analysis of variance (ANOVA) test results of the mean *p,p'*-DDD contaminant indicated a statistically significant difference among sampled stations ($p < 0.05$; $F = 7.631$; $p = 0.036$). Furthermore, spatial mean concentrations of *p,p'*-DDT metabolite in fish ponds water samples collected in target sampled stations indicated a statistically significant difference ($p < 0.05$) at the 95% confidence level. Tukey's *post hoc* test for separation of means revealed that mean *p,p'*-DDD residue level for station E varied significantly from mean *p,p'*-DDD residue level observed at sampling stations C and F.

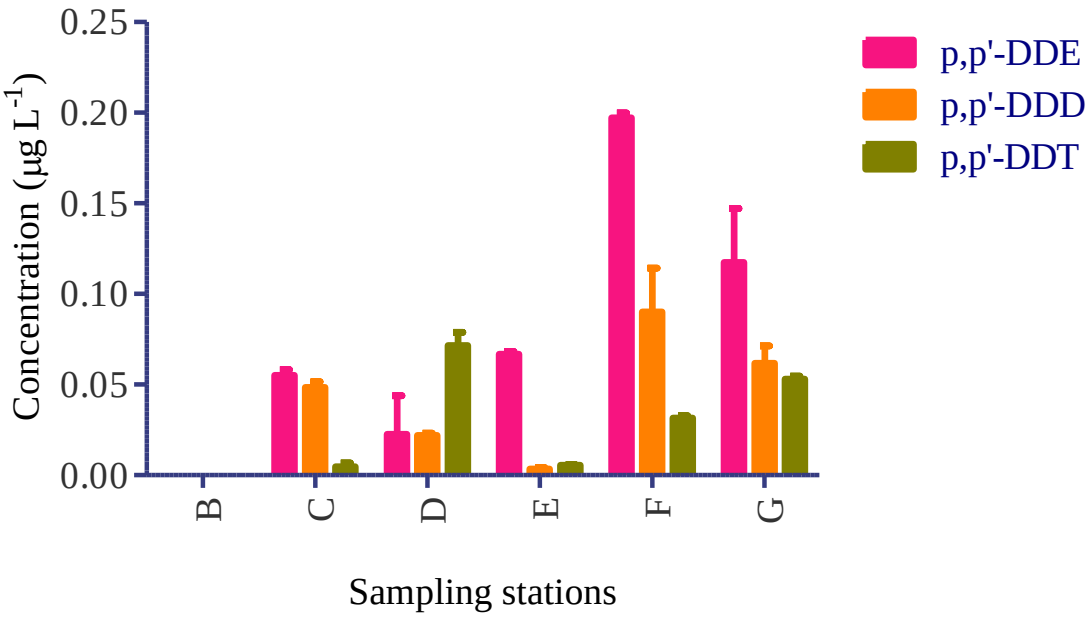

Figure 4.3: **Spatial mean (± SE) concentrations of the DDT and its metabolites in the earthen fish ponds water**.

Figure 4.4 represents observed temporal pesticides variations in both wet and dry seasons. The highest mean concentration level shown was by *p,p'*-DDE (0.371 ±0.055 μgL^{-1}) in fish ponds

water samples during the wet season, while the lowest recorded was by *p,p'*-DDD (0.083 ±0.055 μgL^{-1}) in the dry season. Additionally, results showed that DDT metabolite pesticide concentrations were in the range between 0.083 to 0.571 ±0.005 μgL^{-1} and 0.021 to 0.039 ±0.0002 μgL^{-1} in both wet and dry seasons, respectively. Furthermore, mean DDT pesticides concentrations showed high concentrations during the wet season. The independent sample *T*-test statistical method on the mean *p,p'*-DDE results showed statistically significant differences between the wet and dry seasons ($p < 0.05$; $p = 0.016$), at the 95% confidence level imit (Figure 4.4). Overall observations on the data presented indicates that differences in the mean (± SE) concentration of *p,p'*-DDT metabolite did not show any significant difference ($p > 0.05$; $t = 1.679$; $p = 0.316$) between the wet and dry seasons.

Further analysis of DDT metabolite residue levels recorded in the dry season were as follows; *p,p'*-DDE: 0.039 ±0.001 μg L^{-1}; *p,p'*-DDD: 0.021 ±0.006 μgL^{-1} and *p,p'*-DDT: 0.041 ±0.006 μgL^{-1} for fish ponds water samples in the dry season, respectively (Figure 4.4). In decreasing order, the mean concentrations were:- *p,p'*-DDT< *p,p'*-DDE< *p,p'*-DDD, for the samples collected during the dry season. Independent sample *T*-test results indicated that mean *p,p'*-DDD concentrations obtained during the wet and dry seasons were not statistically significant ($p > 0.05$; $t = 1.673$; $p = 0.119$), at the 95% confidence level.

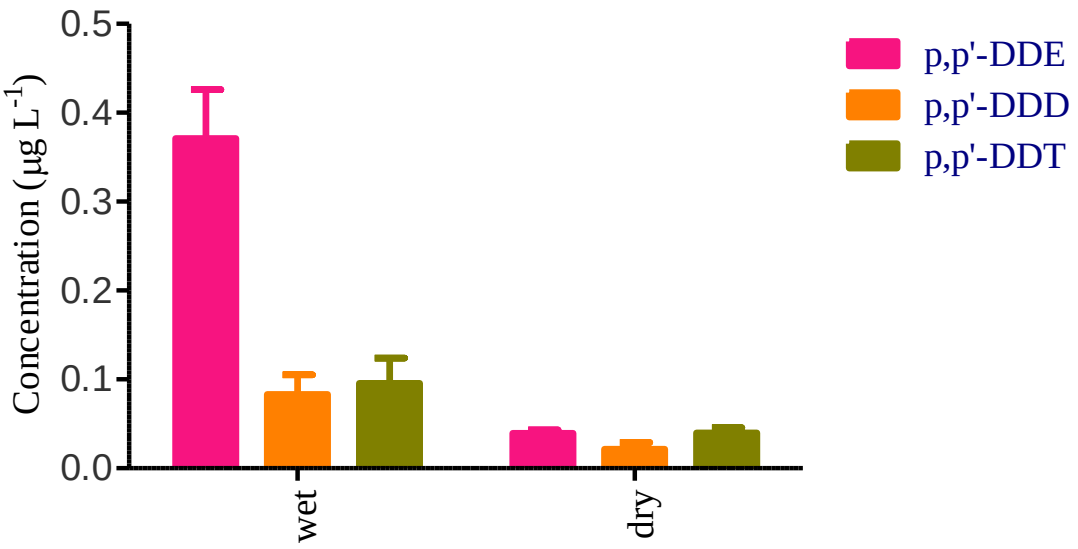

Figure 4.4: **Temporal mean (± SE) concentrations of the DDT and its metabolites in the earthen fish ponds water**.

Table 4.2 indicates correlation between DDT metabolite pesticide residues and water quality parameters in fish ponds over the wet and dry seasons. Significant positive and negative correlation ($p < 0.05$) of the metabolites with physico-chemical parameters were observed over the sampling period. All the three DDT metabolites indicated a strong positive correlation towards total suspended solids (TSS). *p,p'*-DDD also had a strong positive correlation with turbidity (r = 0.716; $p = 0.046$) in the wet season. Similarly, a strong positive correlation was also observed between *p,p'*-DDE metabolite and total suspended solids (TSS) and the relationship was noted to be statistically significant (r = 0.746; $p = 0.034$) in the wet season. However, *p,p'*-DDE metabolite showed a weak negative correlation to temperature, conductivity and total nitrogen (TN) in the wet season. In addition, *p,p'*-DDD metabolite showed a strong positive correlation towards turbidity and TSS (r = 0.716, $p = 0.046$; r = 0.833; $p = 0.010$). The relationship was noted to be statistically significant ($p < 0.05$). Furthermore, *p,p'*-DDE was observed to be negatively correlated to other measured water quality parameters during the wet season. All negative correlations of the measured DDT metabolites with

physico-chemical parameters were not statistically significant ($p > 0.05$; $p = 0.531$) at the 95% confidence level.

During the dry season, all positive correlations between the DDT metabolites and the physico-chemical parameters were not significantly different (Table 4.2). This was contrary to the wet season observations, where all the three metabolites had strong positive correlations with physico-chemical parameters. *p,p'*-DDD and *p,p'*-DDT metabolites showed strong negative correlation with total phosphorus (TP) (r = -0. 722; $p = 0.043$) and total nitrogen (TN) (r = -0.932; $p = 0.001$) and the relationship was statistically significant ($p < 0.05$). The positive correlation value of 0.476 was the highest, then followed by 0.422, and 0.001 was the lowest value.

Table 4.2: **Pearson correlation coefficients between the DDT metabolites and water quality parameter measurements in the earthen fish ponds during wet and dry seasons**.

Wet season	**Temp** (°C)	**Cond** (μScm^{-1})	**TSS** (μgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (μgL^{-1})	**TN** (μgL^{-1})
p,p'-	r =-.487	r =-.313	r =0.746	r =0.342	r =0.486	r =0.576	r =0.589	r =-.247
DDE	p=0.221	p=0.451	p=**0.034**	p=0.407	p=0.222	p=0.135	p =0.124	p=0.556
p.p'-	r =-.522	r =-.418	r =0.833	r =-.134	r =0.371	r =0.716	r =0.524	r =-.666
DDD	p=0.185	p=0.303	p=**0.010**	p=0.751	p=0.365	p=**0.046**	p =0.1818	p=0.072
p,p'-	r =-.417	r =-.451	r =0.739	r =0.149	r =0.372	r =0.612	r =0.471	r =-.439
DDT	p=0.305	p=0.263	p=**0.036**	p=0.723	p=0.365	p=0.107	p =0.239	p=0.276
Dry season								
p,p'-	r =0.147	r =0.318	r =-.161	r =-.394	r =0.398	r =-.385	r =-0.199	r =-.663
DDE	p=0.729	p=0.443	p=0.703	p=0.335	p=0.329	p=0.347	p =0.636	p=0.073
p,p'-	r =0.273	r =0.381	r =-.138	r =-.459	r =0.031	r =-.139	r =-0.140	r =-.743
DDD	p=0.513	p=0.352	p=0.745	p=0.252	p=0.942	p=0.743	p =0.741	p=**0.035**
p,p'-	r =0.106	r =0.422	r =-.556	r =0.001	r =-.071	r =-.593	r =-0.722	r =-.932
DDT	p=0.803	p=0.298	p=0.152	p=0.998	p=0.867	p=0.121	p =**0.043**	p=**0.001**

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

4.2.3 Concentration of the cyclodiene compounds in the earthen fish ponds water

Cyclodiene compounds are chlorinated insecticides whose molecular structures are based on cyclodiene rings, formerly used in agriculture to control pests and for public health purposes. They are stable compounds and due to this, poisoning of organisms in the habitat is attributed to them when applied for pest control. In this study 10 cyclodiene compounds, namely aldrin, endrin, endrin aldehyde, dieldrin, heptachlor, heptachlor epoxide, endosulfan I, endosulfan II, endosulfan sulfate and methoxychlor compounds were studied.

The spatial variations in mean (± SE) residue levels of cyclodiene compounds in fish ponds (μgL^{-1}) water samples between various sampled stations is presented in Figure 4.5 and in Appendix X. Endrin pesticide showed highest mean concentration of 0.513 ±0.150 μgL^{-1} in station G while in stations B, C and D it indicated a BDL concentration. Results showed that heptachlor, aldrin, heptachlor epoxide, endrin, endosulfan II and methoxychlor cyclodiene compounds exhibited below detection limit in B, D, E and G sampling stations while concentrations of endosulfan I were above detection limit at all sampling stations. In addition, dieldrin cyclodiene pesticide compound showed a below detection limit (BDL) level in sampled stations (B to G). The spatial distribution of the cyclodienes encountered during the study period ranged between BDL to 0.506 ±0.150 μgL^{-1}, with endrin pesticide recording highest residue values of 0.471 ±0.082 μgL^{-1} and 0.506 ±0.150 μgL^{-1} in stations E, F and G, respectively. Results indicate that the cyclodiene pesticides compound with the highest concentration was endrin (0.506 ±0.150 μgL^{-1}) at station G. A one-way analysis of variance (ANOVA) test indicated that mean endrin aldehyde concentrations were statistically significant among sampling stations ($p < 0.05$; $F = 25.351$; $p = 0.004$), at the 95% confidence level.

Tukey's *post hoc* test for separation of means revealed that mean endrin aldehyde concentration for station B varied significantly from mean endrin aldehyde concentration observed at sampling stations E and G. Furthermore, lowest concentration recorded in the target area was dieldrin in the range of BDL to 0.0180 μgL^{-1}, as it registered below detection limit concentrations in all sampled stations, while methoxychlor also exhibited (BDL to 0.506 μgL^{-1}) at station B, C and at station D.

The cyclodiene compound with widest distribution (Figure 4.5) in River Kuja watershed was heptachlor and endosulfan I which were detected in target sampling stations B to G. In summary, the spatial distribution of cyclodiene pesticide compounds with highest residue level concentrations in fish ponds were observed to be endrin at station G and endosulfan I pesticide ($0.114 \pm 0.002\ \mu gL^{-1}$) at station G and methoxychlor showed ($0.307 \pm 0.007\ \mu gL^{-1}$) at station C (Figure 4.5). A one-way analysis of variance (ANOVA) test indicated that mean methoxychlor pesticide concentrations were not statistically significant among sampling stations ($p < 0.05$; $F = 3.841$; $p = 0.074$) at the 95% confidence level. Further analysis indicated that mean concentration values for endosulfan II pesticide residue levels were not significantly different between stations ($p > 0.05$; $p = 0.072$), at the 95% confidence level.

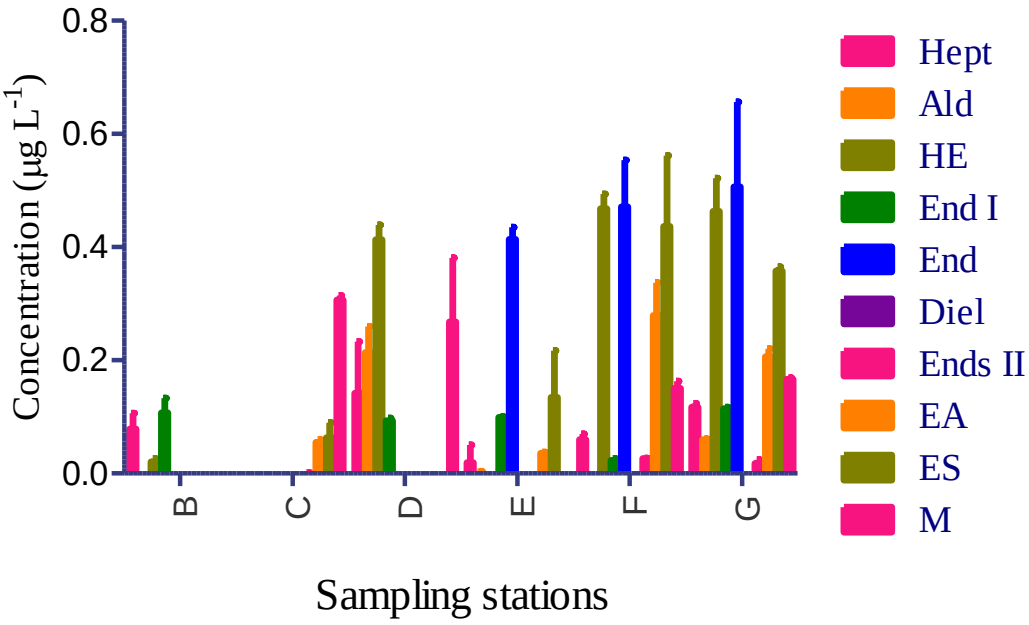

Figure 4.5: **Spatial mean (± SE) distributions of the cyclodiene compounds in the earthen fish ponds water**.

Mean (± SE) temporal distribution of cyclodiene organochlorine pesticides in fish ponds water samples is presented in Figure 4.6. Mean pesticides concentrations of dieldrin and heptachlor epoxide showed contaminant residue levels of between 0.002 to 0.194 ±0.00014 μgL^{-1} as shown by pesticides in the wet season respectively, while in the dry season, the residue level concentration was in the range between 0.002 ±0.0004 μgL^{-1} to 0.062 ±0.0001, as obtained by methoxychlor and endrin cyclodiene pesticides, respectively. Overall lowest mean levels were those of endosulfan II (0.008 ±0.004 μgL^{-1}) and dieldrin 0.002 ±0.001 μgL^{-1} while heptachlor epoxide compound showed highest mean of 0.194 ±0.076 μgL^{-1} in fish ponds during the wet season. The Independent sample *T*-test statistical method indicated that there was a statistical significant difference ($p < 0.05$; t = 1.831; $p = 0.003$) between mean endosulfan sulfate pesticide over wet and dry seasons. The distribution of cyclodiene pesticide compounds in the wet season showed that endrin aldehyde (0.103 ±0.024 μgL^{-1}), endosulfan I (0.187 ±0.008 μgL^{-}

^{1}) and II as well as endrin (0.187 ±0.008 μgL^{-1}) cyclodiene pesticides compounds indicated high concentrations in the wet season (Figure 4.6), while endosulfan II and dieldrin indicated lowest pesticides contaminant levels in fish ponds during the wet season. Independent sample *T*-test statistical method indicated that mean endosulfan I concentration obtained in fish ponds water samples was statistically significant ($p < 0.05$; t = 2.052; $p = 0.003$) between wet and dry seasons.

Additionally, mean (± SE) temporal distribution of cyclodiene pesticide compounds in the dry season indicated that endrin (0.069 ±0.002 μgL^{-1}), dieldrin (0.047 ±0.005 μgL^{-1}) and endosulfan II (0.044 ±0.002 μgL^{-1}) contaminant levels in fish ponds had high mean scores while residue levels that were lower was by methoxychlor, endosulfan sulfate and heptachlor epoxide, at mean levels of 0.002 μgL^{-1} in the dry season months. Further analysis of the cyclodienes in the dry season indicated a mean score range to be 0.002 ±0.00015 μgL^{-1} by methoxychlor pesticide, to a concentration of 0.069 ±0.003 μgL^{-1} by endosulfan pesticide compound (Figure 4.6). The cyclodiene compound with a wide distribution in the study area during the dry season was heptachlor. Significance level ($p < 0.05$) of means of aldrin pesticide over the two year study period using independent sample *T*-test indicated that mean aldrin pesticide level recorded in fish ponds water samples over the two year period was significantly different ($p < 0.05$; t = 1.158; $p = 0.001$) between wet and dry seasons.

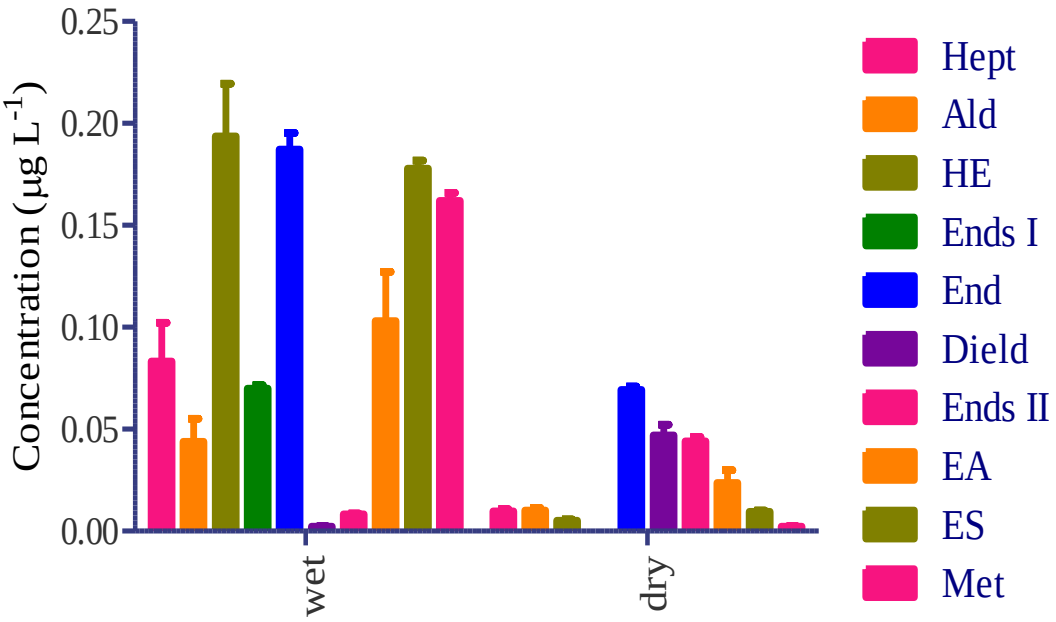

Figure 4.6: **Temporal mean (± SE) distributions of the cyclodiene compounds in the earthen fish ponds water**.

Strong positive and negative correlations (Table 4.3) was obtained for cyclodiene pesticides concentrations against water quality parameters at various sampling stations during the wet season. Endosulfan II compound was strongly positively correlated to turbidity (r = 0.915; p = 0.03), total phosphorus (r = 0.782; p = 0.025), total suspended solids (0.655; p = 0.044) in the wet season and the relationship was noted to be statistically significant as well ($p < 0.05$). In addition, endosulfan sulfate indicated a strong positive correlation with pH levels in the wet season and was statistically significant (r = 0.883; p = 0.032; $p < 0.05$). Though relationships were statistically significant ($p < 0.05$; p =0.002), heptachlor compound showed a negative correlation with all measured water quality parameters. This correlation was observed to be with temperature and TSS in wet season only (r = -0 .738, p = 0.03; r = -0.905, p = 0.034), respectively. In the dry season, heptachlor was positively correlated towards TSS (r = 0.655, p = 0.022), TP (r = 0.782, p = 0.033) and towards turbidity (r = 0.915, p = 0.03) and the relationship was statistically significant ($p < 0.05$). Heptachlor epoxide and endrin aldehyde

were positively correlated with pH (r = 0.883, p = 0.05) and (r = 0.806, p = 0.016) and the relationship was statistically significant (p < 0.05), in the dry season respectively (Table 4.3). In comparison, heptachlor epoxide was negatively correlated against temperature (r = -0.257, p = 0.539) and towards conductivity (r = -0.059, p = 0.889) while endrin aldehyde was noted as negatively correlated towards turbidity and dissolved oxygen (DO), (r = -0.199, p = 0.637) in the dry season. Both relationships in the dry season were not statistically significant (p > 0.05) at the 95% confidence level.

In addition, Table 4.3 shows that heptachlor pesticide compound was positively correlated with TSS (r = 0.776; p = 0.121) but not statistically different in the dry season. However, it was strongly correlated to turbidity (r = 0.915; p = 0.033) and to TP (r = 0.782; p = 0.033) in water column during the dry season, and the relationship was statistically significant in the dry season (p < 0.05). These results illustrated the fact that both both heptachlor pesticide increased positively as the water parameters TSS, turbidity and TP increased. Alternatively, heptachlor epoxide was positively correlated with pH (r = 0.883; p = 0.05). Endrin aldehyde showed a positive correlation with pH (r = 806, p = 0.016) in the dry season but was negatively correlated with turbidity (r = -0.199, p = 0.637) in the dry season, respectively.

Table 4.3: **Pearson correlation coefficients between the cyclodiene pesticides concentrations and the water quality parameter measurements in the earthen fish ponds during the wet and dry seasons**.

Wet season	**Temp** (°C)	**Cond** (μScm^{-1})	**TSS** (μgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (μgL^{-1})	**TN** (μgL^{-1})
Heptachlor	r =-.738	r =-0.439	r =-.905	r =-.167	r =-.410	r =-.531	r =-0.675	r =-0.413
	p =**0.03**	p =0.275	p=**0.034**	p=0.692	p=0.313	p=0.176	p =0.066	p =0.309
Aldrin	r =0.087	r =0.163	r =0.035	r =-.525	r =0.526	r =-.161	r =0.160	r =-0.269
	p=0.838	p =0.699	p=0.934	p=0.182	p=0.181	p=0.704	p =0.705	p =0.519

Heptachlo	r =0.147	r =0.318	r =-.161	r =-.394	r =0.398	r =-.385	r =-0.199	r =-0.663
r Epoxide	p=0.729	p =0.443	p=0.703	p=0.335	p=0.329	p=0.347	p =0.636	p =0.073
Endosulfa	r =0.273	r =0.381	r =-.138	r =-.459	r =0.031	r =-.139	r =-0.140	r =-0.743
n I	p=0.513	p =0.352	p=0.745	p=0.252	p=0.942	p=0.743	p =0.741	p =**0.035**
Endrin	r =0.106	r =0.422	r =-.556	r =0.001	r =-.071	r =-.593	r =-0.722	r =-0.932
	p=0.803	p =0.298	p=0.152	p=0.998	p=0.867	p=0.121	p =**0.043**	p =**0.021**
Dieldrin	r =-.592	r =0.339	r =0.480	r =0.650	r =0.380	r =0.261	r =0.678	r =0.193
	p=0.123	p =0.412	p=0.229	p=0.081	p=0.353	p=0.533	p =0.065	p =0.647
Endosulfa	r =-.889	r =0.082	r =0.655	r =-.025	r =0.233	r =0.915	r =0.782	r =-0.250
n II	**p=0.003**	p =0.847	p=**0.044**	p=0.953	p=0.579	p =**0.03**	p =**0.025**	p =0.550
Endrin	r = -.527	r = -0.069	r =0.219	r =0.151	r =0.596	r =0.247	r =0.575	r =0.041
Aldehyde	p =.180	p = 0.871	p=0.602	p=0.720	p=0.119	p=0.556	p =0.136	p =0.923
Endosulfa	r = -.257	r = -0.059	r =0.121	r =-.195	r =0.883	r =-.015	r =0.441	r =-0.073
n sulfate	p=0.539	p = 0.889	p=0.776	p=0.644	p=**0.032**	p=0.973	p =0.274	p =0.864
Methoxyc	r = -.799	r = 0.177	r =0.402	r =0.089	r =0.544	r =0.651	r =0.837	r =-0.059
hlor	p=**0.037**	p = 0.675	p=0.323	p=0.833	p=0.163	p=0.080	p =**0.019**	p =0.889
Dry season								
Heptachlo	r =-.889	r =0.082	r =0.655	r =-.025	r =0.233	r =0.915	r =0.782	r =-0.250
r	**p=0.003**	p =0.847	p=**0.022**	p=0.953	p=0.579	p =**0.03**	p =**0.033**	p =0.550
Aldrin	r = -.527	r = -0.069	r =0.219	r =0.151	r =0.596	r =0.247	r =0.575	r =0.041
	p=0.180	p = 0.871	p=0.602	p=0.720	p=0.119	p=0.556	p =0.136	p =0.923
Heptachlo	r = -.257	r = -0.059	r =0.121	r =-.195	r =0.883	r =-.015	r =0.441	r =-0.073
r Epoxide	p=0.539	p = 0.889	p=0.776	p=0.644	p =**0.05**	p=0.973	p =0.274	p =0.864
Endosulfa	r = -.136	r =-0.602	r =0.558	r =-.394	r =0.609	r =0.101	r =0.154	r =-0.247
n I	p =.748	p =0.115	p=0.151	p=0.335	p=0.109	p=0.812	p =0.716	p =0.556
Endrin	r =0.161	r =0.520	r =-.611	r =0.359	r =-.058	r =-.518	r =-0.616	r =-0.461
	p=0.703	p =0.187	p=0.108	p=0.383	p=0.892	p=0.189	p =0.104	p =0.249
Dieldrin	r =0.100	r =0.128	r =0.298	r =-.113	r =0.445	r =-.022	r =0.242	r =0.025
	p=0.812	p =0.763	p=0.474	p=0.789	p=0.269	p=0.958	p =0.564	p =0.953
Endosulfa	r =0.143	r =0.223	r =0.149	r =-.060	r =0.561	r =-.184	r =0.132	r =-0.097
n II	p=0.735	p =0.596	p=0.725	p=0.888	p=0.148	p=0.663	p =0.756	p =0.819
Endrin	r =0.219	r = 0.334	r =0.063	r =-.199	r =0.806	r =-.199	r =0.277	r =0.067
Aldehyde	p=0.603	p =0.419	p=0.883	p=0.637	p=**0.016**	p=0.637	p =0.506	p =0.875
Endosulfa	r =0.534	r =0.508	r =-.039	r =0.026	r =0.563	r =-.040	r =0.240	r =0.056
n sulfate	p=0.173	p =0.199	p=0.927	p=0.951	p=0.146	p=0.924	p =0.567	p =0.896

Methoxyc	r =0.672	r =0.471	r =-.439	r =0.167	r =-.394	r =0.715	r =0.404	r =-0.437
hlor	p=0.107	p =0.239	p=0.276	p=0.693	p=0.335	**p=0.046**	p =0.322	p =0.125

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

4.2.4 Concentration of the HCHs in the earthen fish ponds sediment

Figure 4.7 shows mean (± SE) HCHs isomer residue levels detected in fish ponds sediment obtained from the sub-catchments area over the study period. Overall lowest mean level was exhibited by δ-HCH isomer (0.628 ±0.5946 μgKg^{-1}) in station E and G while γ-HCH compound showed a high mean of 19.51 ±3.292 μgKg^{-1} in station G fish pond sediment sample during the study period. Mean residue levels of HCHs compounds in pond sediment were in the range from below detection limit (BDL) to 51.706 ±8.403 μgKg^{-1} (γ-HCH) between stations (stations D and G). In addition, isomer γ-HCH indicated high concentration levels in stations B, D and E during the study period. A one-way ANOVA test showed that the mean γ-HCH pesticide concentration was not statistically significant among the sampling stations ($p > 0.05$; F = 1.534; $p = 0.261$), at the 95% confidence level. Sampling stations D, E and G showed above average mean value of HCH pesticides detected in sediment samples between stations. Sampling stations C, D, F and G recorded lowest HCH pesticides residue levels of β-HCH having below detection limit (BDL) as well as stations E and G with δ-HCH recording lower levels in fish pond sediment samples. In addition, Figure 4.7 and in Appendix XII exhibit lowest pesticide residue levels as was indicated by β-HCH (stations C, D, E and G). A similar trend was observed by δ-HCH isomer whereby lower contaminant levels were observed between observed stations, respectively. Furthermore, analysis of variance (ANOVA) statistical run showed that the mean β-HCH residue level was statistically significant ($p < 0.05$; F = 6.427; $p = 0.003$) among sampling stations. Tukey's *post hoc* test for separation of means revealed

that mean β-HCH concentration for station B varied significantly from mean β-HCH concentration observed at sampling stations E and F. Sampling stations C, D and G indicated widespread distribution of the HCH organochlorine pesticide compounds in the range between BDL limit to 24.207 μgKg^{-1} in the study period. Mean range pesticides concentrations were in the range 1.932 ±1.520 μgKg^{-1} (δ-HCH) to 8.612 ±3.000 μgKg^{-1} (γ-HCH) between the stations (Figure 4.7) and in Appendix IX. Station E showed lindane (γ-HCH) with a mean isomer residue level of 8.612 ±3.000 μgKg^{-1} while δ-HCH indicated low pesticides residue levels from BDL to 1.193 ±0.153 μgKg^{-1} and below in station F, respectively. Sampling station C did not record any positive HCH pesticides residues during the sampling period (all values were below detection limit). Mean differences between the sampled stations were not signicantly different ($p > 0.05$) as results of analysis of variance test did not produce any statistically significant difference in mean α-HCH isomer residue concentration among sampling stations ($p < 0.05$; F = 8.521; $p = 0.073$), at the 95% confidence level.

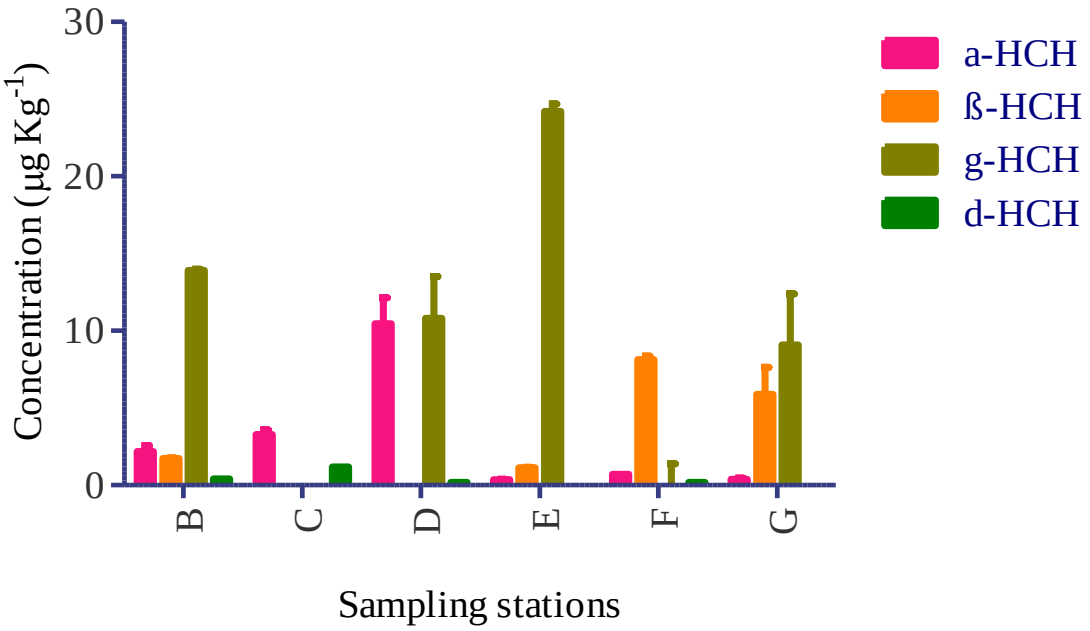

Figure 4.7: **Spatial mean (± SE) distributions of the HCH compounds in the fish ponds sediment**.

The results of the four HCH organochlorine pesticide compounds mean (± SE) temporal distributions in wet and dry seasons are shown in Figure 4.8 below. HCH isomer mean residue values in the wet season ranged between 2.296 ±0.176 (β-HCH) to 12.501 ±0.824 μgKg^{-1} (δ-HCH) while in the dry season the range was between 0.401 ±0.139 (*δ*-HCH) to 13.911 ±3.288 μgKg^{-1} (γ-HCH). Isomer γ-HCH indicated highest pesticides residue level in both wet (20.7 ±7.357 μgKg^{-1}) and dry (8.612 ±3.00 μgKg^{-1}) seasons, while lowest concentration was detected in *δ*-HCH. The independent sample *T*-test showed that mean β-HCH concentration in fish ponds sediment was not significant between wet and dry seasons (p = > 0.05; t = 2.805; p = 1.152). In addition, results indicated that *δ*-HCH (12.501 ±0.824 μgKg^{-1}) and α-HCH recorded residue value of (9.021 ±0.2.137 μgKg^{-1}) while γ-HCH (lindane) recorded zero value in fish ponds sediment samples analysed during the sampling period. Further analysis indicated that fish ponds HCH sediment pesticide concentrations during the dry season was in a range slightly higher than than values obtained in the rain season. The temporal distribution of the pesticides in the dry season show lindane isomer with high contaminant levels in the fish pond sediments while δ-HCH contaminant residue level was the lowest in the dry season. Independent sample *T*-test analysis showed that mean *δ*-HCH concentration in fish ponds sediment samples was statistically significant between sampling seasons ($p < 0.05$; t = 1.462; p = 0.0157) in both wet and dry seasons (Figure 4.8).

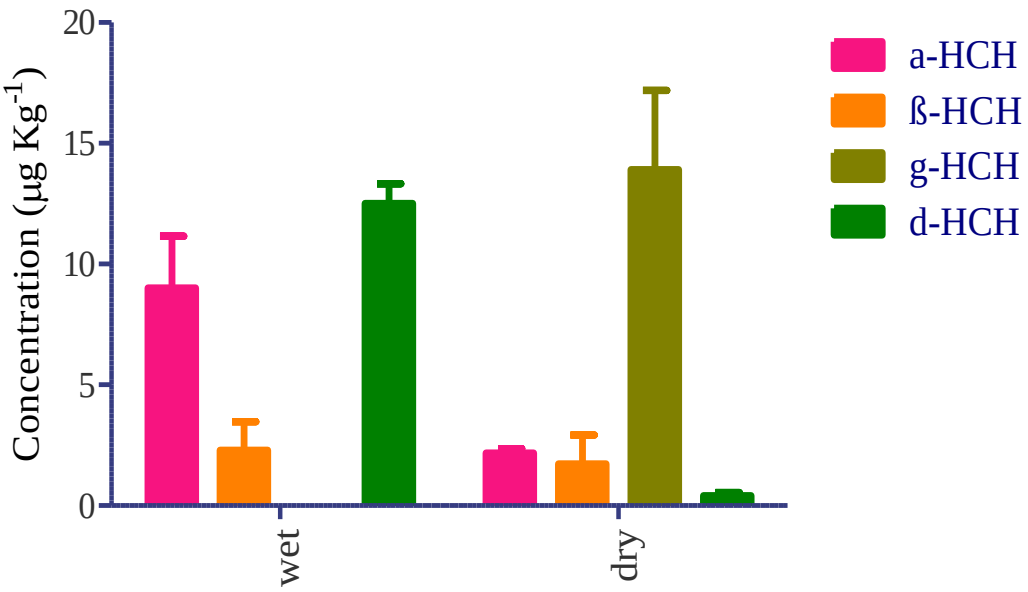

Figure 4.8: **Temporal mean (± SE) concentrations of the HCH isomers in the fish ponds sediment**.

Table 4.4 below show that HCH isomers concentration detected in fish pond sediments showed varied negative and positive bivariate Pearson correlation coefficients from 0.008 – 0.813 during the dry season. Apart from δ-HCH which had a significant correlation with water conductivity in the wet season (r = 0.813; p = 0.014), the rest of the isomers were not positively correlated with physico-chemical parameters during the study period, except for δ-HCH which showed a significant and positive correlation with conductivity (r = 0.813; p = 0.04). Although γ-HCH levels were high in dry and wet seasons, α, β and δ-HCH isomers did not show strong positive correlation during wet and dry seasons. The highest correlation value of 0.813 was obtained, while lowest value of 0.511 observed. However, α-HCH isomer showed positive correlation towards total nitrogen (TN) ions in the water column (r = 0.717; p = 0.046) but β-HCH isomer whose concentrations values in dry and wet season were low, had a strong negative correlation towards TN (r =-0.726; p = 0.041) and the relationship was significantly different, at $p < 0.05$.

Table 4.4: **Pearson correlation coefficients between the HCH isomer concentrations and the water quality parameters measurements in the earthen fish pond sediments samples during the wet and dry seasons**.

Wet season	**Temp** (°C)	**Cond** (μScm^{-})	**TSS** (μgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (μgL^{-1})	**TN** (μgL^{-1})
α-HCH	r =-.552	r =0.037	r =0.668	r =0.643	r =0.271	r =0.518	r = 0.604	r =0.229
	p=0.156	p=0.931	p=0.070	p=0.086	p=0.516	p=0.189	p = 0.113	p=0.584
β-HCH	r =-.097	r =0.552	r =-.538	r =-.088	r =-.328	r =-.109	r = -0.047	r =0.510
	p=.819	p=0.156	p=0.169	p=0.836	p=0.429	p= .798	p = 0.912	p=0.196
γ-HCH	r =0.445	r = -.184	r =-.425	r =0.209	r =0.013	r =-.467	r = -0.378	r =0.536
	p=0.269	p=0.662	p=0.294	p=0.619	p=0.975	p=0.243	p= 0.357	p=0.171
d-HCH	r =-.576	r =0.813	r =-.174	r =0.229	r =-.225	r =0.216	r = 0.428	r =0.437
	p=0.135	p=**.014**	p=0.677	p=0.584	p=0.591	p=0.608	p = 0.289	p=0.279
Dry season								
α-HCH	r =-.583	r = -.626	r =0.197	r =0.141	r =0.265	r =-.002	r =0.244	r =0.717
	p=0.129	p= .097	p=0.640	p=0.739	p=0.526	p=0.996	p =0.561	p=**0.046**
β-HCH	r =0.223	r =0.218	r =-.079	r =-.427	r =0.078	r =-.141	r =-.143	r =-.726
	p=0.596	p=0.604	p=0.851	p=0.292	p=0.855	p=0.738	p =0.736	p=**0.041**
γ-HCH	r =-.177	r = -.100	r =-.519	r =0.211	r =-.513	r =-.108	r =-0.387	r =-.065
	p=0.674	p=0.813	p=0.187	p=0.617	p=0.193	p=0.799	p =0.344	p=0.878
d-HCH	r =.024	r =0.036	r =0.172	r =-.168	r =0.678	r =0.008	r =0.465	r =0.452
	p=0.955	p=0.932	p=0.683	p=0.691	p=0.065	p=0.985	p =0.246	p=0.262

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

4.2.5 Concentration of the DDT metabolites in the earthen fish ponds sediment

Figure 4.9 shows the mean (± SE) spatial distribution of DDT and its metabolites detected in fish ponds sediment over the study period. Overall mean DDT pesticides residue levels between sampled stations was 6.120 ±5.974 μgKg^{-1}; 12.252 ±1.595 μgKg^{-1} and 23.510 ±6.693

μgKg^{-1} for *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT in fish ponds sediment residue levels during the study period (Figure 4.9). DDT residue levels detected in fish ponds sediment (μgKg^{-1}) samples were in varying concentrations and results show that concentrations of DDT and its metabolites in stations B to G ranged between 0.563 to 43.403; BDL to 13.367 and BDL to 46.995 μgKg^{-1} for *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT, respectively. One-way ANOVA test showed that the mean *p,p'*-DDT concentration in fish ponds sediment was not significant between the sampling stations ($p > 0.05$; $F = 2.117$; $p = 0.241$).

Sampling station F recorded highest mean metabolite concentration of (43.60 ±2.387 μgKg^{-1}) for *p,p'*-DDT, while at sampling station C, it registered a mean concentration of 39.0384 ±2.247 μgKg^{-1}. At sampling station E, the pesticide value obtained was 30.458 ±5.364 μgKg^{-1} indicated by *p,p'*-DDE metabolite concentration over the study period, while the lowest residue level of *p,p'*-DDT was registered at station B and D. Results indicate fluctuations in contaminant levels recorded over the study period with consistency of high values by *p,p'*-DDT and *p,p'*-DDE in C, F and G. A one-way analysis of variance (ANOVA) test indicated that mean *p,p'*-DDD was statistically significant among the sampling stations ($p < 0.05$; $F = 52.243$; $p = 0.001$). Tukey's *post hoc* test for separation of means revealed that mean *p,p'*-DDD concentration for station B varied significantly from mean *p,p'*-DDD observed at sampling stations C, D and F.

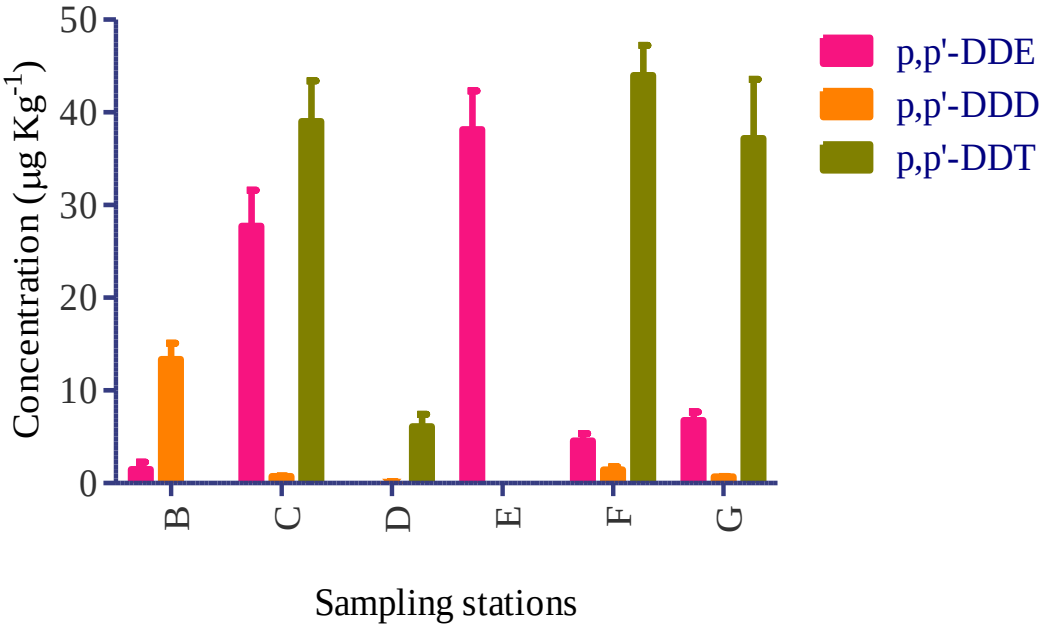

Figure 4.9: **Spatial mean (± SE) concentrations of the DDT metabolites in the fish ponds sediment**.

Figure 4.10 provides an illustration of mean (± SE) temporal distributions of DDT metabolites in fish ponds sediment samples during the wet and dry seasons. Temporal variations observed within DDT metabolites' concentrations in fish ponds sediment samples (µgKg^{-1}) during the dry season gives varied observed differences. Out of the three DDT metabolites observed, none was below detection limit in the two seasons. Contaminant levels during the dry season was in mean range between 8.317 ±1.483 (*p,p'*-DDE) to 36.121 ±6.091 µgKg^{-1} concentration level observed as indicated by *p,p'*-DDT. Similarly, the lowest mean value was registered by *p,p'*-DDE at 1.013 ±0.106 µgKg^{-1} in the wet season. A *T*-test statistical run indicated that temporal distributions of mean *p,p'*-DDT metabolite concentration levels were not significantly different between wet and dry seasons ($p > 0.05$; $t = 2.053$; $p = 0.0976$), at the 95% confidence level. Overall, results showed that the dry season had slightly higher DDT mean (± SE) pesticides residue levels than in the wet season. In addition, results show that in the wet season, mean DDT pesticide variations were noted to be in varying range as well but lower. However, in the

wet season, overall mean for metabolites was 9.461 ±2.931 (*p,p'*-DDE), 21.217 ±3.426 (*p,p'*-DDD) and 36.324 ±1.739 μgKg^{-1} (*p,p'*-DDT) in fish pond sediment residue levels respectively, indicating residue variations in sediment sample obtained during the study period. The independent sample *T*-test statistical run showed that mean temporal distributions of *p,p'*-DDD metabolite concentration levels were significantly different ($p < 0.05$; t = 1.371; $p = 0.017$) between wet and dry seasons.

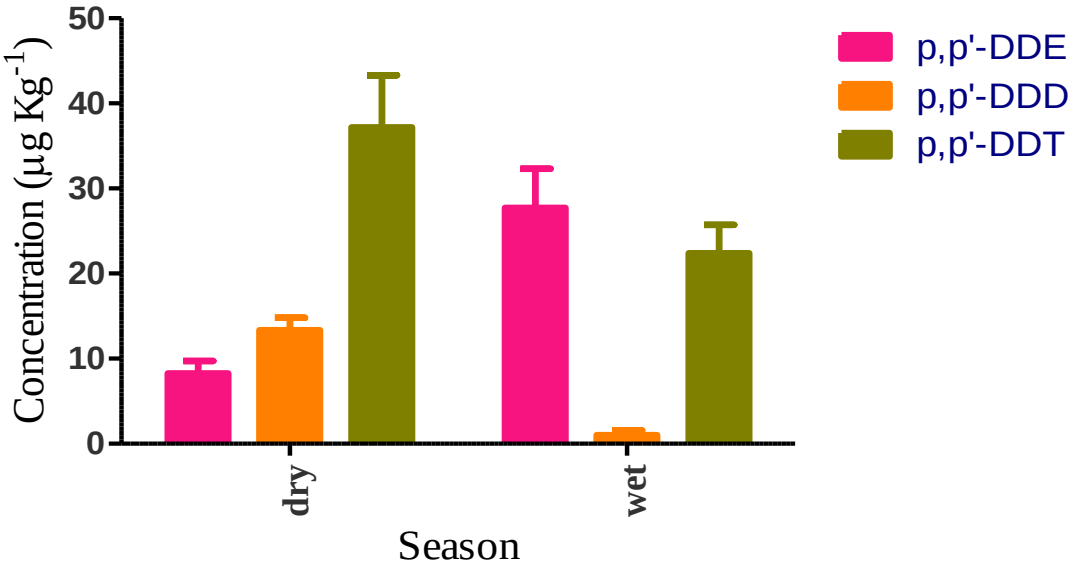

Figure 4.10: **Temporal mean (± SE) distributions of the DDT metabolites in the fish ponds sediment**.

Table 4.5 below shows correlation between DDT pesticide residues and water quality parameters in fish ponds sediment during wet and dry seasons. Negative and positive correlations were observed during the study. The strong positive correlation was in the range of 0.674 to 0.757, but with no significant difference (Table 4.5) in the wet season ($p > 0.05$). In dry season, a weak positive correlation range was observed to be between 0.25, to 0.561. But in the dry season, the relationship did not show any statistical significant relationship ($p > 0.05$) between the metabolites and water quality parameters (Table 4.5). Strong and highest positive correlation was observed between *p,p'*-DDT isomer and TSS (r = 0.757; $p = 0.029$)

during the wet season and the relationship was observed to be significantly different ($p < 0.05$) at the 95% confidence level. The correlation value of 0.561 was highest (*p,p'*-DDT against pH) level in the dry season, followed by 0.445 (*p,p'*-DDD against pH) and the lowest value was 0.025 (*p,p'*-DDD against TN) in the dry season.

Table 4.5: **Pearson correlation coefficients between the DDT metabolite concentrations and the water quality parameter measurements during the wet and dry seasons**.

	Temp (°C)	**Conduc** (μScm^{-1})	**TSS** (mgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (mgL^{-1})	**TN** (mgL^{-1})
Wet season								
p,p'-	r =0.188	r=-0.196	r =0.158	r=-.238	r =0.674	r=-0.015	r =0.124	r=-0.408
DDE	p=0.656	p =0.641	p =0.708	p=0.571	p=0.067	p =0.971	p =0.770	p=0.315
p,p'-	r =0.422	r=-0.397	r=-0.445	r=-.479	r=-.154	r=-0.472	r =-0.573	r =0.227
DDD	p=0.298	p =0.330	p =0.269	p=0.230	p=0.715	p =0.238	p =0.137	p =0.589
p,p'-	r=-0.477	r=-0.261	r =0.757	r=-.238	r =0.314	r =0.536	r =0.449	r=-0.657
DDT	p=0.233	p =0.533	**p=0.029**	p=0.571	p=0.449	p=0.171	p =0.265	p =0.077
Dry season								
p,p'-	r =0.161	r =0.520	r=-0.611	r =0.359	r=-.058	r=-0.518	r =-0.616	r=-0.461
DDE	p=0.703	p =0.187	p =0.108	p=0.383	p=0.892	p =0.189	p =0.104	p =0.249
p,p'-	r =0.100	r =0.128	r =0.298	r=-.113	r =0.445	r=-0.022	r =0.242	r =0.025
DDD	p=0.812	p =0.763	p =0.474	p=0.789	p=0.269	p =0.958	p =0.564	p =0.953
p,p'-	r =0.143	r =0.223	r =0.149	r=-.060	r =0.561	r=-0.184	r =0.132	r=-0.097
DDT	p=0.735	p =0.596	p =0.725	p=0.888	p=0.148	p =0.663	p =0.756	p =0.819

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

4.2.6 Concentration of the cyclodienes in the earthen fish ponds sediment

The spatial distribution of cyclodienes in fish ponds sediment between sampled stations is presented in Figure 4.11 below. Mean (± SE) concentrations of endrin (14.18 ±3.678 μgKg^{-1},

dieldrin (14.800 ±8.000 μgKg^{-1} and endrin aldehyde (18.47 ±5.382 μgKg^{-1}) detected in fish pond sediments were noted to be generally high as shown in stations B, C and E as compared to values obtained in sampling station D, F and G, Figure 4.11 and in Appendix XII. The cyclodiene pesticide concentrations in fish ponds sediment ranged between BDL to 54.674 μgKg^{-1} with dieldrin pesticide showing highest concentration at station E, followed by aldrin pesticide in station E as well. A one-way analysis of variance (ANOVA) test indicated that mean dieldrin cyclodiene pesticide in fish ponds sediment was statistically significant among sampling stations ($p < 0.05$; F = 7.625; $p = 0.004$). Tukey's *post hoc* test for separation of means revealed that mean dieldrin concentration for station B varied significantly from mean dieldrin concentration observed at sampling stations E and G. Lowest mean residue level observed between stations B to G was by heptachlor epoxide, methoxychlor, followed by endosulfan I cyclodiene pesticide levels. Results indicate that endosulfan I and II, heptachlor (3.583 ±0.753 μgKg^{-1}) and heptachlor epoxide (1.918 ±0.978 μgKg^{-1}) and endrin aldehyde occupied lower residue concentrations in the study period. A one-way analysis of variance (ANOVA) test indicated that mean aldrin pesticide in fish ponds sediment was statistically significant among sampling stations ($p < 0.05$; F = 25.836; $p = 0.002$). Tukey's *post hoc* test for separation of means revealed that mean aldrin residue level for station E varied significantly from mean aldrin residue level observed at sampling stations D, F and G.

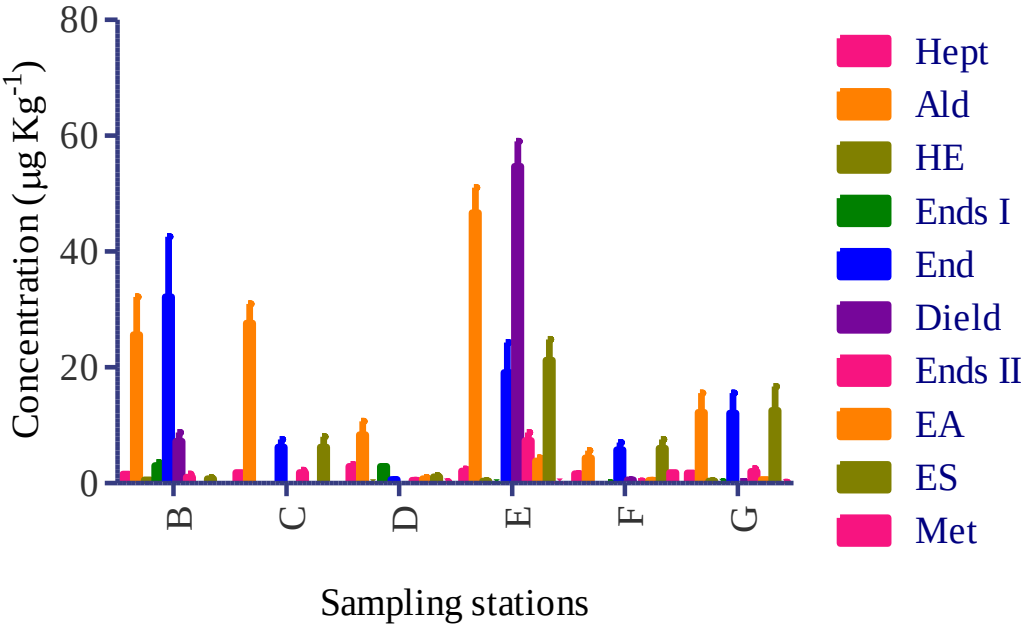

Figure 4.11: **Spatial mean (± SE) concentrations of the cyclodiene compounds in the fish ponds sediment**.

Figure 4.12 represents mean (± SE) temporal concentrations of cyclodiene compounds in fish ponds sediment samples obtained during wet and dry seasons. Observations showed that endrin aldehyde and methoxychlor pesticide residue levels was below detection limit (BDL) in fish ponds sediment during the dry season. However, aldrin and heptachlor epoxide (0.232 ±0.115 µgKg^{-1}) in the dry season level was low in the same sampling period, while higher residue level in sediment was shown by endrin cyclodiene pesticide with a mean of 19.682 ±4.718 µgKg^{-1} in the dry season. Independent sample *T*-test showed that contaminant mean endrin pesticide residue levels in pond sediments was not statistically significant ($p > 0.05$) between wet and dry seasons. Lowest mean concentration in the wet season was obtained by heptachlor epoxide (0.232 ±0.115 µgKg^{-1}) in the wet season while highest was indicated by methoxychlor cyclodiene pesticide with a mean of 42.782 ±7.421 µgKg^{-1} in the wet season. A general observation of results indicate that cyclodiene pesticides residue levels obtained in the wet season was higher than levels recorded in the dry season indicating probably environmental

contaminants recent use in the area (Figures 4.12). Independent sample *T*-test statistical run indicated that mean endosulfan I was statistically significant between wet and dry seasons ($p < 0.05$; t = 7.251; $p = 0.032$), at the 95% confidence level.

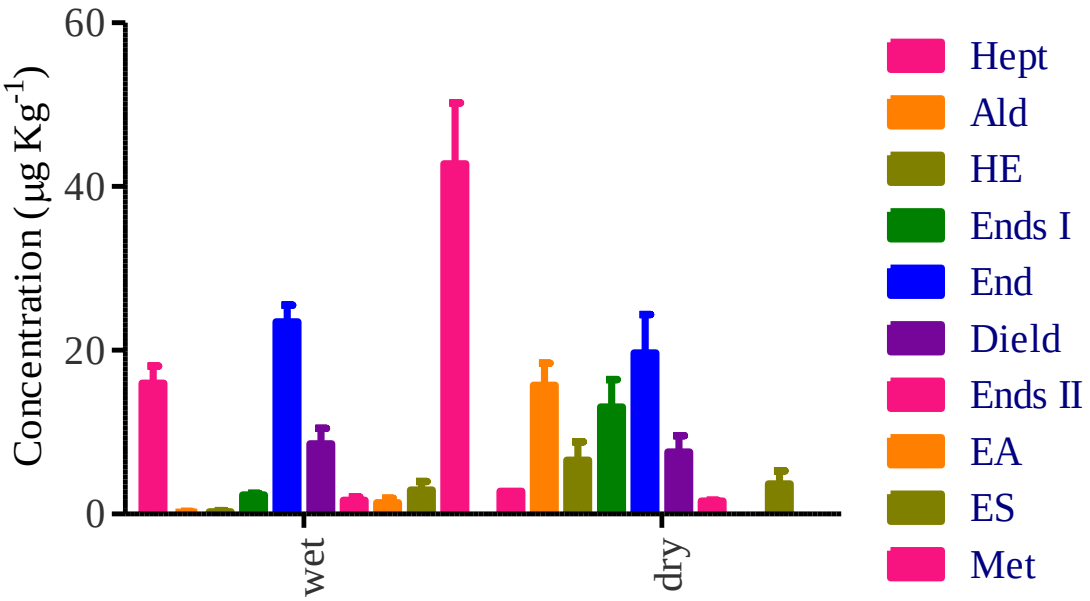

Figure 4.12: **Temporal mean (± SE) distributions of the cyclodienes in the earthen fish ponds sediment**.

4.2.7 Concentrations of the HCH and its isomers in the muscle tissue of Nile tilapia (*O. niloticus*) in the earthen fish ponds

The mean lipid content, length, moisture, and weight of the fish analysed in study area is shown in Table 4.6. The spatial mean (± SE) spatial concentrations of HCH and its isomers in the muscle tissue of Nile tilapia (*O. niloticus*) fish samples in the earthen fish ponds are presented in Figure 4.13. Fluctuations of the mean (± SE) residue levels were observed in fish tissue during the study period. For instance, in station D residue level exhibited by β-HCH was 1.313 ±0.3097 μgKg^{-1} d.w and in station C the level shown by γ-HCH isomer was below detection limit (BDL). Pesticides residue levels ranged between 0.552 to 2.722; BDL to 5.1179; BDL to

7.858 and 0.4237 to 3.460 μgKg^{-1} d.w for α-HCH, β-HCH, γ-HCH and δ-HCH pesticides, at stations C, E and F, respectively.

Table 4.6: **Mean lipid content, length, moisture, and weight of fish analysed in study area (n = 186).**

Parameters	Length (cm)	Weight (g)	Lipid content (%)	Moisture content (%)
O. niloticus	27.6± 3.2	268.6 g	0.84 %	78.2 %

Mean ±SE, n = 186

A one-way analysis of variance (ANOVA) indicated a significant difference between overall means of β-HCH isomer in *O. niloticus* tissue between sampled stations ($p < 0.05$; F = 6.261; $p = 0.025$). Additionally, the spatial distribution of the residue level fluctuated between one station and another, for example, α-HCH had a mean value of 0.094 ±0.001 μgKg^{-1} in station E to 1.947 ±0.471 μgKg^{-1} in station D, while δ-HCH had a low mean residue level of 0.423 ±0.010 μgKg^{-1} to 2.846 ±0.773 μgKg^{-1} in station G. Analysis of variance (ANOVA) test of the mean γ-HCH isomer obtained indicated a no significant difference between sampled stations in both wet and the dry seasons, respectively ($p > 0.05$; p =0.08).

Observations of the HCH pesticides residue levels in the analysed samples were in the decreasing order of γ-HCH>β-HCH>δ-HCH>α-HCH. Stations B, D F and H showed a greator frequency of detection of the HCH residues in fish samples in the dry season. Stations B, D and F showed high contaminant values of detection in fish samples, for instance, at station G, all isomers pesticide levels were greator than > 1.0 μgKg^{-1}. A one-way analysis of variance (ANOVA), showed that mean α-HCH differences were statistically significant between sampling stations ($p < 0.05$; F = 5.723; $p = 0.020$), at the 95% confidence level. Tukey's *post hoc* test for separation of means revealed that mean α-HCH for station D varied significantly from mean α-HCH observed at sampling stations C, E and G.

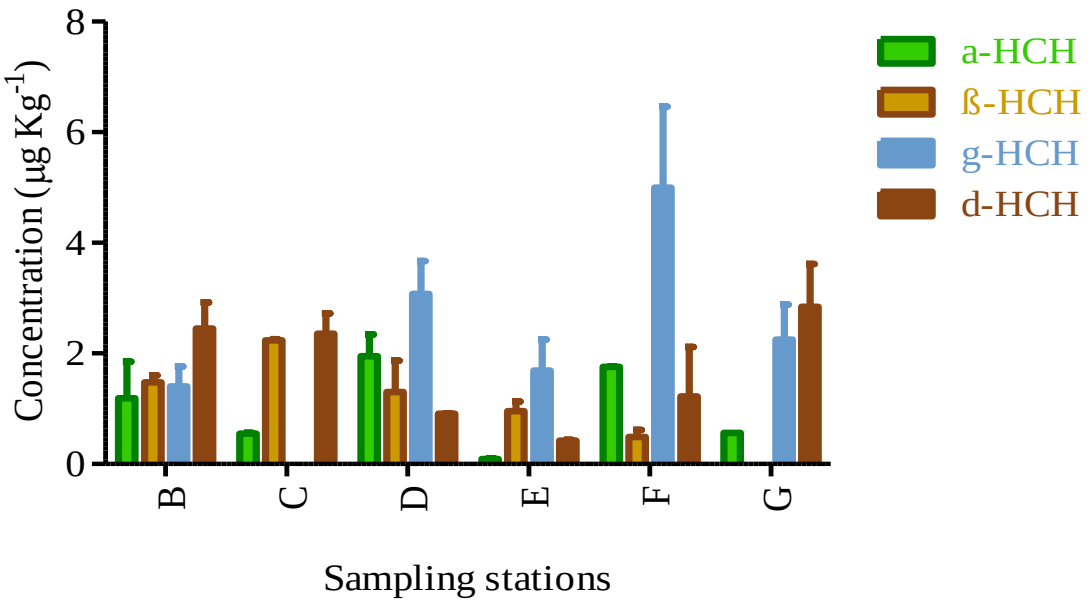

Figure 4.13: **Spatial mean (± SE) distributions of the HCH isomers in the muscle tissue of *O. niloticus* in earthen fish ponds**.

The study investigated mean (± SE) temporal distributions of HCH isomer concentrations in muscle tissue of *O. niloticus* in earthen fish pond samples between wet and dry seasons and the results are shown in Figure 4.14. Variations between stations were noted whereby the lowest mean residue level was exhibited by β-HCH (2.098 ±0.544 µgKg^{-1}) while γ-HCH isomer recorded a high mean of (6.157 ±0.9831 µgKg^{-1}) in the wet season. The independent sample *T*-test showed that mean of β-HCH concentration was not significant between wet and dry seasons ($p > 0.05$; t= 12.412; $p = 0.274$) at the 95% confidence level. Mean concentrations for HCHs residue levels in sampled fish during dry season of (February, July) and wet season (October, November) in the study area showed a range of between 1.410 ±0.968 µgKg^{-1} to 6.860 ±0.411 µgKg^{-1} delta and gamma isomers in wet season, respectively, while in the dry season, levels fluctuated between 0.420 ±0.095 µgKg^{-1} to 2.44 ±0.372 µgKg^{-1} for alpha and delta isomers, respectively. These results showed that mean concentrations obtained in the wet

season were higher than those recorded in the dry season. Independent sample *T*-test showed that mean γ-HCH concentration in *O. niloticus* tissue were significantly different between the wet and dry seasons ($p < 0.05$; t = 3.740; $p = 0.0246$) at the 95% confidence level. The lowest mean concentration was for δ-HCH (1.410 ±0.4103 μgKg^{-1}) and highest mean level was for lindane (γ-HCH) isomer (2.541 ±0.8252 μgKg^{-1}) in *O. niloticus* fish sample. In addition, temporal differences were observed in mean contaminant residue levels of δ-HCH and γ-HCH in fish tissues (Figure 4.14). The independent sample *T*-test showed that δ-HCH means concentrations was not significantly different between wet and dry seasons.

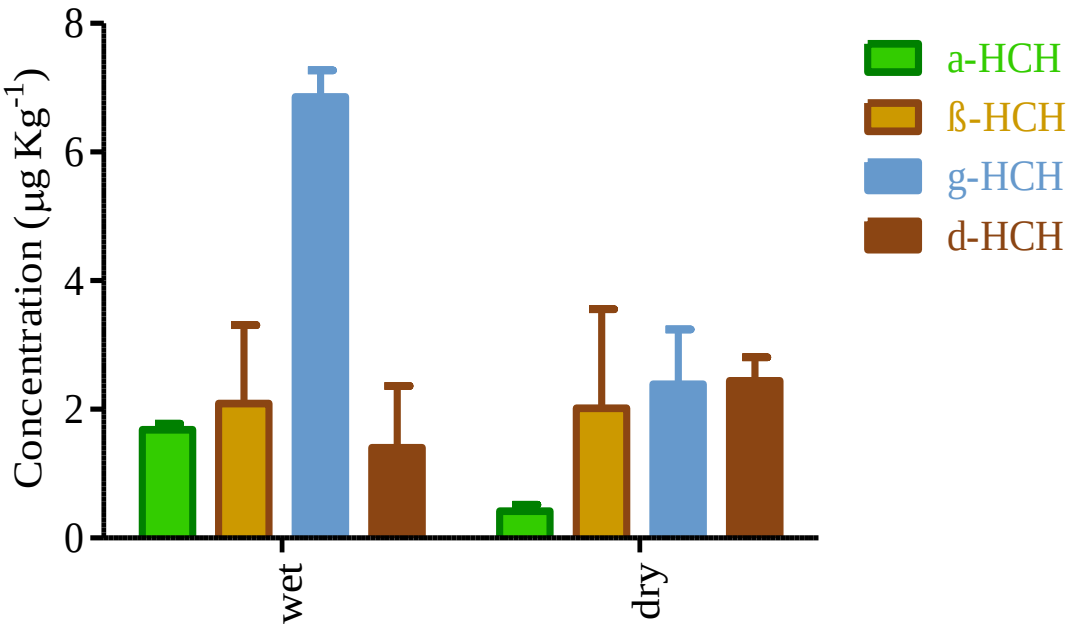

Figure 4.14: **Temporal mean (± SE) distributions of the HCH isomers in the muscle tissue of *O. niloticus* in earthen fish ponds**.

4.2.8 Concentration of the DDT metabolites in the muscle tissue of *O. niloticus* in earthen fish ponds.

The spatial distributions of the mean (± SE) concentrations of DDT pesticide and its metabolite residue in *O. niloticus* observed between the different stations in fish ponds is shown in Figure

4.15. Metabolite *p,p'*-DDD showed overall mean concentration level of 0.631 ±0.157 μgKg^{-1} between stations in fish tissue but ranged from BDL (station C) to 1.098 ±0.496 μgKg^{-1} (station G). A one-way analysis of variance (ANOVA) test showed that *p,p'*-DDD mean levels were significantly different among sampled stations in the study period ($p < 0.05$; F = 4.261; p = 0.024), at the 95% confidence level. Furthermore, *p,p'*-DDT mean concentration observed was from 0.105 ±0.002 μgKg^{-1} (station B) to 3.518 ±0.839 μgKg^{-1} (station G) with an overall mean of 1.616 ±0.498 μgKg^{-1}. The mean levels for *p,p'*-DDT were lower at stations B, D, and F, than those observed in stations (E and F). A one-way analysis of variance (ANOVA) test of mean *p,p'*-DDT metabolite indicated that the differences were significantly different among sampling stations ($p < 0.05$; F = 3.952; p = 0.031), at the 95% confidence level. Tukey's *post hoc* test for separation of means revealed that mean *p,p'*-DDT concentration for station G varied significantly from those at sampling stations B and E. The results of *p,p'*-DDE metabolite mean residue level showed a range of 0.918 ±0.012 μgKg^{-1} (station E) to 2.138 ±0.839 μgKg^{-1} (station D), with an overall mean concentration of 1.51 ±0.303 μgKg^{-1} in the fish tissue samples, among different sampling stations. Sampling station B, C and F recorded the highest residue concentrations of *p,p'*-DDE metabolite between stations, although the overall mean indicated a lower value (Figure 4.15). A one-way analysis of variance (ANOVA) test of the mean residue level of the *p,p'*-DDE metabolite showed no statistically significant difference among the sampling stations ($p > 0.05$) at the 95% confidence level.

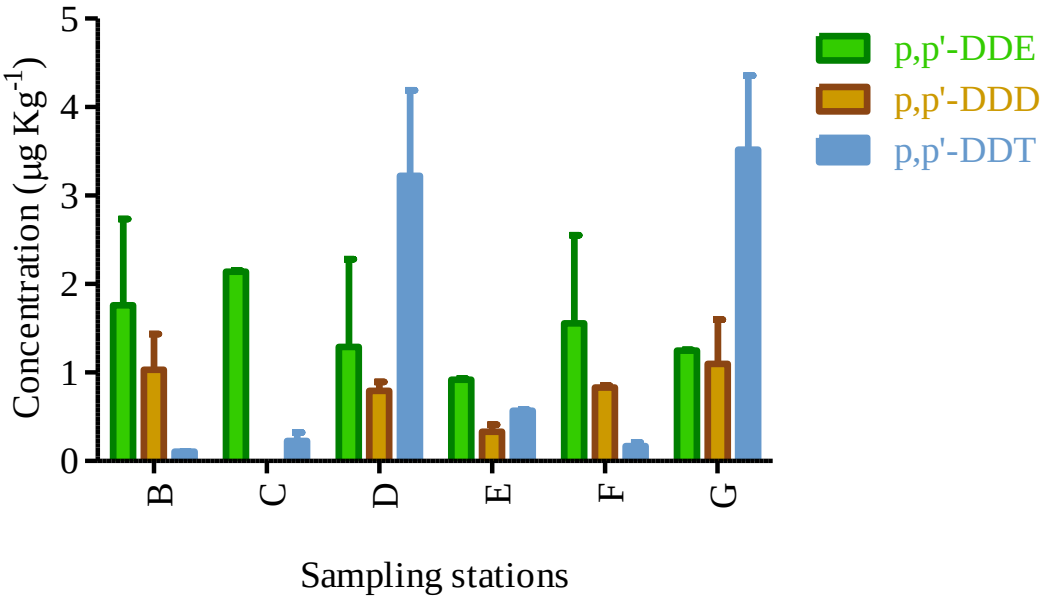

Figure 4.15: **Spatial mean (± SE) distributions of the DDT metabolites in the muscle tissue of *O. niloticus* in earthen fish ponds**.

The temporal mean (± SE) distributions of DDT metabolites in the muscle tissue of *O. niloticus* in fish earthen ponds in both the wet and dry seasons is shown in Figure 4.16. The results showed that the DDT metabolite mean values in *O. niloticus* fish samples varied consistently during the study period. The mean concentrations of *p,p'*-DDD, *p,p'*-DDD and *p,p'*-DDT were: 1.529 ±0.370 µgKg^{-1}, 0.63 ±0.157 µgKg^{-1}, and 1.316 ±0.498 µgKg^{-1}, dry weight, respectively. Overall DDT metabolites mean levels during the dry season of February and July were 1.529 ±0.373 µgKg^{-1} (*p,p'*-DDE), while lowest mean DDT metabolite residue levels in fish tissue during dry months of February and July were for *p,p'*-DDD with mean residue value at BDL. The independent sample *T*-test of *p,p'*-DDE metabolite concentrations showed a statistically significant difference between wet and dry seasons ($p < 0.05$; t = 5.381; $p = 0.0361$).

The mean (± SE) results for *p,p'*-DDD showed a lower concentration during the wet season (0.028 ±0.004 µgKg^{-1}), while *p,p'*-DDT pesticide exhibited a high residue level (2.084 ±0.017

μgKg^{-1}) in *O. niloticus* during the dry season months. The independent sample *T*-test showed that mean of *p,p'*-DDT concentration in the months of February and July was not significantly different ($p > 0.05$; $p = 0.264$). In addition, mean *p,p'*-DDE concentrations in *O. niloticus* between the wet and dry seasons were compared, and the results indicated a no significant difference ($p > 0.05$; $p = 0.072$), (Figure 4.16) but the *T*-test analysis of the mean *p,p'*-DDD concentration showed a statistically significant ($p < 0.05$; t = 3.036; $p = 0.003$) difference at the 95% confidence level.

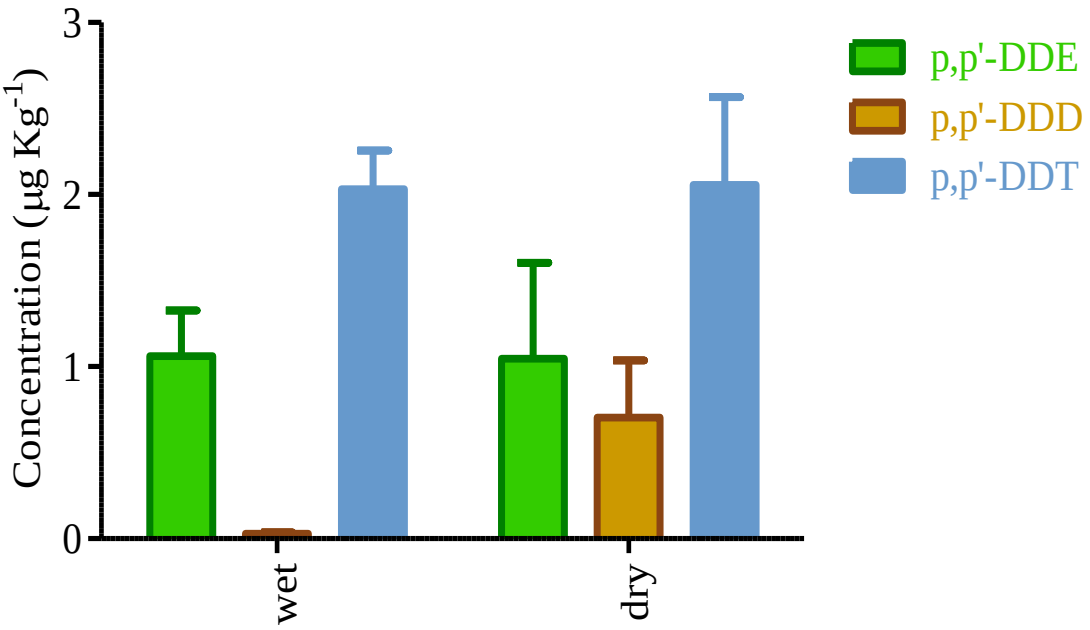

Figure 4.16: **Temporal mean (± SE) concentrations of the DDT metabolites in the muscle tissue of *O. niloticus* in earthen fish ponds**.

Table 4.7 shows the Pearson correlation coefficient between the DDT metabolite pesticide residues and the water quality parameters in earthen fish ponds over wet and dry seasons. Water samples were obtained at the same time the fish was being collected for analysis. Statistically significant negative and positive correlations were observed between the variables determined. There was a strong negative statistically significant correlation observed between *p,p'*-DDE with TP during the wet season (r = -0.822; $p = 0.012$). Metabolite *p,p'*-DDT indicated a strong

positive correlation cefficient with DO (r = 0.865; p = 0.006), and the relationship was observed to be statistically significant ($p < 0.05$). No other metabolite indicated a significant relationship between DDT metabolites with water quality parameters in fish ponds during the wet season (Table 4.7). A strong positive correlation was observed between *p,p'*-DDE isomer and TSS in the dry season, though the relationship was not statistically significant (r = 0.658; p = 0.076; p = > 0.05). The lowest negative correlation value was observed between DO against *p,p'*-DDD (r = -0.027; p = 0.949), whereas the highest correlation emerged between *p,p'*-DDT and DO (r = 0.865; p = 0.006) during the wet season.

Table 4.7: **Pearson correlation coefficient between the DDT metabolite concentrations and the water quality parameter measurements during the wet and dry seasons**.

Wet season	**Temp** (°C)	**Cond** (μScm^{-1})	**TSS (**μgL^{-1}**)**	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (mgL^{-1})	**TN** (mgL^{-1})
p,p'-DDE	r= 0.630 p=0.094	r=-0.326 p= 0.431	r = -0.561 p = 0.148	r= -0.397 p = 0.330	r= -0.473 p = 0.236	r =-0.680 p = 0.063	r=-0.822 p=**0.012**	r =0.168 p=0.692
p,p'-DDD	r= 0.080 p=0.850	r=-0.652 p= 0.079	r = 0.431 p = 0.287	r= -0.027 p = 0.949	r = 0.249 p = 0.552	r = 0.266 p = 0.524	r =0.061 p=0.887	r=-0.047 p=0.913
p,p'-DDT	r= 0.534 p=0.173	r= 0.496 p= 0.211	r = 0.328 p = 0.428	r = 0.865 p = **0.006**	r= -0.196 p = 0.643	r = 0.332 p = 0.421	r =0.469 p=0.240	r =0.596 p=0.119
Dry season								
p,p'-DDE	r= 0.628 p=0.096	r= 0.269 p= 0.519	r = 0.658 p = 0.076	r = 0.261 p = 0.533	r = 0.073 p = 0.864	r = 0.564 p = 0.146	r= 0.509 p=0.197	r= 0.365 p=0.374
p,p'-DDD	r= 0.184 p=0.662	r= 0.163 p= 0.699	r = -0.229 p = 0.584	r = 0.413 p = 0.309	r = 0.052 p = 0.903	r =-0.274 p = 0.511	r=-0.329 p=.426	r=-0.327 p=0.429
p,p'-DDT	r=-0.337 p=0.415	r=-0.114 p= 0.788	r = -0.427 p = 0.291	r = 0.523 p = 0.183	r = 0.312 p = 0.451	r= -0.512 p = 0.195	r=-0.335 p=0.417	r= 0.303 p=0.466

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

4.3 Concentration of the organochlorine pesticides (OCPs) in the rivers

4.3.1 Concentrations of the hexachlorocyclohexanes (HCH) in surface water of rivers

Figure 4.17 represents the spatial mean (± SE) distributions of HCH isomers in surface water of rivers receiving fish pond effluents in the River Kuja watershed. The mean residue levels of HCHs compounds in river water samples was from below detection limit (stations C and E) to 0.955 ±0.003 μgKg^{-1}, with both the lowest and the highest values obtained for isomer δ-HCH. The mean concentration values observed for α-HCH pesticide were: 0.001 ±0.0004 μgL^{-1} in station C to 0.332 ±0.073 μgL^{-1} in station D, whereas the mean contaminant level for β-HCH residue was between 0.097 ±0.003 μgL^{-1} (station D) to 0.955 ±0.002 μgL^{-1} (station F) (Figure 4.17). A one-way analysis of variance (ANOVA) test showed that the mean β-HCH concentration levels were not significantly different among sampled stations ($p > 0.05$; F = 1.426; $p = 0.063$). Additionally, mean concentration for isomer δ-HCH was between 0.239 ±0.026 μgL^{-1} in station B to 0.955 ±0.152 μgL^{-1} in station F while isomer γ-HCH showed mean residue level from below detection limit (BDL) in sampling station C and E to 0.225 ±0.032 μgL^{-1} in sampling station G. A one-way analysis of variance (ANOVA) test indicated that the mean γ-HCH concentration levels were not significantly different between sampled stations ($p > 0.05$; F = 2.241; $p = 0.205$). The overall mean variations of contaminant levels of δ-HCH and γ-HCH isomer in river surface water samples were observed to be 0.428 ±0.013 μgL^{-1} and 0.791 ±0.010 μgL^{-1}, respectively.

The mean (± SE) residue level variations were observed within stations; for instance, at station C and D, α -HCH recorded residue levels of 0.332 μgL^{-1}, while at station D it indicated a value of 0.001 μgL^{-1} in water. Although much higher residue level of HCH pesticide compounds in river water were recorded at stations D and F (where contaminant levels were above 0.5 μgL^{-1}) HCH isomers recorded a level of < 1.0 μgL^{-1} in all target stations. A one-way analysis of

variance test showed that the mean γ-HCH concentration levels were significantly different between the different sampling stations ($p < 0.05$; F = 8.326; $p = 0.003$). Tukey's *post hoc* test for separation of means revealed that mean γ-HCH concentration for station C varied significantly from those observed at sampling station G. Further analysis of the isomer residue values indicated that there was no statistical difference between mean isomer levels in station G and the mean values were almost at equal magnitude ($p > 0.05$; F = 2.052; $p = 0.941$) at the 95% confidence level.

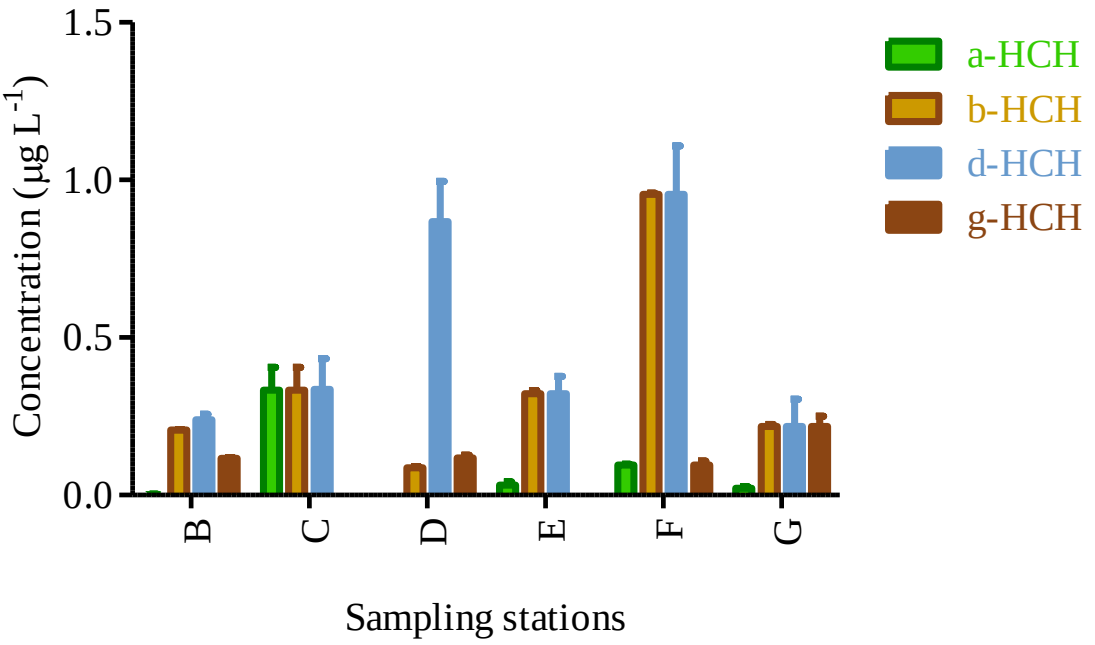

Figure 4.17: **Spatial mean (± SE) distributions of the HCH isomers in the river water**.

The results of the temporal mean (± SE) distributions of the four HCH isomer concentrations in waters receiving fish pond effluents in River Kuja watershed during wet and dry seasons is presented in Figure 4.18. In the dry season, the mean isomer value recorded was 1.0 ±0.038 μgL^{-1}, for β-HCH and a low observation was noted for γ-HCH isomer (BDL) in the river water samples during the dry season months.

Concentrations of γ-HCH and δ-HCH in the dry season were at BDL as shown in Figure 4.18 while the concentrations of the other two other isomers (α-HCH and β-HCH) were above the detection limits, at 1.324 ±0.617 μgL^{-1} and 0.847 ±0.0.035 μgL^{-1} (mean levels), during the dry season, respectively. The independent sample *T*-test showed that mean β-HCH concentration was significantly different between wet and dry seasons ($p < 0.05$; 1.749; $p = 0.021$) at the 95% confidence level. From residue level observations, the dry season months had a high percentage of detection than the wet season (Figures 4.18). Overall, the mean residue levels of the organochlorine pesticides (HCHs) in river water samples receiving fish pond effluents in River Kuja watershed collected during the dry season of February and July were significantly higher than those of the wet season, especially for α-HCH which had a wider contaminant range in between seasons (Figure 4.18).

Further, a *T*-test method indicated significantly different ($p < 0.05$; t = 1.940; $p = 0.013$) result in means of α-HCH isomer concentrations in river waters receiving fish ponds effluent between wet and dry seasons. In addition, further *T*-test analysis showed no statistically significant difference in mean residual level of β-HCH ($p > 0.05$; t = 1.639; $p = 0.149$) between the wet and dry seasons. Further analysis indicated the mean contaminant level of delta and gamma HCH pesticides ranged between BDL to a low value of 0.001 ±0.000 μgL^{-1} in both the wet and dry seasons. The independent sample *T*-test showed no statistically significantl difference in the mean δ-HCH during wet and dry seasons ($p < 0.05$; t = 4.291; $p = 0.271$) at the 95% confidence level.

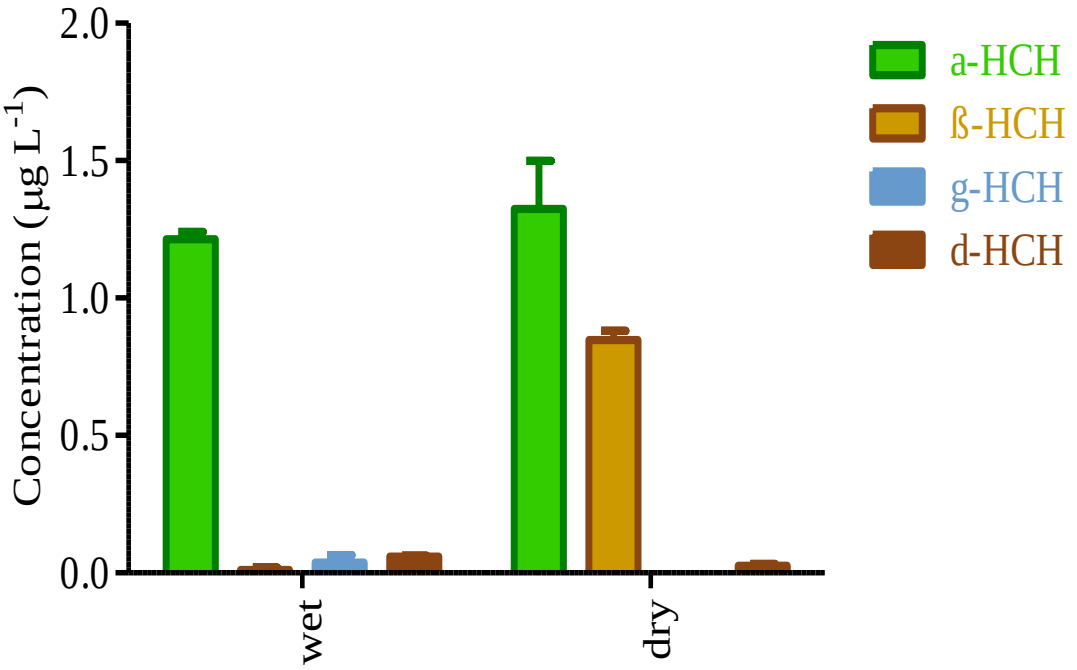

Figure 4.18: **Temporal mean (± SE) distributions of the HCH isomers in the rivers.**

In order to measure the strength of the association between pesticides in water column, a Pearson correlation test, with an *r* coefficient range of -1≤1.0 was carried out to elaborate on the hydrophobic and hydrophilic strengths of the OCPs (Table 4.8). Selected HCH isomers in river waters receiving fish ponds effluents showed strong positive and negative correlation with water quality parameters during the wet season. Isomer α-HCH had a strong positive correlation with total nitrogen (r = 0.815, p = 0.014) and was observed to be significantly different (p < 0.05) in the wet season (Table 4.8), but it was negatively correlated to temperature, TP, pH and TSS. β-HCH and δ-HCH also showed a strong positive correlation with temperature and turbidity respectively, during the wet season months of April and May. Overall, HCH pesticide residue levels in river water samples in the wet season showed a strong positive and negative correlations with physico-chemical parameters; for example, α-HCH with total nitrogen (TN), β-HCH with turbidity and TSS, δ-HCH with temperature and δ-HCH with turbidity (Table 4.8) in the range of 0.798 to 0.819 and were significantly different (p <

0.05). In comparison, some of the concentrations of HCH isomers had weak negative correlations with physico-chemical parameters during the dry season.

Table 4.8: **Pearson correlation coefficients between the HCH isomer concentrations and the water quality parameters in river surface water samples, during the wet and dry seasons**.

Wet season	**Temp** (°C)	**Cond** (μScm^{-1})	**TSS** (μgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (μgL^{-1})	**TN** (μgL^{-1})
α-HCH	r =-.075	r =0.401	r =-.579	r =0.358	r =-.204	r =-.377	r =-0.052	r =0.815
	p=0.859	p=0.324	p=0.132	p=0.383	p=0.628	p=0.357	p =0.903	p=**0.014**
β-HCH	r =-.366	r =-.521	r =0.844	r =-.243	r =0.438	r =0.798	r =0.451	r =-.671
	p=0.372	p=0.185	**p=0.008**	p=0.561	p=0.277	p=**0.018**	p =0.262	p=0.069
γ-HCH	r =-.643	r =-.209	r =0.472	r =-.317	r =0.561	r =0.523	r =0.579	r =-.085
	p=0.086	p=0.619	p=0.238	p=0.444	p=0.148	p=0.184	p =0.133	p=0.842
d-HCH	r =-.819	r =0.331	r =0.503	r =0.202	r =-.172	r =0.813	r =0.646	r =-.047
	p=**0.013**	p=0.423	p=0.204	p=0.631	p=0.684	p=**0.014**	p =0.084	p=0.911
Dry season								
α-HCH	r=0.025	r=0.167	r =-.394	r=0.715	r=0.404	r =-.519	r =-.363	r=0.116
	p=0.954	p=0.693	p=0.335	**p=0.046**	p=0.322	p=0.187	p =0.377	p=0.784
β-HCH	r=0.102	r =-.090	r= 0.134	r =-469	r =-.119	r =0.355	r =0.363	r =-.048
	p=0.809	p=0.831	p=0.752	p=0.241	p=0.778	p=0.388	p =0.376	p=0.911
γ-HCH	r =0.225	r =0.179	r =-.113	r =0.443	r =0.177	r =-.281	r =-0.291	r =-.299
	p=0.593	p=0.672	p=0.791	p=0.272	p=0.676	p=0.500	p =0.485	p=0.472
d-HCH	r =-.001	r =0.070	r =0.092	r =-.548	r =0.497	r =-.111	r =0.207	r =-.150
	p=0.999	p=0.868	p=0.829	p=0.159	p=0.211	p=0.794	p =0.624	p=0.723

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

Strong positive correlations may imply that imply that an increase in the levels of the physico-chemical parameters favoured the accumulation of the concentrations of some of the HCHs

isomers in the river waters. Taking $p < 0.05$, results indicated a no significant relationship between all the four isomers and the water quality variables except for α-HCH with the DO levels during the dry season.

4.3.2 Concentrations of the DDT metabolites in the rivers

Figure 4.19 below represents the concentration of DDT metabolites between different sampling stations in waters receiving fish pond effluents in River Kuja watershed. The metabolite with the highest mean residue concentration was *p,p'*-DDT and which was from 0.0375 ±0.014 μgL^{-1} (station B) and 0.967 ±0.073 μgL^{-1} (station G), while *p,p'*-DDD metabolite was below the detection limit (BDL) to 0.296 ±0.002 μgL^{-1} (station B and G). However, a one-way analysis of variance (ANOVA) test showed that the mean *p,p'*-DDD metabolite concentration was not significant among the sampling stations ($p > 0.05$; $F = 1.247$; $p = 0.635$). In addition, only *p,p'*-DDD had concentrations which were at BDL at two stations, whereas the other two metabolites: *p,p'*-DDE and *p,p'*-DDT were detectable in all the sampling stations (B and D). The metabolite with the widest distribution range was *p,p'*-DDT which was recorded in all sampled stations (B to G) during the study period. The metabolite with the narrowest distribution range was *p,p'*-DDD (BDL in stations B, D and 0.327 ±0.003 μgL^{-1} in station F). Further, a one-way analysis of variance showed that the mean concentrations of *p,p'*-DDT were not significantly different ($p > 0.05$) between stations C and D, but the mean variation was significantly different among stations B and C (Figure 4.19).

Additionally, Figure 4.19 presents illustrations for the spatial DDT metabolite distributions in rivers receiving fish ponds effluent in River Kuja watershed. The range of the concentrations in the target compound was from BDL (*p,p'*-DDT) (as indicated at station B and D) to 1.751 μgL^{-1} (station D), while that of *p,p'*-DDE the range was between 0.034 ±0.051 (at station E) to 0.851 ±0.026 μgL^{-1} (at station A) in the river water during the study period. A one-way analysis

of variance (ANOVA) test showed that the mean *p,p'*-DDE` concentrations were not significantly different ($p > 0.05$; F = 1.538; $p = 0.398$) among the sampling stations.

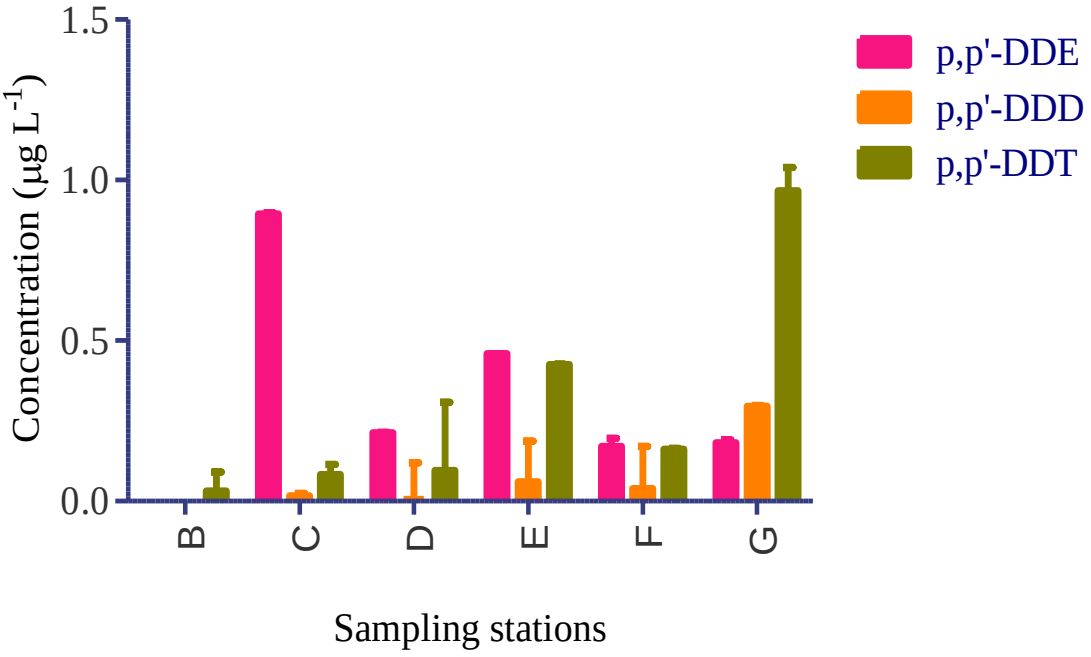

Figure 4.19: **Spatial mean (± SE) distributions of DDT metabolites in the river water**.

Figure 4.20 indicates the temporal mean DDT metabolite concentrations for the sampling stations during the dry and wet seasons in river waters receiving fish pond effluents. The metabolite with the highest mean concentration in the river water samples was *p,p'*-DDT metabolite (1.086 ±0.294 μgL^{-1}) during the dry season months, while the metabolite with the lowest mean concentration was *p,p'*-DDD, which was below the detection limit. The independent sample *T*-test showed that the mean *p,p'*-DDT metabolite concentrations were significantly different between the wet and dry seasons ($p < 0.05$; t = 4.204; $p = 0.010$), at the 95% confidence level. Furthermore, mean DDT pesticide level variations were observed in the study area. Overall means of *p,p'*-DDE and *p,p'*-DDT metabolites in the wet and dry seasons were observed to be significantly different ($p < 0.05$; t = 1.634; $p = 0.014$), (Figure 4.20). During the dry season, the residue level was in the range (0.030 to 0.851; BDL to 0.982; 0.011

to 0.975 µgL^{-1}) for *p,p'*-DDE , *p,p'*-DDD and *p,p'*-DDT in river water, respectively. The lowest DDT metabolite detection level in river waters during the dry season was of the *p,p'*-DDD metabolite, which was below detection limit. The independent sample *T*-test showed that mean *p,p'*-DDE metabolite concentrations was significantly different between wet and dry seasons ($p < 0.05$; t = 1.290; $p = 0.004$) at the 95% confidence level.

The concentrations of *p,p'*-DDD were at BDL in both the dry and wet seasons whereas the concentrations of the other two metabolites (*p,p'*-DDE and *p,p'*-DDT) were above detection limits in both seasons. The metabolite with the widest distribution range was *p,p'*-DDT (0.063 to 1.82 µgL^{-1}) while the one with the narrowest distribution range was *p,p'*-DDE (0.0302 to 0.851 µgL^{-1}) in both seasons. Temporal mean distributions of the DDT metabolites was much wider and had high concentrations in the dry season than during the wet season. The independent sample *T*-test showed that the mean *p,p'*-DDD metabolite concentrations were not significant between the wet and dry seasons ($p > 0.05$; t = 2.581; $p = 0.083$).

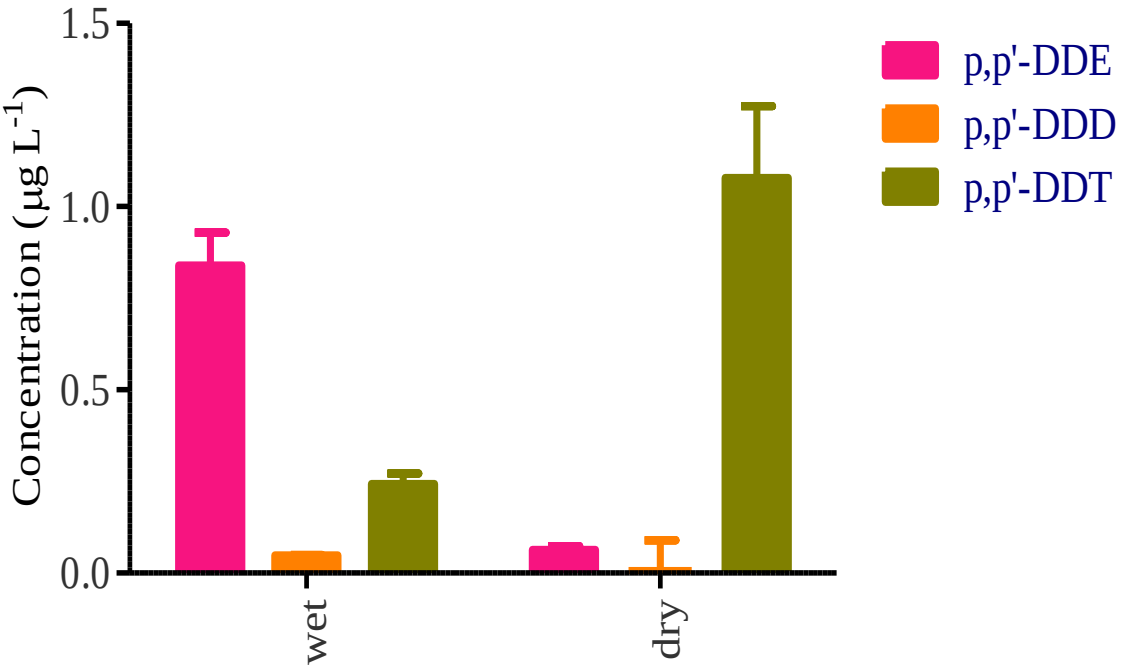

Figure 4.20: **Temporal mean (± SE) distributions of the DDT metabolites in the rivers**.

Table 4.9 shows correlation coefficients between the DDT metabolite residue concentrations and the water quality parameters in the water samples from rivers receiving fish pond effluents during wet and dry seasons. All the positive correlation coefficients were insignificant (p > 0.05) except the correlation between *p,p'*-DDD and conductivity, r = 0.757; p = 0.029, which in this case was the highest observed coefficient during the wet season. The lowest correlation coefficient in the wet season was between *p,p'*-DDT and conductivity (r = 0.017; p = 0.968). Weak and positive associations between DDT metabolites with physico-chemical parameters ranged from 0.481 to 0.516 (Table 4.9) and they were observed for *p,p'*-DDD metabolite and total phosphorus (TP) (r = 0.481; p = 0.228), whereas pH was also weakly correlated with *p,p'*-DDE metabolite (r = 0.516 with p = 0.190) during the wet season.

During the dry season, the Pearson moment correlations (Table 4.9) were positive and ranged from weak to strong, with three of them being statistically significant (p < 0.05). These were between *p,p'*-DDT with DO (r = 0.724; p = 0.043) and the highest observed coefficient was between *p,p'*-DDE and pH (r = 0.749; p = 0.032). The lowest positive correlation observed was between the *p,p'*-DDT metabolite and conductivity (r = 0.025; p = 0.952) but the relationship insignificant (p > 0.05). The highest negative correlation (r = -0.729; p = 0.022) was observed for *p,p'*-DDT metabolite with total phosphorus (TP) during the dry season. However, all the negative correlations during the wet season were insignificant. The lowest correlation was between *p,p'*-DDE and temperature (r =-0.026; p = 0.950) while the highest was between *p,p'*-DDD with temperature (r= -0.614; p = 0.105). Weak negative correlation were observed for the metabolite *p,p'*-DDE and total nitrogen (TN) (r = -0.365; p = 0.374) concentrations in water receiving effluents from fish ponds. All the other correlations were insignificant with the lowest being *p,p'*-DDD with pH (r =-0.014; p = 0.974).

Table 4.9: **Pearson correlation coefficient between the DDT metabolite concentrations and the physico-chemical parameters in the river water during the wet and dry seasons**.

Wet season	**Temp** (°C)	**Conduc** (µScm^{-1})	**TSS** (µgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (µgL^{-1})	**TN** (µgL^{-1})
p,p'-	r =-.026	r =-.272	r =0.185	r =0.116	r =0.516	r =0.255	r =0.281	r =-.365
DDE	p=0.950	p=0.515	p=0.661	p=0.784	p=0.190	p=0.542	p =0.501	p=0.374
p,p'-	r =-.614	r =0.757	r =-.082	r =0.162	r =-.207	r =0.368	r =0.481	r =0.288
DDD	p=0.105	p=**0.029**	p=0.847	p=0.701	p=0.622	p=0.369	p =0.228	p=0.489
p,p'-	r =0.279	r =0.017	r =0.173	r =-.123	r =-.092	r =0.018	r =-0.175	r =-.252
DDT	p=0.504	p=0.968	p=0.683	p=0.772	p=0.828	p=0.967	p =0.679	p=0.548
Dry season								
p,p'-	r =0.120	r =0.161	r =0.127	r =-.193	r =0.749	r =-.068	r = 0.405	r =0.303
DDE	p=0.776	p=0.704	p=0.765	p=0.647	p=**0.032**	p=0.872	p = 0.319	p=0.466
p,p'-	r =-.045	r =0.211	r =-.582	r =-.249	r =-.014	r =-.232	r = -0.165	r =-.151
DDD	p=0.915	p=0.616	p=0.131	p=0.553	p=0.974	p=0.579	p = 0.696	p=0.722
p,p'-	r =-.311	r =0.025	r =-.623	r =0.724	r =-.118	r =-.667	r = -0.779	r=0.205
DDT	p=0.454	p=0.952	p=0.099	p=**0.043**	p=0.782	p=0.071	p = **0.022**	p=0.626

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

It was observed that the correlations were generally stronger during the dry season than in the wet season. There were three significant correlations during the dry season, while there was only one during the wet season.

4.3.3 Concentration of the cyclodiene compounds in the rivers

The mean (± SE) cyclodiene concentration compounds in the riverwater and among the stations were analysed to illustrate spatial differences in the period under assessment (Figure 4.21). The mean range variations for heptachlor epoxide, endosulfan II, dieldrin and methoxychlor cyclodiene pesticides were: 0.233 ± 0.010 µgL^{-1} to 1.244 ± 0.003 µgL^{-1}; 0.001 to 0.098 ± 0.004

μgL^{-1}; BDL to 2.125 ± 0.073 $\mu gL^{-1}$and 0.097 to 5.101 ± 0.251 μgL^{-1}, respectively, and were observed in the sampling stations B, D and E indicating that cyclodiene compounds residues encountered in river water samples contained high concentrations. Residue levels observed during the study period ranged from BDL to 5.101 ± 0.007 μgL^{-1}, with highest value recorded for methoxychlor (station E). The compounds that registered below the detection limit (BDL) levels included endrin, (station D), dieldrin (station C and D) as well as endosulfan II, (at sampling stations B, C and D). A one-way analysis of variance (ANOVA) test showed that the mean concentrations of methoxychlor were significantly different ($p < 0.05$; F = 6.381; p = 0.013), among sampling stations. Tukey's *post hoc* test for separation of means revealed that the mean methoxychlor concentrations for station D varied significantly from those observed at sampling stations C and F. Further investigation using a one-way analysis of variance (ANOVA) test showed that heptachlor epoxide mean concentrations were not significantly different ($p > 0.05$; F = 1.642; p = 0.398) among sampling stations. The data obtained in the different sampling stations showed that the mean residue level for methoxychlor compound was the highest (5.024 ± 0.756 μgL^{-1}) followed by dieldrin (1.002 ±0.293 and 2.241 ±0.118 $\mu gL^{-1)}$) in sampling stations G and E. The mean concentrations of endosulfan II cyclodiene pesticide in river waters receiving fish ponds effluent in River Kuja watershed varied from BDL (in stations C, D and E) to 0.044 ±0.183 μgL^{-1} (station F). In combination, endosulfan II cyclodiene pesticides showed a mean concentration that was significantly different among sampling stations ($p < 0.05$; F = 21.631; p = 0.001), at 95% confidence level.

Further data analysis showed that the mean cyclodiene pesticides contaminant levels ranged between 0.0440 ±0.018 to 2.234 ±0.756 μgL^{-1} for endosulfan II and methoxychlor, respectively, between sampled stations; whereas the mean residue level of endosulfan I and methoxychlor was 0.075 ±0.039 μgL^{-1} in the river water. ANOVA statistical test showed that the means of aldrin concentrations were significantly different among sampling stations ($p <$

0.05). Tukey's *post hoc* test for separation of means revealed that mean aldrin residue level for station G varied significantly from that observed at sampling stations B, D and E.

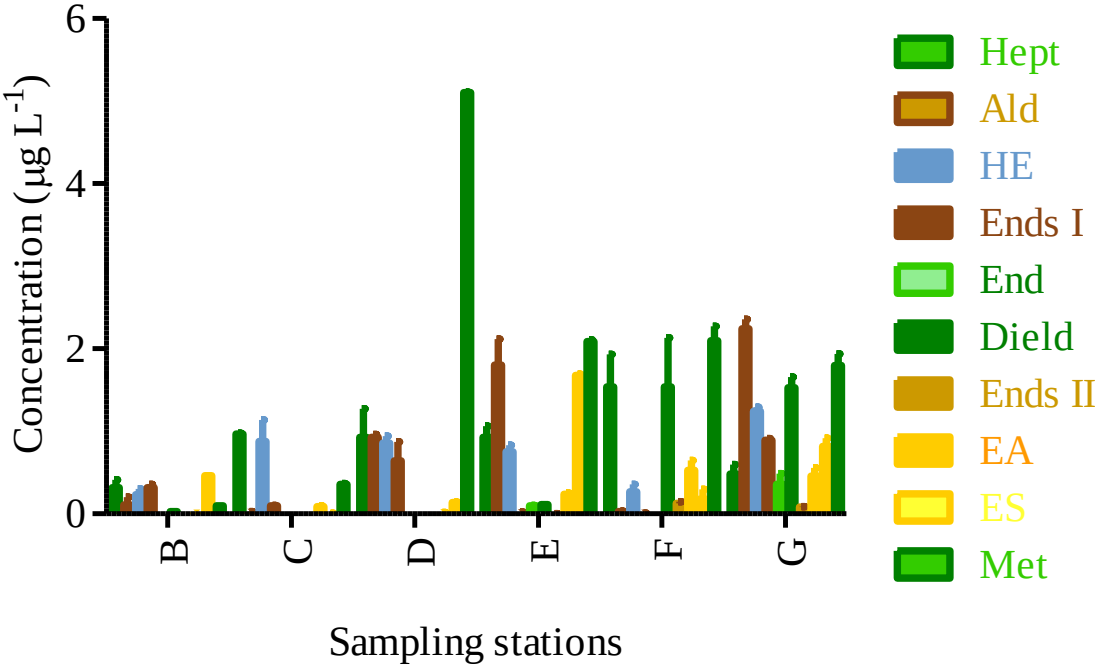

Figure 4.21: **Spatial mean (± SE) distributions of the cyclodienes in the river water**.

Figure 4.22 represents the temporal distribution of cyclodiene compounds levels in the wet and dry seasons. Cyclodienes concentrations ranged from the below detection limit, (endrin aldehyde), to 2.373 µgL^{-1} (endosulfan II) during both the wet and dry seasons. The independent sample *T*-test showed that the endosulfan II mean concentrations were significantly different between (wet and dry) seasons ($p < 0.05$; t = 1.782; $p = 0.016$) at the 95% confidence level. Aldrin, endosulfan II, endrin aldehyde and heptachlor means conceentrations in river water were 0.078 ±0.004, 2.102 ±0.2021, 0.001 ±0.0008 and 1.584 ±0.451 µgL^{-1}, respectively; indicating that the cyclodiene compounds residues encountered in river waters receiving fish pond effeluents in both wet and dry seasons were in slightly lower as compared to those encountered spatially. Taking $p < 0.05$, the temporal distribution differences of the mean levels of dieldrin residues were statistically significant in both wet and dry seasons but not for

heptachlor (Figure 4.22). Further analysis showed that dieldrin cyclodiene compound mean levels were significantly different ($p < 0.05$; t = 7.271; $p = 0.0001$) in the wet and dry seasons. In addition, sample *T*-test procedures on cyclodiene pesticides encountered indicated significant seasonal variation, especially for endosulfan sulfate ($p < 0.05$; t = 4.291; $p = 0.0423$), endosulfan II ($p < 0.05$; $p = 0.0087$) and aldrin ($p < 0.05$; t = 5.418; $p = 0.0006$) during the study period.

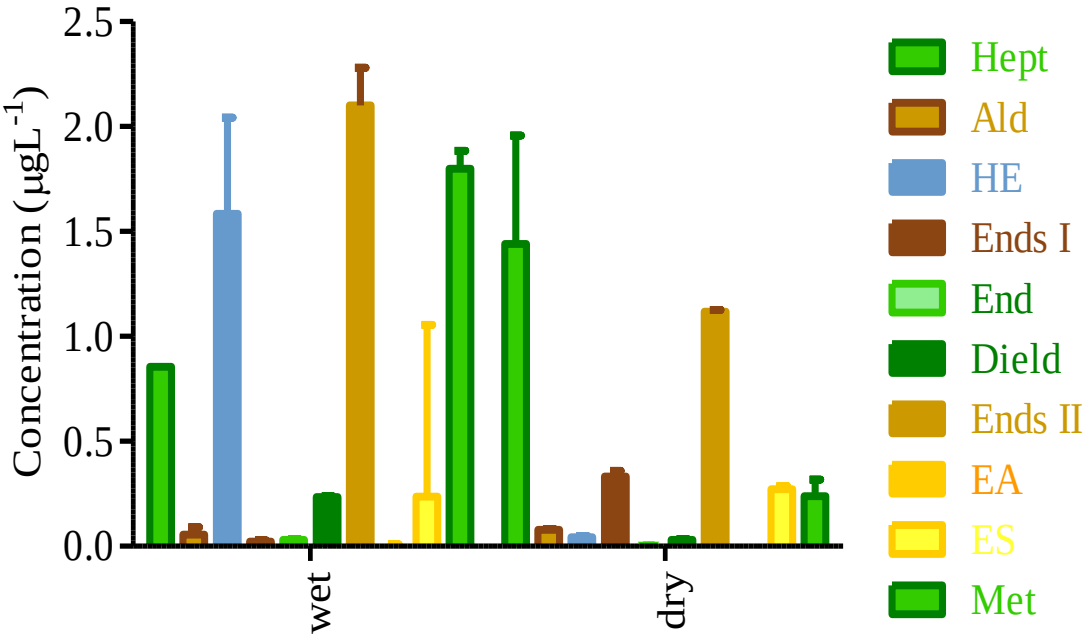

Figure 4.22: **Temporal mean (± SE) distributions of the cyclodienes in the river water**.

Table 4.10 below shows correlation between cyclodiene pesticide residues and water quality parameters in river water over wet and dry seasons. A strong and positive correlation was observed in the wet season between heptachlor and TP, though not statistically significant (r = 0.509, $p = 0.197$. However, methoxychlor was positively significantly correlated with DO (r = 0.765; $p = 0.036$). Negative but insignificant correlation were observed (r = -0.229, $p = 0.584$ to r = -0.241, $p = 0.566$) between endosulfan sulfate mean residue levels against TSS; and endosulfan I against turbidity in the dry season (Table 4.10). However, the relationship between

endosulfan I and DO were noted to be significant (at $p < 0.05$), in the dry season. In the dry season, there was no significant correlation between endrin aldehyde against pH ($r = 0.497$, $p = 0.211$ to $r = -0.017$, $p = 0.969$) and also between dieldrin and temperature. Negative and significant correlations were observed between endrin aldehyde against temperature ($r = -0.001$, $p = 0.999$ to $r = -0.816$ with $p = 0.031$) as well as between heptachlor against turbidity in the dry season. However, heptachlor was positively and significantly ($p < 0.05$) correlated with pH in the water column. Differences and significant correlations in pesticide residue averages in water column were noted to be significantly different between heptachlor with pH ($r = 0.778$; $p = 0.042$) and with turbidity ($r = 0.816$; $p = 0.032$) and similar to heptachlor epoxide and turbidity levels ($r = 0.748$; $p = 0.023$).

Table 4.10: **Pearson correlation coefficient between the cyclodiene pesticides concentrations and the water quality parameter measurements in the river water during the wet and dry seasons**.

Wet season	**Temp** (°C)	**Cond** (μScm^{-1})	**TSS** (μgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (μgL^{-1})	**TN** (μgL^{-1})
Heptachlo	r =0.628	r =0.269	r = 0.658	r =0.261	r =.073	r =0.564	r = 0.509	r =0.365
r	p=0.096	p=0.519	p = 0.076	p=0.533	p=0.864	p=0.146	p = 0.197	p=0.374
Aldrin	r =0.184	r =0.163	r = -0.229	r =0.413	r =0.052	r =-.274	r =-0.329	r =-.327
	p=0.662	p=0.699	p = 0.584	p=0.309	p=0.903	p=0.511	p = 0.426	p=0.429
Heptachlo	r =-.337	r =-.114	r = -0.427	r =0.523	r =0.312	r =-.512	r =-0.335	r =0.303
r Epoxide	p=0.415	p=0.788	p = 0.291	p=0.183	p=0.451	p=0.195	p = 0.417	p=0.466
Endosulfa	r =-.582	r =0.142	r = 0.689	r =-.728	r =-.389	r =-.281	r = 0.160	r =-.269
n I	p=0.130	p=0.737	p = 0.059	p=**0.044**	p=0.341	p=0.501	p = 0.705	p=0.519
Endrin	r =-.548	r =0.691	r =-0.616	r =0.123	r =0.055	r =0.427	r = -0.455	r =0.439
	p=0.159	p=0.058	p = 0.104	p=0.772	p=0.897	p=0.292	p = 0.257	p=0.277
Dieldrin	r =-.532	r =0.592	r = 0.582	r =-.068	r =-.183	r =-.211	r = 0.119	r =-.282
	p=0.173	p=0.122	p = 0.130	p=0.872	p=0.665	p=0.616	p = 0.778	p=0.498
Endosulfa	r =0.256	r =0.234	r = 0.005	r =0.471	r =0.366	r =-.318	r = -0.261	r =0.139
n II	p=0.541	p=0.577	p = 0.990	p=0.239	p=0.373	p=0.442	p = 0.533	p=0.744

Endrin	r =0.343	r =-.549	r =-0.183	r =-.211	r =0.119	r =-.282	r = -0.367	r =0.246
Aldehyde	p=0.406	p=0.159	p = 0.665	p=0.616	p=0.778	p=0.498	p = 0.371	p =.557
Endosulfa	r =-.017	r =0.691	r =-0.616	r =0.123	r =-.417	r =-.439	r = -0.137	r =0.528
n sulfate	p=0.967	p=0.058	p = 0.104	p=0.772	p=0.305	p=0.275	p = 0.746	p=0.179
Methoxyc	r =0.534	r =.496	r = 0.328	r =0.765	r =-.196	r =0.332	r =0.469	r =0.596
hlor	p=0.173	p=0.211	p=0.428	p=**0.036**	p=0.643	p=0.421	p=0.240	p=0.119
Dry season								
Heptachlo	r =0.055	r =0.427	r = -0.455	r =0.439	r =0.778	r =-.816	r = -0.443	r =-.213
r	p=0.897	p=0.292	p= 0.257	p=0.277	p=**0.042**	p=**0.031**	p= 0.272	p=0.613
Aldrin	r =-.017	r =0.196	r = -0.060	r =0.459	r =0.359	r =-.309	r = -0.149	r =.263
	p=0.969	p=0.641	p = 0.888	p=0.253	p=0.383	p=0.456	p = 0.724	p=0.529
Heptachlo	r =-.128	r =0.213	r =-0.387	r =0.142	r =0.689	r =-.748	r = -0.389	r =-.281
r Epoxide	p=0.763	p=0.612	p= 0.344	p=0.737	p=0.059	p=**0.023**	p = 0.341	p=0.501
Endosulfa	r =0.457	r =0.495	r = 0.061	r =0.735	r =0.249	r =-.241	r = -0.266	r =-.116
n I	p=0.255	p=0.212	p= 0.885	p=**0.008**	p=0.551	p=0.566	p = 0.524	p=0.784
Endrin	r =0.025	r =0.167	r =-0.394	r =0.715	r =0.404	r =-.519	r =-0.363	r =0.116
	p=0.954	p=0.693	p =0.335	**p=0.046**	p=0.322	p=0.187	p =0.377	p=0.784
Dieldrin	r =0.102	r =-.090	r =0.134	r =-.469	r =-.119	r =0.355	r =0.363	r =-.048
	p=0.809	p=0.831	p =0.752	p=0.241	p=0.778	p=0.388	p =0.376	p=0.911
Endosulfa	r =0.225	r =0.179	r =-0.113	r =0.443	r =0.177	r =-.281	r =-0.291	r =-.299
n II	p=0.593	p=0.672	p =0.791	p=0.272	p=0.676	p=0.500	p =0.485	p=0.472
Endrin	r =-.001	r =0.070	r =0.092	r =-.548	r =0.497	r =-.111	r =0.207	r =-.150
Aldehyde	p=0.999	p=0.868	p =0.829	p=0.159	p=0.211	p=0.794	p =0.624	p=0.723
Endosulfa	r =0.184	r =0.163	r = -0.229	r =0.413	r =0.052	r =-.274	r =-0.329	r =-.327
n sulfate	p=0.662	p=0.699	p = 0.584	p=0.309	p=0.903	p=0.511	p = 0.426	p=0.429
Methoxyc	r =-.337	r =-.214	r = -0.427	r =0.523	r =0.312	r =-.512	r =-0.335	r =0.303
hlor	p=0.415	p=0.788	p = 0.291	p=0.183	p=0.451	p=0.195	p = 0.417	p=0.466

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

4.3.4 Concentration of the HCHs isomers in the river sediments

Concentrations of HCH and its isomers in river sediments between different stations is illustrated in Figure 4.23. The spatial distributions of detected HCH pesticides levels (μgKg^{-}

^{1}) in river sediment samples were higher than those found in the water (μgL^{-1}). The overall mean (± SE) ranged between below detection limit (BDL) to a high value of 32.564 ±5.501 μgKg^{-1} in river bottom sediments. Residue levels of the α-HCH, δ-HCH and γ-HCH isomers in river sediments varied from low to a high level in sampling stations B, D, F and G. The highest mean contaminant level in river sediments from the study area was for α-HCH isomer. Alpha (α-HCH) residue level varied from BDL, (in stations C and D) to 32.564 ±5.501 μgKg^{-1} in station G whereas the mean concentration for the beta (β-HCH) isomer varied from 0.822 ±0.008 μgKg^{-1} (in station D) to 12.838 ±1.754 μgKg^{-1} (in sampling station F). The data was subjected to a one-way analysis of variance (ANOVA) test and results indicated that the mean β-HCH concentration was not significantly different between the sampled stations ($p > 0.05$; F = 1.747; $p = 0.061$) at the 95% confidence level. The mean for gamma (γ-HCH) isomer varied from below detection limit (in station D) to a high value of 19.453 ±3.934 μgKg^{-1} in station E, whereas the δ-HCH indicated a mean residue level of BDL (in sampling station E) to 13.381 ±2.231 μgKg^{-1} in sampling station G. A one-way ANOVA test showed that α-HCH mean concentration was significantly different among the sampling stations ($p < 0.05$; F = 5.382; p = 0. 018) at the 95% confidence level. Tukey's *post hoc* test for separation of means revealed that mean α-HCH concentration for station B varied significantly from that observed at sampling stations D, F and G. Additionally, the spatial distributions of HCH organochlorine pesticide compounds in the river sediments showed mean concentrations for beta and delta ranging between 1.932 ±1.520 μgKg^{-1} to 8.612 ±3.000 μgKg^{-1} in stations B, C, F and G (Figure 4.23) and in Appendix IX. A one-way analysis of variance of mean concentrations obtained for γ-HCH residue in the river sediments sampled in River Kuja watershed indicated that the concentrations were not significantly different between sampling stations ($p > 0.05$; F = 1.215; $p = 0.320$) at the 95% confidence level.

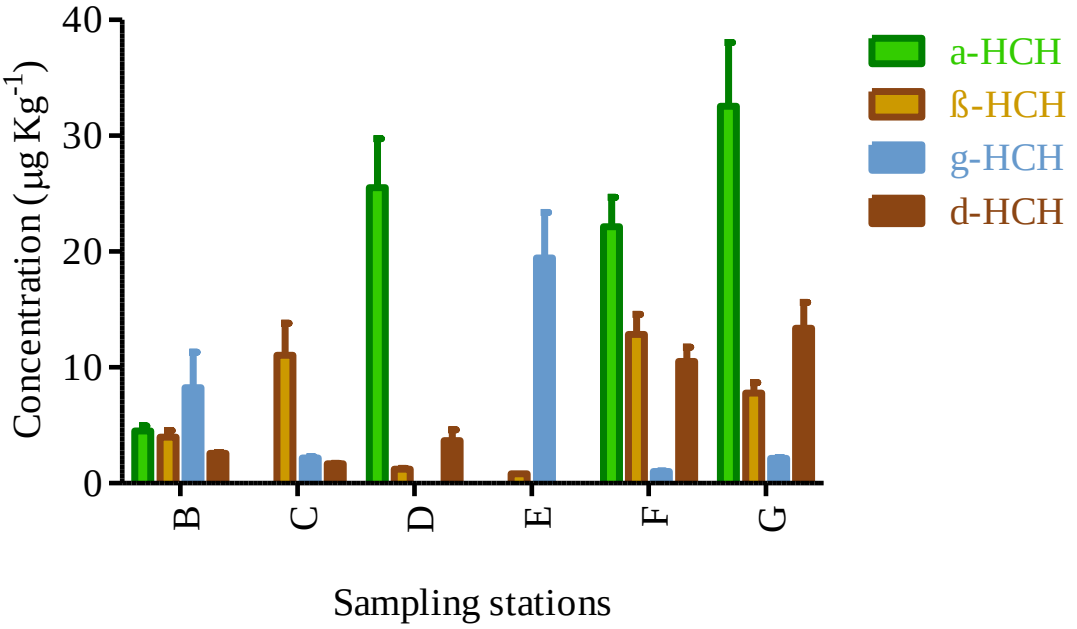

Figure 4.23: **Spatial mean (± SE) concentrations of the HCH isomers in the river sediments**.

Figure 4.24 represents mean temporal variations of the HCH isomers obtained in the river sediment samples over wet and dry seasons. Results obtained from the wet season data ranged between (0.618 to 22.254 ±2.825; BDL to 4.801 ±0.825; 0.053 to 8.310 ±0.325 and 1.502 to 10.389 ±1.025 µgKg^{-1}) for α-HCH, β-HCH, γ-HCH and δ-HCH isomers, respectively (Figure 4.24). Overally, the sampled pesticides residues recorded high mean concentration of α-HCH, γ-HCH and δ-HCH in the wet season than those values observed in the dry season. The independent sample *T*-test showed that mean α-HCH concentrations were significantly different between (wet and dry) seasons ($p < 0.05$; t = 1.632; $p = 0.010$) at the 95% confidence level. Residue levels of α-HCH, β-HCH, δ-HCH and γ-HCH isomers in river sediments were all above detection limits in the wet season. The highest mean residue levels of HCH pesticide compounds in river sediments receiving fish ponds effluent in River Kuja watershed during the dry season were α-HCH and δ-HCH (19.840 ±4.4201; 10.980 ±2.825 µgKg^{-1}), Figure 4.24.

The mean range recorded was from a low concentration value of 2.299 ±0.6514 μgKg^{-1} to the highest residue value of 8.1231 ±3.749 μgKg^{-1}. The independent *T*-test analysis showed that mean γ-HCH concentrations were significantly different between the wet and dry seasons ($p < 0.05$; t = 3.620; $p = 0.006$) at the 95% confidene limit.

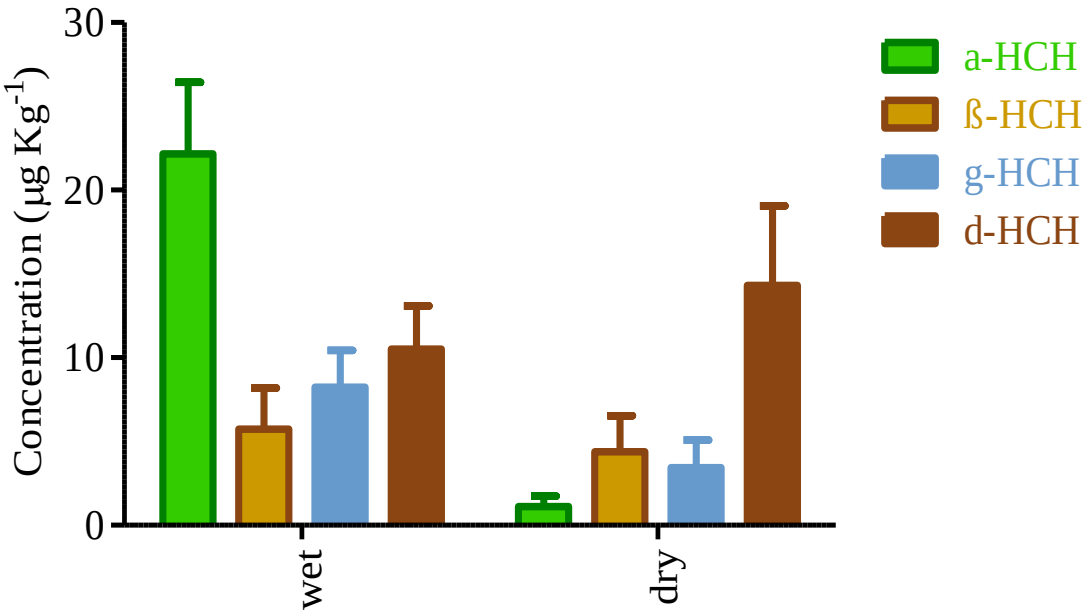

Figure 4.24: **Temporal mean (± SE) distributions of the HCH isomers in the river sediments**.

Table 4.11 shows that the HCH pesticide isomer concentrations detected in river sediments exhibit a strong positive bivariate correlation ($p < 0.05$) in the range of 0.003 to 0.875 during the wet season. A strong negative correlation was noted to be between α-HCH and TP in the river sediment (r = 0.875; $p = 0.004$) during the wet season (Table 4.11) implying that the concentration of the α-HCH in the water column increased and that of TP decreased, or vice versa. There was a statistical significant association between α-HCH pesticide residues in river sediments and temperature, turbidity and TP concentrations in river water, indicating that these physico-chemical parameter variations influenced the high α-HCH pesticides levels recorded

in river water sediments during sampling period in the area under study. During the dry season, only α-HCH showed significant relationship with pH level in the river water ($p < 0.05$). The highest correlation value of 0.875 was obtained for TP in the wet season, the lowest value of 0.003 was obtained for δ-HCH and dissolved oxygen (DO).

Table 4.11: **Pearson correlation coefficient between the HCH isomer concentrations and the water quality parameter measurements in the river water sediments during the wet and dry seasons**.

Wet season	**Temp** (°C)	**Cond** (μScm^{-1})	**TSS** (μgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (μgL^{-1})	**TN** (μgL^{-1})
α-HCH	r =-.866	r =0.066	r =0.791	r =0.404	r =0.475	r =0.706	r =0.875	r =-0.009
	p=**0.006**	p=0.877	p =**0.019**	p=0.321	p=0.235	p=**0.050**	p =**0.004**	p =0.984
β-HCH	r =-.218	r =-.411	r =0.522	r =-.489	r =0.146	r =0.316	r =0.132	r =-0.739
	p=0.605	p=0.312	p =0.185	p=0.218	p=0.731	p=0.446	p =0.756	p =**0.036**
γ-HCH	r =-.016	r =0.643	r =-0.479	r =0.014	r =-.309	r =-.009	r =-.007	r = 0.365
	p=0.969	p=0.086	p =0.229	p=0.973	p=0.455	p=0.984	p =0.987	p = 0.374
d-HCH	r =-.369	r =0.313	r =0.264	r =0.003	r =0.131	r =0.640	r =0.469	r =-0.136
	p=0.368	p=0.451	p =0.528	p=0.995	p=0.757	p=0.087	p =0.240	p = 0.748
Dry season								
α-HCH	r =0.219	r =0.334	r = 0.063	r =-.199	r =0.806	r =-.199	r = 0.277	r = 0.067
	p=0.603	p=0.419	p = 0.883	p=0.637	p=**0.016**	p=0.637	p= 0.506	p = 0.875
β-HCH	r =0.534	r =0.508	r =-0.039	r =0.026	r =0.563	r =-.040	r = 0.240	r = 0.056
	p=0.173	p=0.199	p = 0.927	p=0.951	p=0.146	p=0.924	p= 0.567	p = 0.896
γ-HCH	r =-.438	r =-.594	r = 0.179	r =0.531	r =-.131	r =0.031	r =-.055	r = 0.514
	p=0.278	p=0.121	p = 0.670	p=0.176	p=0.757	p=0.941	p= 0.896	p = 0.192
d-HCH	r =-.078	r =-.064	r = 0.126	r =-.226	r =.653	r =-.068	r = 0.371	r = 0.332
	p=0.855	p=0.879	p = 0.766	p=0.591	p=0.079	p=0.874	p =0.365	p = 0.422

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

4.3.5 Concentration of the DDT metabolites in the river sediments

The spatial mean (± SE) distribution of DDT and its metabolite pesticides residue levels detected in river sediment (μg Kg^{-1}) receiving fish ponds effluent in River Kuja watershed are displayed in Figure 4.25. The results show the variations in residue concentrations. The overall means (± SE) for *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT were 3.020 ±1.754 μgKg^{-1}, 6.237 ±1.612 μgKg^{-1} and 22.347 ±7.582 μgKg^{-1} respectively, for the river sediments in the target stations B to G. The *p,p'*-DDE metabolite concentrations ranged between 0.491 to 13.558 μgKg^{-1} in station B, to 1.232 to 15.648 μgKg^{-1} (*p,p'*-DDD) in station B and 0.978 to 42.012 μgKg^{-1} (*p,p'*-DDT) in sampling station C. A one-way analysis of variance (ANOVA) test showed that the mean *p,p'*-DDE metabolite concentrations were not significantly different among sampled stations ($p > 0.05$; $F = 1.163$; $p = 0.529$) at the 95% confidence level (Figure 4.25).

The mean residue concentrations of the *p,p'*-DDD metabolite among the stations ranged between 4.262 ±0.634 μgKg^{-1} (in sampling station C) to 15.655 ±4.521 μgKg^{-1} (in station B). The range for *p,p'*-DDT concentration was between 8.856 ±0.634 μgKg^{-1} at station G to 41.112 ±7.425 μgKg^{-1} at station C while that of *p,p'*-DDE the range was between 0.354 at station D to 13.893 μgKg^{-1} (at station G) in the river sediments among sampled stations. A one-way analysis of variance test showed that mean *p,p'*-DDD metabolite concentrations were not significantly different among sampled stations ($p > 0.05$; $F = 1.326$; $p = 0.124$) at the 95% confidence level. Spatially, it was observed that there was a significant difference in *p,p'*-DDT metabolite concentrations among the target sampling stations ($p < 0.05$; $F = 8.638$; $p = 0.028$) at the 95% confidence level. Tukey's *post hoc* test for separation of means revealed that mean *p,p'*-DDT residue level for station C varied significantly from mean *p,p'*-DDT residue level observed at sampling stations D and F.

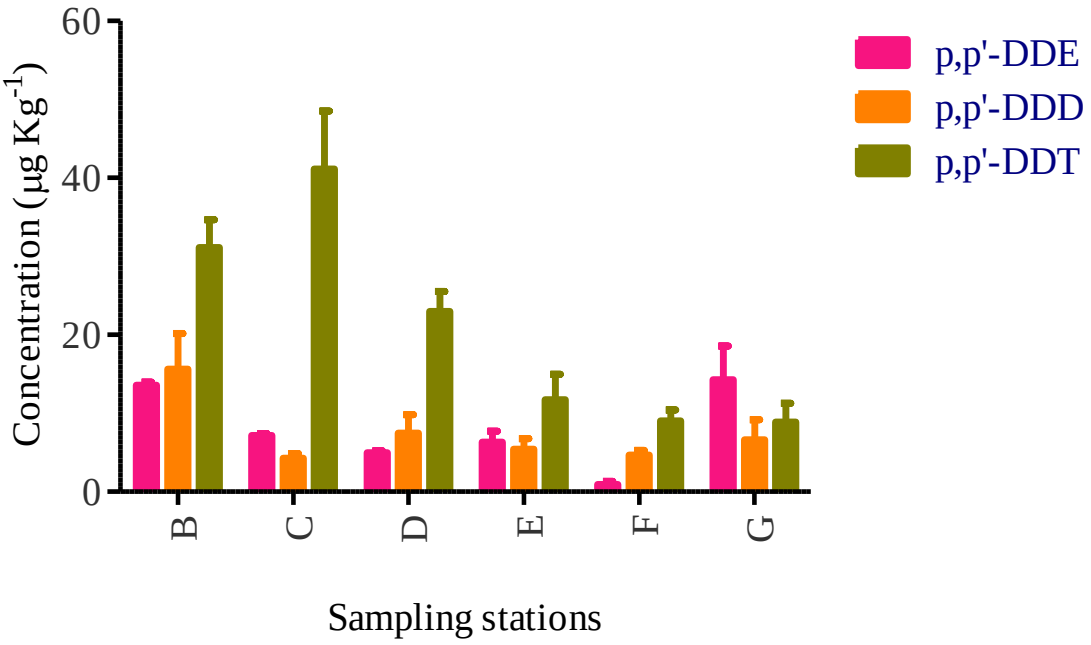

Figure 4.25: **Spatial mean (± SE) concentrations of the DDT metabolites in the river sediments**.

The temporal mean (± SE) distribution of the DDT metabolites assessed over the wet and dry seasons are presented in Figure 4.26. There were variations observed in contaminant levels and the overall mean *p,p'*-DDE was 1.232 ±9.804 µgKg^{-1} during the wet season. However, in the dry season, residue levels were much higher (3.823 ±0.019 µgKg^{-1}). The concentrations of the *p,p'*-DDD metabolite residue was 5.641 ±0.010 µgKg^{-1} (wet season), whereas *p,p'*-DDT metabolite registered a residue level of 12.971 ±4.761 µgKg^{-1} in river sediment. The independent sample *T*-test showed that the mean *p,p'*-DDD concentrations was significantly different between (the wet and dry) seasons ($p < 0.05$; t = 6.390; $p = 0.001$) at the 95% confidence level. Generally, it was observed that mean (± SE) values for the metabolites detected in the river sediment receiving fish pond effluent in River Kuja watershed were lower during the dry season than the wet season. Temporal distribution differences between the contaminants level were observed to be significant in the wet season months. The independent

sample *T*-test showed that the *p,p'*-DDE mean concentrations were not significantly different between (the wet and dry) seasons ($p > 0.05$; $p = 0.073$) at the 95% confidence level.

Seasonally, the mean concentration of *p,p'*-DDT shown in Figure 4.26 was lower during the wet season as compared to the level indicated in the dry months. Analysis of variance statistical test indicated that the means of *p,p'*-DDT were statistically significant between the (wet and dry) seasons ($p < 0.05$; t = 1.482; $p = 0.030$) at the 95% confidence level.

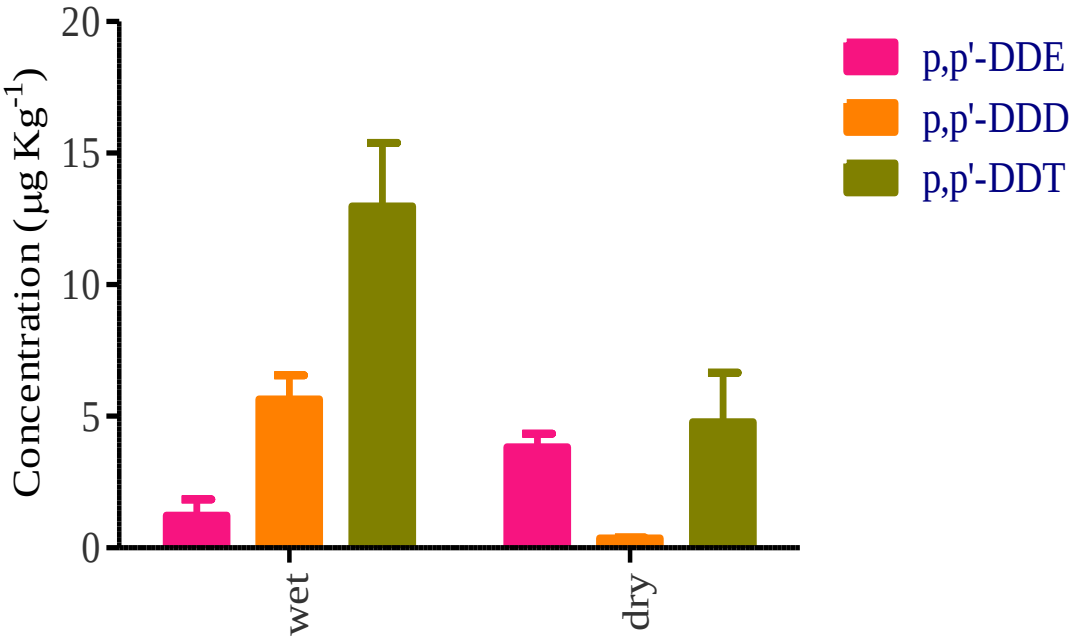

Figure 4.26: **Temporal mean (± SE) concentrations of the DDT metabolites in the river sediments**.

Table 4.12: illustrates correlations between the DDT metabolite concentrations and the water quality parameter measurements in the river sediments receiving fish pond effluents in River Kuja watershed during the wet and dry seasons. DDT metabolite residues in the river water sediments showed a positive and significant correlation ($p < 0.05$) (r = 0.119 and 0.691) between *p,p'*-DDD with pH and *p,p'*-DDT with conductivity during the wet season. The

highest correlation value of r = 0.691 was between *p,p'*-DDT metabolite against the TSS (in the wet season) whereas the lowest positive correlation was r = 0.005 between *p,p'*-DDT and the conductivity of river water during the dry season (Table 4.12). Negative correlation were also observed (r = -0.046 to 0.233) between *p,p'*-DDD and turbidity during the dry season, as well as between *p,p'*-DDT and the water temperature levels during the wet season (r = -0.017 to -0.616). The correlation observed between water quality parameters and DDT metabolites were not significantly different ($p > 0.05$) during seasons except for *p,p'*-DDE and pH (r = 0.808; $p = 0.015$).

Table 4.12: **Pearson correlation coefficient between the DDT metabolite concentrations and the water quality parameter measurements in the river sediment during the wet and dry seasons**.

Wet season	**Temp** (°C)	**Conduc** (μScm^{-1})	**TSS** (mgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (mgL^{-1})	**TN** (mgL^{-1})
p,p'-	r =0.256	r = -.482	r =-.242	r =-.508	r =.366	r =-.318	r = -0.261	r =0.139
DDE	p=0.541	p=0.227	p=0.563	p=0.199	p=0.373	p= .442	p = 0.533	p=0.744
p,p'-	r =0.343	r = -.549	r =-.183	r =-.211	r =0.119	r =-.282	r = -0.367	r =0.246
DDD	p =.406	p=0.159	p=0.665	p=0.616	p=0.778	p=0.498	p= 0.371	p=0.557
p,p'-	r =-.017	r=0.691	r=-0.616	r= 0.123	r=-.417	r =-.439	r = -0.137	r=0.528
DDT	p=0.967	p=0.058	p=0.104	p=0.772	p=0.305	p=0.275	p =0.746	p=0.179
Dry season								
p,p'-	r =0.432	r =0.389	r =0.229	r =-.046	r =0.808	r =0.048	r = 0.516	r =0.335
DDE	p=0.285	p=0.341	p=0.585	p=0.915	p=**0.015**	p=0.910	p = 0.191	p=0.417
p,p'-	r =0.592	r =0.582	r =-.068	r =0.584	r =0.333	r =-.233	r = -0.203	r =-.203
DDD	p=0.122	p=0.130	p=0.872	p=0.129	p=0.419	p=0.579	p = 0.629	p=0.629
p,p'-	r =0.234	r =0.005	r =0.471	r =-.013	r =0.559	r =0.286	r = 0.606	r =0.578
DDT	p=0.577	p=0.990	p=0.239	p=0.976	p=0.149	p=0.492	p =0.112	p=0.134

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond:

Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

4.3.6 Concentration of the cyclodienes in the river sediments

Figures 4.27 illustrates spatial mean (± SE) distributions of cyclodiene pesticide compounds in river sediments during the wet and dry seasons. The overall mean concentrations of endosulfan I was 29.840 ±10.220 μgKg^{-1} across the sampled stations, whereas methoxychlor recorded a lower mean of 13.470 ±6.757 μgKg^{-1} between the target sampling stations (Figures 4.27). Residue concentrations of cyclodiene pesticide compounds in the river sediments varied significantly among the stations. The cyclodiene compounds ranged from below detection limit (in sampling stations B and C), to detectable levels of endosulfan II as well as endrin aldehyde (in station B), to a high contaminant level of 73.355 ±6.501 μgKg^{-1} (by endosulfan I) in station F. A one-way analysis of variance (ANOVA) test showed that the mean endosulfan I concentrations were statistically and significantly different among the sampled stations ($p < 0.05$; F = 5.427; $p = 0.027$) at the 95% confidence level. Tukey's *post hoc* test for separation of means revealed that the mean endosulfan I for station D varied significantly from the levels at sampling stations C and F. Additionally, the analysis of variance test revealed that the mean concentrations for endrin aldehyde among sampling stations were not significantly different ($p > 0.05$; $p = 0.076$), at the 95% confidence level. Further analysis of the mean aldrin, endosulfan II and endosulfan sulfate (18.44 ±4.628 μgKg^{-1} and 29.84 ±1.032 μgKg^{-1} and 26.95 ±8.425 μgKg^{-1}) revealed variations between sampling stations B, D, F and G, respectively. Analysis of variance test showed that mean for endosulfan sulfate cyclodiene compound concentrations were not significantly different between stations ($p > 0.05$; F = 2.143; $p = 0.064$), at the 95% confidence level.

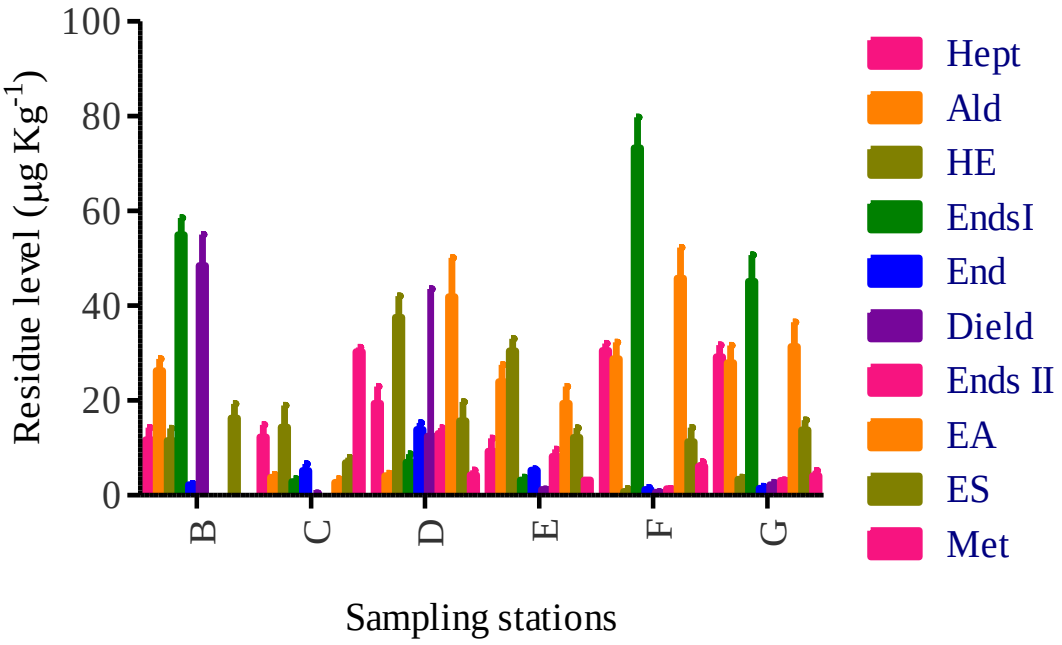

Figure 4.27: **Spatial mean (± SE) distributions of the cyclodiene compounds in the river sediments**.

The mean (± SE) residue levels of the cyclodienes in river sediment detected during wet and dry seasons is shown in (Figure 4.28). Endosulfan I, heptachlor and endrin aldehyde mean concentrations in the wet season showed high residue levels compared to those obtained in the dry season. The residue levels of methoxychlor in the wet and dry seasons was 12.420 ±1.622 µgKg^{-1} and 2.641 ±0.025 µgKg^{-1}, respectively, indicating variations during the sampling months. The independent sample *T*-test showed that methoxychlor mean concentrations were significantly different between the wet and dry seasons ($p < 0.05$; t = 3.193; $p = 0.002$) at the 95% confidence level. Statistical differences were noted to exist in the mean dieldrin, endrin, aldrin and heptachlor residue levels between seasons in river sediments.

Generally, the cyclodiene concentrations in the wet season were lower (Figure 4.28), and ranged between 0.349 ± 0.185 µgKg^{-1} (endrin pesticide) to 14.471 ±3.231 µgKg^{-1}, with an overall mean concentration of 6.574 ± 2.687 µgKg^{-1} in both seasons. Significant statistical differences in the mean levels of cyclodienes were evident for (independent sample *T*-test)

methoxychlor during the wet and dry seasons (p < 0.05; t = 2.053; p = 0.014) at the 95% confidence level.

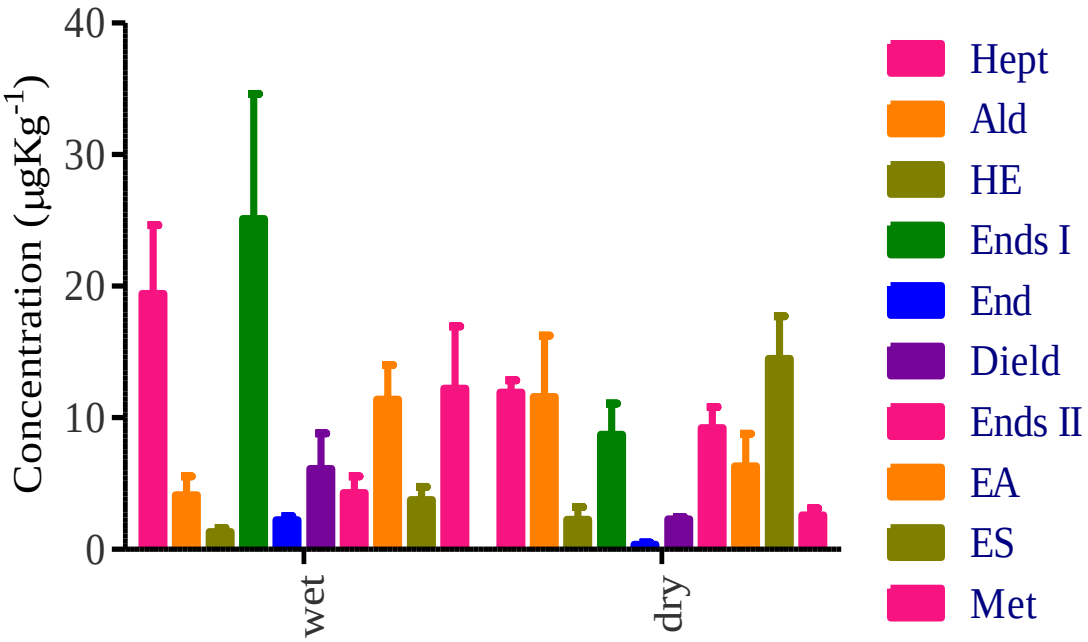

Figure 4.28: **Temporal mean (± SE) distributions of the cyclodiene compounds in the river sediments**.

Table 4.13 shows the correlation between cyclodiene pesticide compound residues and the water quality parameters in river sediment during the wet and dry seasons. Strong positive and negative correlations (p < 0.05) were observed during the study. A few pesticides, that is, methoxychlor, heptachlor, aldrin, endosulfan I and endrin aldehyde indicated strong positive correlation in the range of 0.715 to 0.957 and the relationship were statistically significant (for instance, methoxychlor compound versus turbidity, TP and TSS during the wet season) and endosulfan I versus conductivity but the remaining four pesticides indicated a statistically significant relationship during the dry season (p < 0.05).

***Table 4.13: Pearson c*orrelation coefficient between the cyclodiene pesticides concentrations and the water quality parameter measurements in the river sediment during the wet and dry seasons**.

Wet season	**Temp** (°C)	**Cond** (μScm^{-s})	**TSS** (μgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (μgL^{-1})	**TN** (μgL^{-1})
Heptachlor	r =-.552 p=0.156	r = 0.037 p = 0.931	r =0.668 p=0.070	r =0.643 p=0.086	r =0.271 p=0.516	r =0.518 p=0.189	r =0.604 p= 0.113	r = 0.229 p = 0.584
Aldrin	r =-.097 p=0.819	r = 0.552 p = 0.156	r =-.538 p=0.169	r =-.088 p=0.836	r =-.328 p=0.429	r =-.109 p=0.798	r = -.047 p= 0.912	r = 0.510 p = 0.196
Heptachlor epoxide	r =0.445 p=0.269	r = -0.184 p = 0.662	r =-.425 p=0.294	r =0.209 p=0.619	r =0.013 p=0.975	r =-.467 p=0.243	r = .378 p= 0.357	r = 0.536 p = 0.171
Endosulfan I	r =-.576 p=0.135	r = 0.813 p = **0.015**	r =-.174 p=0.677	r =0.229 p=0.584	r =-.225 p=0.591	r =0.216 p=0.608	r =0.428 p= 0.289	r = 0.437 p = 0.279
Endrin	r =0.025 p=0.954	r =0.167 p =0.693	r =-.394 p=0.335	r =0.715 **p=0.046**	r =0.404 p=0.322	r =-.519 p=0.187	r =-.363 p =0.377	r =0.116 p =0.784
Dieldrin	r =0.102 p=0.809	r =-0.090 p =0.831	r =0.134 p=0.752	r =-.469 p=0.241	r =-.119 p=0.778	r =0.355 p=0.388	r =0.363 p =0.376	r =-0.048 p =0.911
Endosulfan II	r =0.225 p=0.593	r =0.179 p =0.672	r =-.113 p=0.791	r =0.443 p=0.272	r =0.177 p=0.676	r =-.281 p=0.500	r =-.291 p =0.485	r =-0.299 p =0.472
Endrin aldehyde	r =-.001 p=0.999	r =0.070 p =0.868	r =0.092 p=0.829	r =-.548 p=0.159	r =0.497 p=0.211	r =-.111 p=0.794	r =0.207 p =0.624	r =-0.150 p =0.723
Endosulfan sulfat	r =-.592 p=0.123	r = 0.339 p = 0.412	r =0.480 p=0.229	r =0.650 p=0.081	r =0.380 p=0.353	r =0.261 p=0.533	r =0.678 p= 0.065	r = 0.193 p = 0.647
Methoxychlor	r =-.889 **p=0.003**	r = 0.082 p = 0.847	r =0.745 p=**0.022**	r =-.025 p=0.953	r =0.233 p=0.579	r =0.905 p=**0.032**	r =0.788 p= **0.020**	r = -0.250 p = 0.550
Dry season								
Heptachlor	r =-.381 p=0.352	r = -0.234 p = 0.578	r =0.394 p=0.334	r= 0.025 p=0.953	r =0.957 p=**0.012**	r =0.235 p=0.575	r= 0.593 p= 0.121	r = -0.081 p = 0.848

Aldrin	r =-.661	r = -0.144	r =0.636	r=-0.173	r=0.144	r =0.812	r =0.567	r = -0.510
	p=0.075	p = 0.733	p=0.089	p=0.682	p=0.733	p=**0.019**	p= 0.143	p = 0.196
Heptachlor epoxide	r =-.592	r = 0.339	r =0.480	r =0.650	r =0.380	r =0.261	r =0.678	r = 0.193
	p=0.123	p = 0.412	p=0.229	p=0.081	p=0.353	p=0.533	p =0.065	p = 0.647
Endosulfan I	r =-.889	r = 0.082	r =0.715	r =-.025	r =0.233	r =0.905	r =0.788	r = -0.250
	p=0.003	p = 0.847	p=**0.024**	p=0.953	p=0.579	p=**0.033**	p =**0.040**	p = 0.550
Endrin	r =0.628	r = 0.269	r= 0.658	r= 0.261	r= 0.073	r= 0.564	r= 0.509	r = 0.365
	p=0.096	p = 0.519	p=0.076	p=0.533	p=0.864	p=0.146	p =0.197	p = 0.374
Dieldrin	r= 0.184	r = 0.163	r=-0.229	r= 0.413	r= 0.052	r=-0.274	r=-0.329	r =-0.327
	p=0.662	p = 0.699	p=0.584	p=0.309	p=0.903	p=0.511	p= 0.426	p = 0.429
Endosulfan II	r =-.337	r= -0.114	r=-0.427	r= 0.523	r= 0.312	r=-0.512	r=-0.335	r = 0.303
	p=0.415	p = 0.788	p=0.291	p=0.183	p=0.451	p=0.195	p= 0.417	p = 0.466
Endrin aldehyde	r =-.128	r = 0.213	r=-0.387	r= 0.142	r= 0.689	r=-0.818	r=-0.389	r = -0.281
	p=0.763	p = 0.612	p=0.344	p=0.737	p=0.059	p = **0.05**	p= 0.341	p = 0.501
Endosulfan sulfate	r= 0.457	r = 0.495	r= 0.061	r= 0.691	r=-0.616	r= 0.123	r=-0.266	r = -0.116
	p=0.255	p = 0.212	p=0.885	p=0.058	p=0.104	p=0.772	p= 0.524	p = 0.784
Methoxychlor	r=-0.643	r=-0.209	r=0.472	r=-0.317	r =0.561	r =0.523	r =0.579	r =-0.085
	p=0.086	p =0.619	p=0.238	p=0.444	p=0.148	p=0.184	p =0.133	p =0.842

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

4.3.7 Concentration of the HCH isomers in the muscle tissue of *O. niloticus* from river water

The spatial mean (± SE) distributions of the HCH isomers in the muscle tissue of (*O. niloticus*) samples collected during the wet and dry seasons is presented in Figure 4.29. The mean range depicted in all the fish sampled from the target stations was between BDL for the α-HCH isomer in station D, and β-HCH (station G) as well the γ-HCH pesticide in stations D and G. The mean residue level of 0.952 μgKg^{-1} was recordedd by γ-HCH in sampling station B. Lindane (γ-HCH) exhibited a lower mean concentration in sampling stations B and G, followed by *δ*-HCH (stations B and F) and α-HCH concentration (station D). A one-way analysis

(ANOVA) test showed that the mean γ-HCH concentrations were statistically and significantly different among the sampled stations ($p < 0.05$; F = 7.351; $p = 0.025$) at the 95% confidence level. The relationship between β-HCH in station C to F as well as between α-HCH in stations C to F among sampled stations in the wet and dry seasons was observed to be statistically significant, at the 95% confidence level. In addition, the mean range of the HCH pesticides was between 0.121 ±0.037 to 0.435 ±0.036 μgKg^{-1} for β-HCH and 0.52 ±0.983 μgKg^{-1} for γ-HCH content in fish samples obtained in the rivers receiving fish ponds effluents within River Kuja watershed. A one-way ANOVA test showed that mean δ-HCH concentration was not significantly different among the sampling stations ($p > 0.05$; F = 1.648; $p = 0.072$).

Alpha (α-HCH) isomer exhibited concentrations that were almost evenly distributed between the sampled stations (μgKg^{-1}) in stations B, D and F, and a similar trend was observed for β-HCH in stations B and F. Analysis of variance test showed that the mean β-HCH concentration was statistically and significantly different ($p < 0.05$; $p = 0.002$) among the sampling stations, but the mean α-HCH level was not significantly different (Figure 4.29) among the sampled stations during the study period ($p > 0.05$; F = 11.512; $p = 0.062$;) at the 95% confidence level.

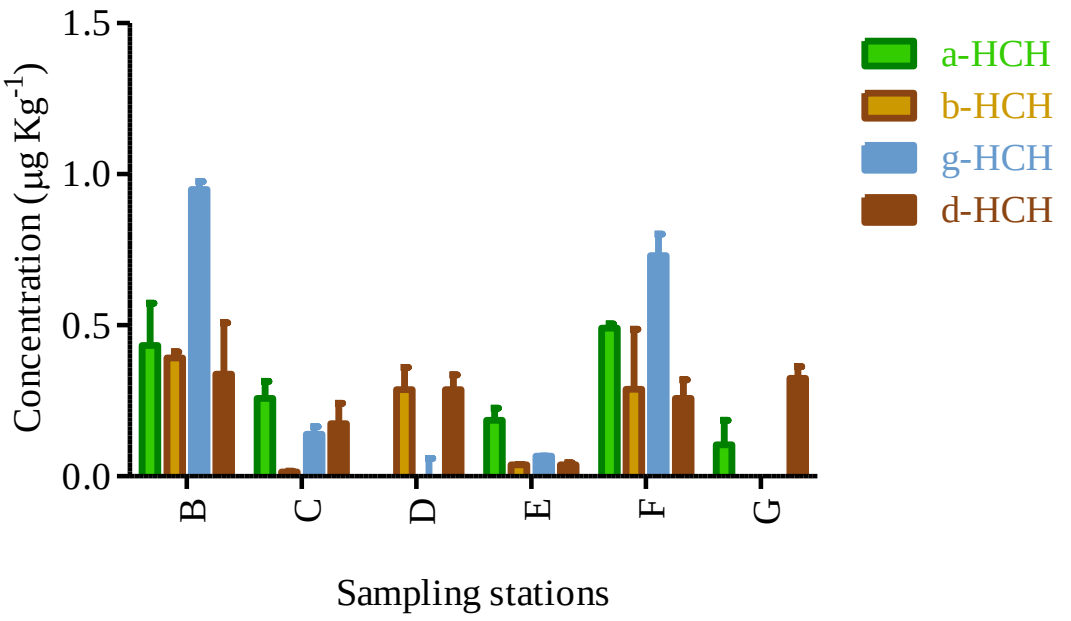

Figure 4.29: **Spatial mean (± SE) distributions of the HCH isomers in the muscle tissue of *O. niloticus* from the river water**.

Figure 4.30 represents mean (± SE) temporal distributions of HCH pesticides residue levels in the muscle tissue *O. niloticus* fish species in river water during the wet and dry seasons. The mean pesticides levels ranged between 0.170 ±0.005 (γ-HCH) to 0.20 ±0.049 µgKg^{-1} (β-HCH) during the wet season. The independent sample *T*-test method showed that the mean δ-HCH concentration was not statistically significant between sampling seasons ($p > 0.05$; t = 5.291; $p = 0.270$) at the 95% confidence level. Furthermore, mean HCH residue levels ranged between 0.324 ±0.005 µgKg^{-1} (β-HCH) to 1.495 ±0.128 µgKg^{-1} (γ-HCH) in the dry season. Independent sample *T*-test analysis test showed that the mean β-HCH contaminant level was not statistically and significantly different between the sampling seasons ($p > 0.05$; t = 4.702'$p = 0.060$) at the 95% confidence level. Additionally, results showed that residue concentration range was between BDL to 1.445 µgKg^{-1} for γ-HCH pesticide in the dry season, although in the dry season. Similarly, the dry season residue range was between 0.410 ±0.062 to 1.063 ±0.001

µgKg^{-1} for α-HCH and γ-HCH isomer pesticides content in the muscle tissue of fish samples in rivers receiving fish ponds effluent in River Kuja watershed.

In addition, the lowest and highest mean residue concentrations was recorded by β-HCH and lindane (γ-HCH) isomers in the muscle tissue of *O. niloticus* during the dry season, respectively. During the period under study, HCH residue concentration in the dry season months were higher than those levels observed in the wet season, and hence all isomer levels detected were in the range of < 1.5 µgKg^{-1} in the muscle tissue of *O. niloticus* fish samples. The seasonal mean levels of γ-HCH (Figure 4.30) were significantly different ($p < 0.05$; t = 2.863; $p = 0.003$) between wet and dry seasons.

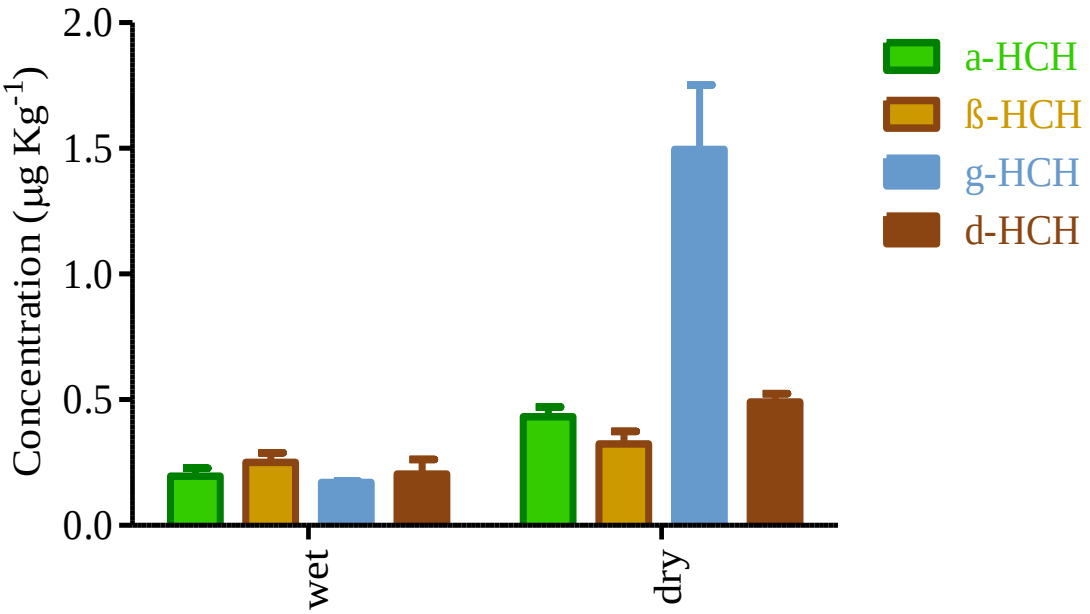

Figure 4.30: **Temporal mean (± SE) distributions of the HCH isomers in the muscle tissue of *O. niloticus* from river water.**

4.3.8 Concentration of DDT metabolites in the muscle tissue of *O. niloticus* from the river water

Residue levels of DDT metabolites in muscle tissue of fish collected from the different sampling stations is presented in Figure 4.31. The spatial mean (± SE) distributions of DDT and its metabolites in *O. niloticus* in rivers receiving fish pond effluent in target sampling stations was between 0.630 ±0.157 µgKg^{-1} (*p,p'*-DDD) to 1.53 ±0.371 µgKg^{-1} (*p,p'*-DDE). Further results showed that the spatial concentrations range in fish tissue 0.041 to 0.210 µgKg^{-1} (*p,p'*-DDD and *p,p'*-DDE) and 0.370 to 0.599 µgKg^{-1} for (*p,p'*-DDD and *p,p'*-DDT) for stations C and F, respectively. A one-way analysis of variance (ANOVA) showed that the mean *p,p'*-DDT residue levels between sampling stations was not statistically and significantly different ($p > 0.05$; $F = 2.163$; $p = 0.075$), at the 95% confidence level (Figure 4.31).

DDT and its metabolites residue values in the muscle tissue of *O. niloticus* fish in river sampling stations is presented in Figure 4.31. The mean pesticides range depicted by all the metabolites was between (BDL by *p,p'*-DDE metabolite in sampling station E) to (0.726 µgKg^{-1} by *p,p'*-DDT metabolite recorded in stations G and D). The mean range was between 0.079 ±0.0301 to 0. 786 ±0.1781 µgKg^{-1} for *p,p'*-DDT and *p,p'*-DDE isomer pesticide content in the muscle tissue of *O. niloticus* fish, collected in river waters receiving fish ponds effluent in River Kuja watershed. The ANOVA test results on the mean DDT metabolite revealed a statistically significant difference between stations ($p < 0.05$; $F = 16.352$; $p = 0.001$) at the 95% confidence level. Tukey's *post hoc* test for separation of means revealed that mean *p,p'*-DDE concentration for station B varied significantly from mean *p,p'*-DDE concentration observed at sampling stations D and G.

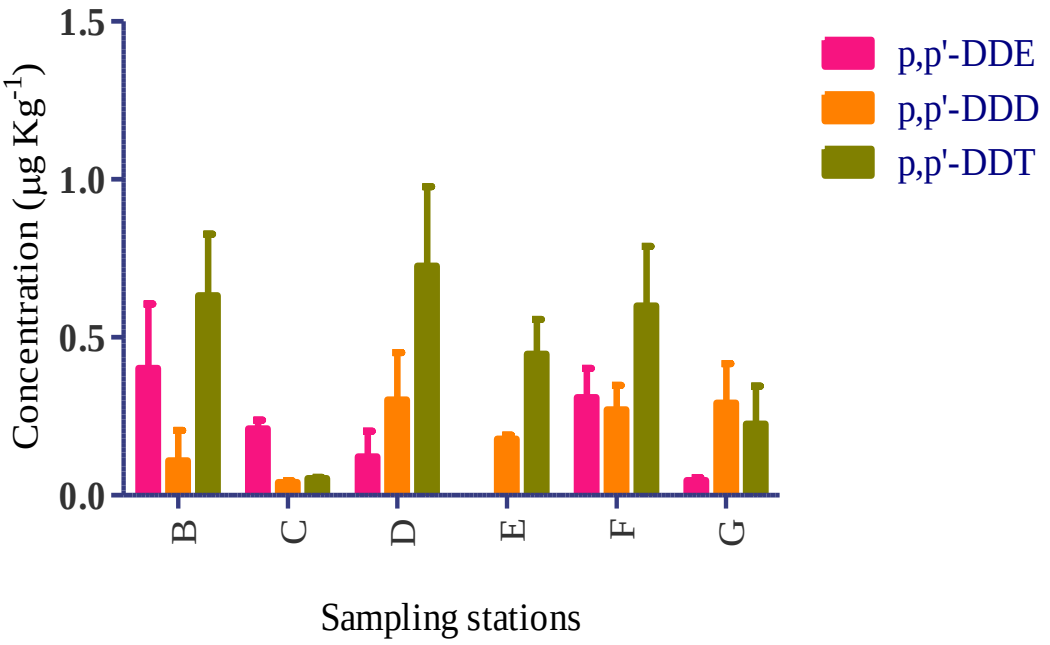

Figure 4.31: **Spatial mean (± SE) distributions of the DDT metabolites concentrations in the muscle tissue of *O. niloticus* from the river water.**

Figure 4.32 provides an illustration of the variation of DDT metabolites and its temporal distribution in the muscle tissue of *O. niloticus* in rivers receiving fish pond effluents within the River Kuja watershed. In decreasing order of magnitude, the mean (± SE) concentrations were: *p,p'*-DDD (5.641 ±0.617 µgKg^{-1}), for *p,p'*-DDT (3.971 ±1.413 µgKg^{-1}) and for *p,p'*-DDE (1.23 ±0.619 µgKg^{-1}), during the wet season, respectively. The independent sample *T*-test showed that mean *p,p'*-DDD metabolite concentrations was statistically and significantly different ($p < 0.05$; t = 1.830; $p = 0.018$) among the sampling stations, at the 95% confidence level. The mean contaminant value observed by DDT metabolites in the dry season were much lower, with highest level at < 0.270 ±0.083 µgKg^{-1} (Figure 4.32). These concentration values were almost three-times lower than the mean values obtained for *p,p'*-DDE during the wet season. Further investigations revealed a temporal distributions of the DDT contaminant concentrations in *O. niloticus* obtained in the waters receiving fish pond effluents within the

River Kuja watershed during the dry season, with a contaminant range of between 0.016 ±0.003 (*p,p'*-DDT) to 0.271 ±0.022 μgKg^{-1} (*p,p'*-DDD). The *p,p'*-DDD isomer recorded the highest mean contaminant level (0.271 ±0.022 μgKg^{-1}) in fish samples collected during the study period. Similarly, the lowest mean value was registered by *p,p'*-DDT at 0.016 ±0.003 μgKg^{-1} in the dry season, (Figure 4.32). Independent sample *T*-test showed that mean *p,p'*-DDT concentrations in the muscle tissue of *O. niloticus* was statistically and significantly different ($p < 0.05$; t = 1.702; $p = 0.004$) between (wet and dry) seasons, at the 95% confidence level.

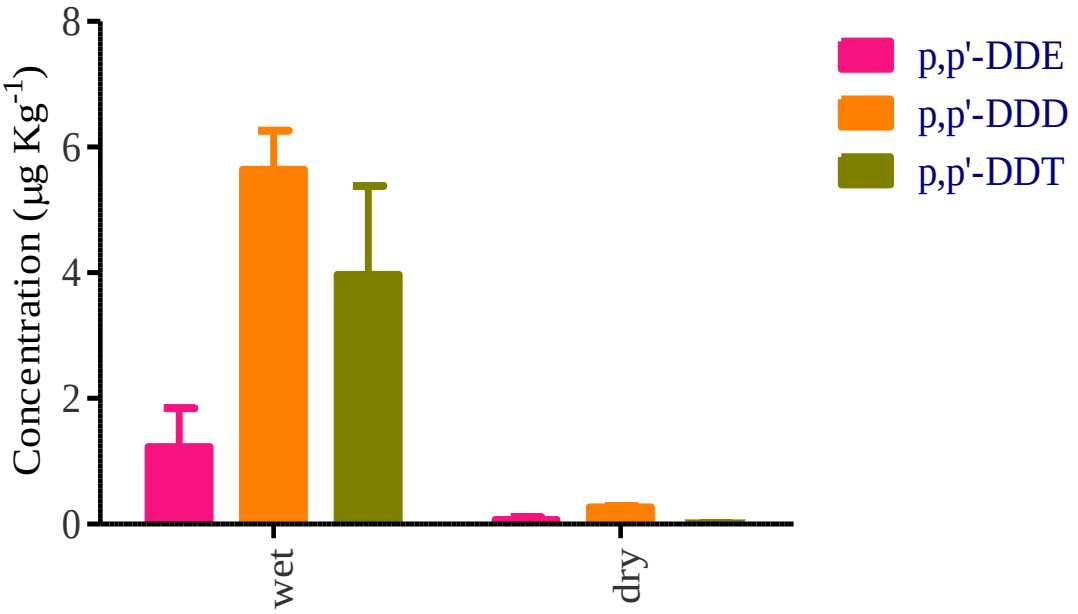

Figure 4.32: **Temporal mean (± SE) distributions of the DDT metabolites in the muscle tissue of *O. niloticus* from the river water.**

Table 4.14 below shows the correlation coefficients between DDT metabolite pesticide residues and the water quality parameters in river water sampled in the River Kuja watershed during wet and dry seasons. There was a strong negative correlation observed between *p,p'*-DDD with TN during the wet season (r = -0.666; $p = 0.072$). The metabolite *p,p'*-DDT indicated a strong positive correlation cefficient with TSS (r = 0.739; $p = 0.016$), and the relationship was observed to be statistically significant ($p < 0.05$). No other DDT metabolite

indicated a significant relationship with turbidity during wet season (Table 4.14), except *p,p'*-DDD. A weak negative correlation was observed between *p,p'*-DDE isomer and TSS in dry season, and the relationship was not significant (r = -0.161; *p* = 0.703; *p* = > 0.05). Observations over the dry season, show a very weak positive correlation value of r = 0.001; *p* = 0.886 (DO against *p,p'*-DDT) followed by a significant positive relationship between TN against *p,p'*-DDT (r = 0.632; *p* = 0.002).

Table 4.14: **Pearson correlation coefficient between the DDT metabolites and the water quality parameter measurements in the muscle tissue of *O. niloticus* fish in the river waters during the wet and dry seasons**.

Wet season	**Temp** (°C)	**Cond** (μScm^{-1})	**TSS** (μgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (μgL^{-1})	**TN** (μgL^{-1})
p,p'-	r =-.487	r =-.313	r =0.846	r =0.342	r =0.486	r =0.576	r =0.589	r =-.247
DDE	p=0.221	p=0.451	p=**0.014**	p=0.407	p=0.222	p=0.135	p =0.124	p=0.556
p.p'-	r =-.522	r =-.418	r =0.833	r =-.134	r =0.371	r =0.716	r =0.524	r =-.666
DDD	p=0.185	p=0.303	p=**0.020**	p=0.751	p=0.365	p=**0.026**	p =0.1818	p=0.072
p,p'-	r =-.417	r =-.451	r =0.739	r =0.149	r =0.372	r =0.612	r =0.471	r =-.439
DDT	p=0.305	p=0.263	p=**0.016**	p=0.723	p=0.365	p=0.107	p =0.239	p=0.276
Dry season								
p,p'-	r =0.147	r =0.318	r =-.161	r =-.394	r =0.398	r =-.385	r =-0.199	r =-.663
DDE	p=0.729	p=0.443	p=0.703	p=0.335	p=0.329	p=0.347	p =0.636	p=0.073
p,p'-	r =0.273	r =0.381	r =-.138	r =-.459	r =0.031	r =-.139	r =-0.140	r =-.743
DDD	p=0.513	p=0.352	p=0.745	p=0.252	p=0.942	p=0.743	p =0.741	p=**0.025**
p,p'-	r =0.106	r =0.422	r =-.556	r =0.001	r =-.071	r =-.593	r =-0.722	r =.632
DDT	p=0.803	p=0.298	p=0.152	p=0.886	p=0.867	p=0.121	p =**0.013**	p=**0.002**

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

4.4 Concentration of the organochlorine pesticides (OCPs) in the wastewater lagoons

4.4.1 Concentration of HCHs in the muscle tissue of fish from the wastewater lagoons

Figure 4.33 represents mean (± SE) levels of HCH isomers and the spatial distributions in the muscle tissue of *O. niloticus* fish from the wastewater sampling stations. Even though the tissue samples analysed from both stations indicated presence of pesticide contaminants, station A had a lower mean range (0.863 ±0.747 μgKg^{-1} to 19.668 ±4.549 μgKg^{-1}) for β-HCH and γ-HCH in station H. Overall, results showed the pesticides concentration ranged between a low of 1.781 ±0.016 μgKg^{-1} (indicated by β-HCH isomer) to a high of 28.495 ±2.495 μgKg^{-1} (γ-HCH isomer), in both sampling stations A and H. A one-way analysis of variance (ANOVA) test showed that mean γ-HCH concentrations was not statistically and significantly different among the sampling stations ($p > 0.05$; $F = 2.263$; $p = 0.205$), at the 95% confidence level. Lindane exhibited the highest concentration in station H followed by mean concentration value at station A (Figure 4.33). Statistical analysis results of ANOVA test indicated that δ-HCH mean concentration was not statistically significant among the sampling stations ($p > 0.05$; $F = 1.573$; $p = 0.074$) at the 95% confidence level. In addition, station A had residue levels that were in the order of magnitude of: 1.781 ±0.016 μgKg^{-1} (β-HCH), 4.766 ±1.801 μgKg^{-1} (γ-HCH), 5.801 ±1.593 μgKg^{-1} (α-HCH),and 19.120 ±4.549 μgKg^{-1} (δ-HCH) in fish collected in wastewater sampling stations during the sampling period. However, the overall mean concentrations in both sampling stations A and H were in the increasing order of magnitude γ-HCH < δ-HCH < α-HCH <β-HCH.

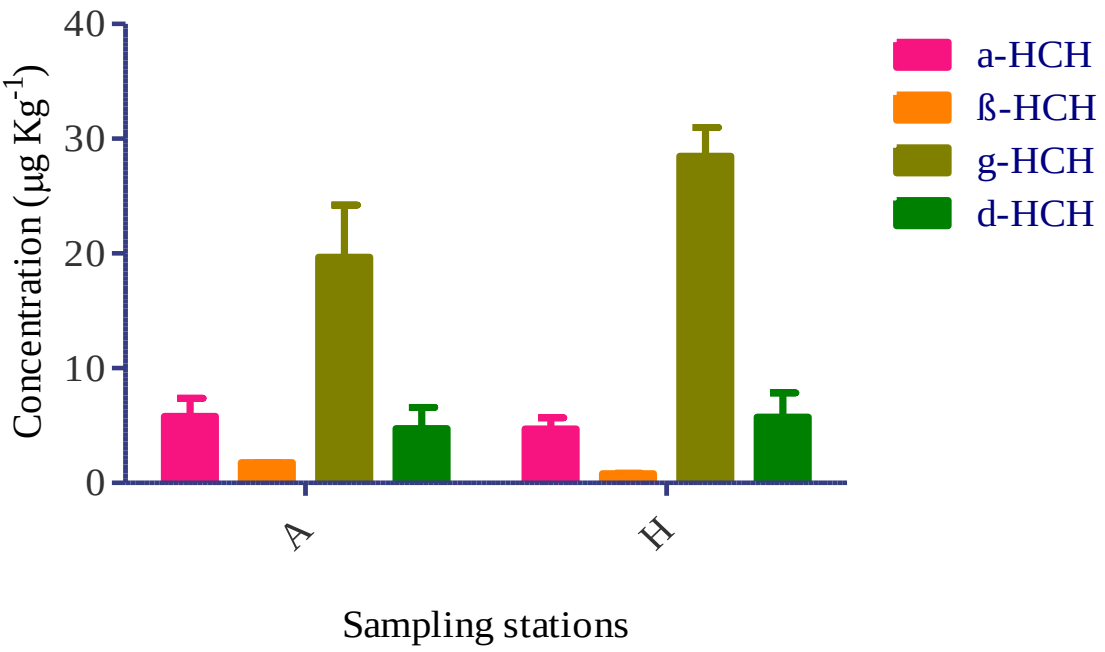

Figure 4.33: **Spatial mean (± SE) distributions of the HCH isomers in the muscle tissue of *O. niloticus* from the wastewater.**

A comparison of the temporal mean (± SE) concentrations of the HCH isomers in wastewater between wet and dry seasons is illustrated in Figure 4.34. HCH isomers pesticide concentrations and their temporal distributions in wastewater ranged from a low of 2.529 ±0.640 µgKg^{-1} (α-HCH) to 9.073 ±2.922 µgKg^{-1} (β-HCH) during the wet season. Independent sample *T*-test showed that mean δ-HCH concentration was not significantly different between the wet and dry seasons ($p > 0.05$; t = 4.721; $p = 0.072$). Further analysis indicated that all the four HCH isomers (both wet and dry) seasons recorded values above > 1.0 µgKg^{-1}. β-HCH and α-HCH pesticide residues recorded the highest and the lowest mean concentrations, respectively, during the wet season (Figure 4.34). The independent sample *T*-test method on the mean α-HCH isomer concentration obtained in wastewater *O. niloticus* fish within River Kuja watershed during the wet season months (May and October) and in the dry months (February and July) indicated that there was no significant difference ($p > 0.05$; t = 6.292; p =

0.063) between the seasons, at the 95% confidence level. However, a *T*-test result showed that mean γ-HCH concentrations between (wet and dry) seasons was significantly different ($p < 0.05$; t = 2.069; $p = 0.006$) at the 95% confidence level.

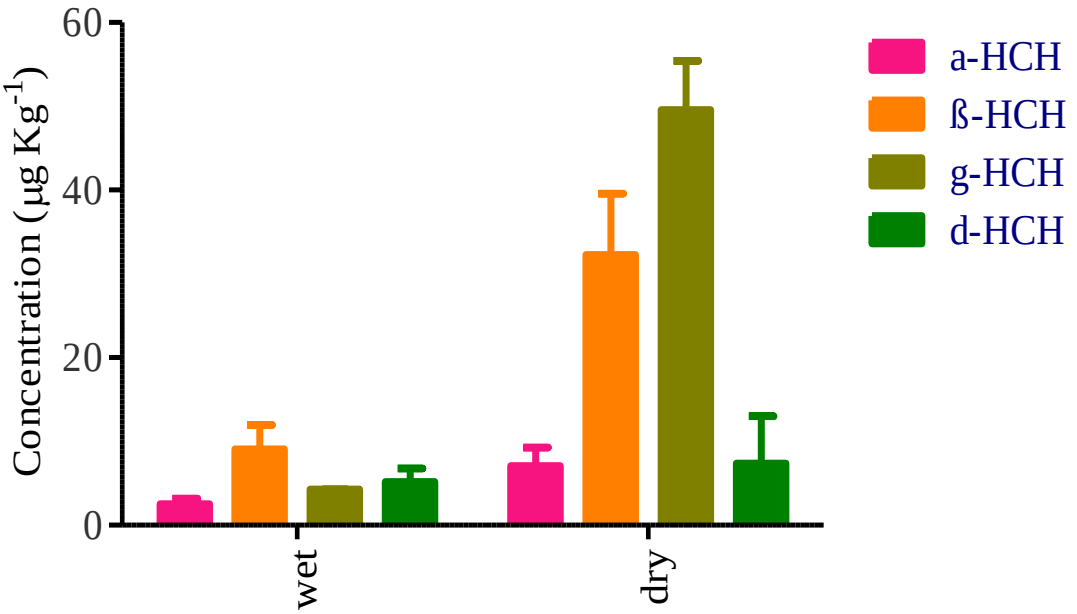

Figure 4.34: **Temporal mean (± SE) distributions of the HCH isomers in the muscle tissue of *O. niloticus* from the wastewater.**

Correlations between HCH isomer concentrations and the water quality parameter measurements in wastewater lagoons samples during the wet and dry seasons is presented in Table 4.15. The highest positive correlation coefficient was in the dry season and this was the association between the isomer δ-HCH and conductivity in the wastewater. The relationship was observed to be statistically significant (r = 0.895; $p = 0.012$) during the dry season. The lowest positive correlation was observed for the relationship between δ-HCH isomer concentration against TSS during the dry season (r = 0.061; $p = 0.785$) but not significant ($p > 0.05$). Positive correlations in the dry season were in the range of 0.061 to 0.895 (Table 4.15). The wet season revealed a fairly strong relationship between physico-chemical parameters

against HCH isomers in wastewater lagoons. In the dry season, both α-HCH and γ-HCH indicated a negative significant relationship with turbidity ($p < 0.05$).

Observations in Table 4.15 indicated strong significant positive relationship between DO versus α-HCH, pH versus β-HCH, and TP versus γ-HCH during the wet season. However, γ-HCH showed a significant negative relationship with wastewater pH (r = -0.744; p = 0.013). There were no significant associations between conductivity, TSS, TN, and turbidity and the HCHs isomers during the wet season ($p > 0.05$). Similarly, the TP. TN, TSS and temperature in the wastewater exhibited no significant relationship between gamma, beta, gamma and alpha HCH isomers in wastewater during the wet season ($p > 0.05$). Strong positive correlations were in the range of 0.745 to 0.957 (Table 4.15) and they were observed for α-HCH isomer and DO (r = 0.721; $p = 0.001$) during the wet season and whose relationship was significantly different ($p < 0.05$) in the wet season. The highest and significant correlation coefficient of r = 0.637 was observed for γ-HCH and the total phosphorus during the wet season. Highest negative significant correlation of r = -0.744 was obtained between γ -HCH and temperature.

Table 4.15: **Pearson correlation coefficient between the HCH isomer concentrations and the water quality parameter measurements in the wastewater during the wet and dry seasons**.

Wet season	**Temp** (°C)	**Cond** (μScm^{-1})	**TSS** (μgL^{-1})	**DO** (mgL^{-1})	**pH**	**Turb** (NTU)	**TP** (μgL^{-1})	**TN** (μgL^{-1})
α-HCH	r=-0.657	r=-0.049	r= 0.219	r= 0.721	r= 0.596	r= 0.247	r = 0.575	r = 0.043
	p= 0.280	p= 0.871	p= 0.602	p= **0.001**	p= 0.119	p= 0.556	p = 0.136	p = 0.923
β-HCH	r=-0.466	r=-0.059	r= 0.121	r=-0.175	r= 0.583	r=-0.015	r = 0.441	r = -0.073
	p= 0.439	p= 0.869	p= 0.776	p= 0.644	p= **0.024**	p= 0.973	p = 0.274	p = 0.794
γ-HCH	r=-0.744	r= 0.312	r= 0.402	r= 0.089	r= 0.544	r= 0.651	r = 0.637	r = -0.068
	p= **0.013**	p= 0.675	p= 0.323	p= 0.833	p= 0.163	p= 0.080	p = **0.003**	p = 0.669
d-HCH	r=-0.136	r=-0.602	r= 0.558	r=-0.394	r= 0.709	r= 0.101	r = 0.154	r = -0.347
	p= 0.875	p= 0.115	p= 0.151	p= 0.335	p= 0.409	p= 0.812	p = 0.716	p = 0.632

Dry season								
α-HCH	r= 0.273	r= 0.427	r=-0.455	r= 0.439	r= 0.778	r=-0.816	r = -0.443	r =-0.483
	p= 0.797	p= 0.292	p= 0.257	p= 0.277	p= **0.003**	p= **0.012**	p = 0.272	p = 0.642
β-HCH	r=-0.017	r= 0.196	r=-0.060	r= 0.459	r= 0.359	r=-0.309	r = -0.149	r = 0.263
	p= 0.869	p= 0.641	p= 0.788	p= 0.253	p= 0.383	p= 0.456	p = 0.724	p = 0.719
γ-HCH	r=-0.128	r= 0.313	r=-0.387	r= 0.142	r= 0.689	r=-0.848	r = -0.389	r = -0.281
	p= 0.673	p= 0.612	p= 0.344	p= 0.737	p= 0.059	p= **0.031**	p = 0.341	p = 0.501
d-HCH	r= 0.617	r= 0.895	r= 0.061	r= 0.735	r= 0.249	r=-0.241	r = -0.266	r = -0.626
	p= 0.255	p= **0.012**	p= 0.785	p= **0.001**	p= 0.551	p= 0.566	p = 0.524	p = 0.494

Note: Boldface represent statistically significant *p*-values of the correlation coefficient as determined by Pearson correlation test. *r* represents Pearson moment correlation coefficient (-1≤1.0). **Key**:- Temp: Temperature; Cond: Conductivity; TSS: Total suspended solids; DO: Dissolved oxygen; Turb: Turbidity; TN: Total nitrogen; TP: Total phosphorus.

4.4.2 Concentration of the DDT metabolites in the muscle tissue of fish from the wastewater

The spatial mean (± SE) concentrations of DDT and its metabolites in the muscle tissue of *O. niloticus* from the wastewater sampling stations are shown in Figure 4.35. The mean concentration levels recorded the highest levels of 43.246 ±1.482 μgKg^{-1} (*p,p'*-DDE) (station H) and the lowest (7.370 ±1.173 μgKg^{-1}) were of *p,p'*-DDT, at station A (Figure 4.35). Metabolite *p,p'*-DDD residue levels in both stations A and H were all above the detection limit. The highest *p,p'*-DDT concentration was detected at station H (28.484 ±7.496 μgKg^{-1}) and had all its concentrations above 1.0 μgKg^{-1}. Except for station H, *p,p'*-DDT metabolite exhibited the highest residue levels in wastewater samples that were > 10 μgKg^{-1} (Figure 4.35) in both sampled stations, followed by *p,p'*-DDD and *p,p'*-DDE metabolites, in that order. A one-way analysis of variance (ANOVA) test showed that mean *p,p'*-DDE concentration in wastewater lagoons *O. niloticus* fish tissue was statistically significant among the sampling stations ($p < 0.05$; $F = 6.239$; $p = 0.018$) at the 95% confidence level. Tukey's *post hoc* test for separation

of means revealed that mean *p,p'*-DDE concentration varied significantly between sampling stations E and G. Overall, results above show that mean pesticides contaminant levels observed differed spatially within the wastewater lagoons sampling stations (Figure 4.35). Analysis of variance (ANOVA) statistical test showed the mean *p,p'*-DDT concentration in wastewater lagoons fish samples to be statistically and significantly different between the sampling stations ($p < 0.05$; F = 8.385; $p = 0.0016$) at the 95% confidence level. Tukey's *post hoc* test for separation of means revealed that mean *p,p'*-DDT residue level at station A varied significantly from those at sampling station H.

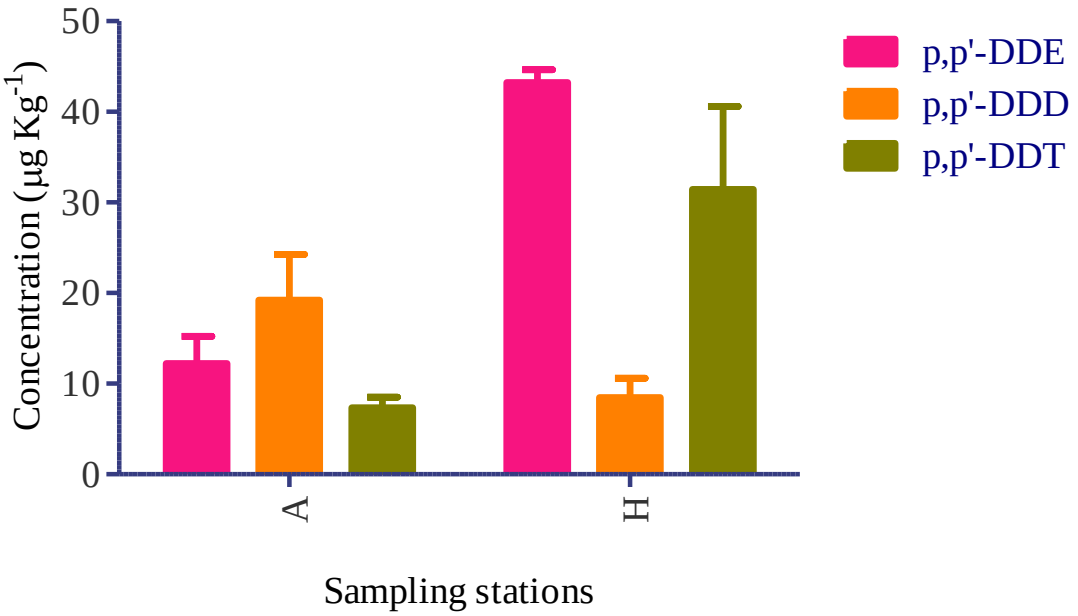

Figure 4.35: **Spatial mean (± SE) distributions of the DDT metabolites in the muscle tissue of *O. niloticus* from the wastewater.**

Figure 4.36 represents the temporal mean (± SE) disributions of DDT metabolites during the wet and dry seasons. The study showed that metabolite *p,p'*-DDD exhibited high mean concentrations during the wet season, followed by *p,p'*-DDT contaminant residue. The temporal mean concentrations ranged between 9.647 ±1.853 µgKg^{-1} (*p,p'*-DDE) to 31.821 ±6.950 µgKg^{-1} (*p,p'*-DDD) during the wet season, whereas the dry season mean residue levels

were lower and ranged between 0.265 ±0.031 µgKg^{-1} (*p,p'*-DDE) to 0.932 ±0.254 µgKg^{-1} (*p,p'*-DDE). The independent sample *T*-test showed that mean *p,p'*-DDE concentration was statistically and significantly different between the wet and dry seasons ($p < 0.05$; t = 1.630; $p = 0.003$). The variations showed that the *p,p'*-DDD residues were higher than the *p,p'*-DDE residue indicating (lowest DDT metabolite) concentrations during the study period. The results of the temporal concentrations of DDT metabolite in fish confirms the residues detected in wastewater (µg Kg^{-1}) in both wet and dry seasons. The temporal distribution of mean DDT and its metabolites in the muscle tissue of *O. niloticus* that inhabit wastewater lagoons areas revealed varied concentrations between the two sampling stations. The independent sample *T*-test showed that the mean *p,p'*-DDT concentration were statistically significant between the wet and dry seasons ($p < 0.05$; t = 4.729; $p = 0.016$), at the 95% confidence level (Figure 4.36).

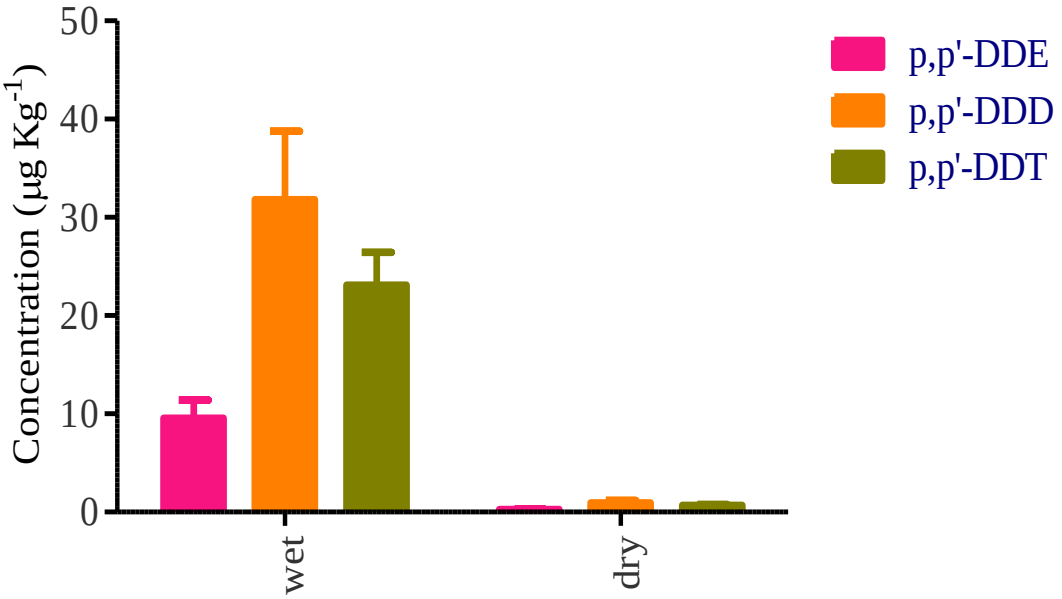

Figure 4.36: **Temporal mean (± SE) distributions of the DDT metabolites in the muscle tissue of *O. niloticus* from the wastewater.**

CHAPTER FIVE

DISCUSSION

The study revealed and identified a total of seventeen different organochlorine pesticides (OCPs) in the order of hexachlorocyclohexanes and its isomers, dichlorodiphenyltrichloroethanes and its metabolites as well as cyclodienes in the order as enumerated: α-HCH, β-HCH, γ-HCH, δ-HCH, *p,p*-DDD, *p,p*-DDE, *p,p*-DDT, aldrin, endrin, dieldrin, endrin aldehyde, endosulfan I, endosulfan II, endosulfan sulfate, heptachlor, heptachlor epoxide, and methoxychlor, in both water, sediment and fish samples over the study period. Variations were observed in pesticides results obtained in that some organochlorine pesticide residue levels were below recommended standards while others indicated values that exceeded existing threshold levels of NEMA and WHO/US EPA thereby, giving an indication that local input of these contaminants within River Kuja watershed existed. Past studies targeting organochlorine pesticides have revealed existence of these OCPs in given catchment and lacustrine areas within Lake Victoria Basin. Madadi et al. (2005), Musa et al. (2009) and Abongo et al. (2014) carried out studies in selected sampling stations of river Sio, Nzoia and Nyando river basins. Further scrutiny of overall isomer results indicate that concentration levels of lindane in the study area were higher than the WHO guidelines (Appendix 4) of 2.0 μgKg^{-1} for daily intake of drinking water and could pose human health challenges if consumed over a considerable length of time.

Both of these investigations revealed existence of HCHs, DDTs and cyclodienes pesticides in different matrices such as water, sediment and in fish. HCH and DDTs pesticides results obtained by Madadi et al. (2005) showed that they were below WHO and NEMA thresholds except some cyclodienes such as aldrin and its oxidized compound dieldrin which were above World Health Organization recommended standards of 0.25 μgL^{-1} in natural water. In addition, investigations by Abon'go et al. (2014) indicated that although HCH values were between below detection limit (BDL) to 3.97 ±0.117 μgL^{-1}, DDT metabolite residues in some sampled

stations were above NEMA and WHO guidelines of 2.0 μgL^{-1} in natural water. This study also indicated cylodiene residues of aldrin, dieldrin, endosulfans, and lindane were all above WHO, US EPA and NEMA recommended standards in water, as the residues were observed to be at 0.97 ±0.106 μgL^{-1} contaminant level. However, spatial and temporal results from this study showed cyclodienes such as heptachlor, aldrin, heptachlor epoxide, endrin, endosulfan II and methoxychlor that were below detection limit (BDL) values, indicative that not all samples analysed contained cyclodienes that were above accepted thresholds in water. For instance, endosulfan I had mean concentrations that were above detection limit in all sampling stations, indicating previous and recent use of the banned pesticides in the sampled area. Mean spatial results from this study on DDTs showed values that were BDL to 0.092 ±0.001 μgL^{-1}, lower than WHO thresholds but overall mean residue value was higher than NEMA recommended standards of 2.0 μgL^{-1} in natural water. In addition, mean HCH pesticides residue levels in wastewater was 3.604 μgKg^{-1} in the wet season. Additionally, this study revealed overall mean residue values for HCHs to be between BDL to 0.571 ±0.62 μgL^{-1} and noted to be below NEMA and WHO of 2.0 μgL^{-1} in sampled water. Additionally, residues analysed in this study indicated cyclodiene pesticides such as aldrin residues were above WHO but dieldrin, an oxidized form of aldrin, was within recommended standards. Temporal HCH average levels detected for α-HCH, β-HCH, δ-HCH, and γ-HCH isomers in *O. niloticus* fish samples in the study area residue variations observed could probably be due to time of use of these pollutants in the area or transportation from other areas or by atmospheric deposition within the vicinity, either by air or by running water as run-offs during rainy spells (Pfeuffer, 2008). However, except for a few sampling stations investigated, the levels obtained were lower than WHO and EPA standards in bottom sediments of 2.0 μgL^{-1} and 5.0 μgKg^{-1} in water and sediment as well as fish (IUPAC, 2003; Kristensen et al., 2018).

These results could mean that some sampled stations had recent application of aldrin in farms, agro-industrial and for domestic use, while others had previous applications. This is due to the fact that dieldrin is a metabolized form of aldrin which has been broken down in the environment over time, after being applied to control occurrence of harmful insects in domestic, agricultural and industrial set-ups. Prolonged exposure of aldrin leads to bioaccumulation by both plants and animals such that it can be found in aquatic plants and in fats of organisms as it is known to be lipophilic. Identification and occurrence of these OCP compounds in the study area therefore show that River Kuja watershed has had its fair share of these toxic organic contaminants availability, probably due to agricultural, industrial or public health requirements.

DDT pesticide and its metabolite concentrations in fish ponds was lower (BDL to 0.550 ±0.031 μgL^{-1}) though higher in wastewater lagoons samples which indicated a higher residue mean of 3.368 ±0.246 μgL^{-1}. Analysed fish ponds sediment samples indicated higher DDT residue range of between 0.491 to 13.558 ±0.721 μgKg^{-1} as compared to BDL to 2.987 ±0.786 μgKg^{-1} in analysed fish samples in the study period. However, further analysis showed that the concentrations were well below the recommended value of 2.0 μgL^{-1} and 1.0 μgL^{-1} for WHO and NEMA in natural water, respectively. However, this was not the case in sediment and fish as results show higher values implying that prolonged exposure would be of public health concern.

Furthermore, high concentrations of DDT and its metabolites in natural water samples in the study area is considered crucial and of significance than in the sediments due to the fact that water is an important resource and its availability for use by humans and fish although in this study the concentrations were below the recommended limit by WHO compared to sediments which were higher than the existing global thresholds. The presence of this pesticide in the sediment environment despite the fact it had been banned from use decades ago is probably

due to previous uses in the catchment (Mbabazi, 1998). Cases of DDT use have been reported previously in vector-borne diseases' control within the Lake Victoria Basin, hence River Kuja watershed study area; and it is known to survive in soils and air up to 30 years, hence thunderstorms and rains could cause residual DDT to be carried as flush floods, ending up in the lacustrine ecosystems (Musa et al., 2011) in the target area. A study carried out by Murty (1986) revealed that the degradation of DDT and mirex in exposed fish was very slow compared to other pesticides and that there was very little excretion of the pesticide via urine and gills even after 48 hours of exposure. Additionally, this may pose serious public health and environmental health risk.

Methoxychlor organic pesticide residues showed consistent high values in fish and sediment. It had the highest overall mean in water samples with 1.69 ±001 μgL^{-1} and a residue mean concentration of 24.67 ±2.751 μgKg^{-1} in sediment samples in the period of study. Investigations by this study showed overall methoxychlor mean value of 1.642 ±0.106 μgL^{-1} in water and 13.470 ±6.757 μgKg^{-1} in fish. These residues observed are lower than WHO and NEMA global standards of 20.0 μgKg^{-1} in fish and sediment. This indicates that either methoxychlor is still being used on crops, livestock, and in animal feed or carried downstream via runoff. According to a 2002 report by the Agency for Toxic Substances and Disease Registry (ATSDR), once methoxychlor is deposited in the ground after its application on forests, food crops and animals, it adheres strongly to the soil particles. These soil particles are either blown by the wind or carried downstream as runoff, thereafter (ATSDR, 2002).

Detection of pesticides such as methoxychlor, endosulphan, heptachlor, endrin and DDT and which had been banned globally and locally, continue to pose serious risks to public health in the study area as results from this investigation unveils their presence, even after two to three decades after use. According to studies by Getenga et al. (2004) and Osoro et al. (2016) in an investigation on impacts of pesticides on human health and environment in the River Nzoia

catchment and Rusinga Island in Lake Victoria, pesticides were responsible for the development of symptoms of ill health where several farmers fell ill after exposure to these pesticides although the authors could not point to any specific pesticide (NCLR, 2013). For example, pesticides such as heptachlor have been reported to be highly toxic to humans causing hyperexcitation of the central nervous system and harm to the liver (Omwenga et al., 2016).

Spatial and temporal distributions of heptachlor and its oxidized compound heptachlor epoxide indicated various residue levels in water, sediment and fish in the study area, with statistically insignificant ($p > 0.05$) differences. Heptachlor and its degradation product heptachlor epoxide residue in fish ponds in the dry season was 0.194 ±0.076 μgL^{-1} concentration and the relationship was observed to be statistically significant. This mean residue value observed is below European Protection Agency (EPA), IUPAC (2003) recommended thresholds in water. However, the vresidue levels were above in analysed fish ponds sediment samples. In fish ponds sediment, the residue value in the dry season was higher (18.47 ±5.382 μgKg^{-1}) while that of its sister dissipated compound heptachlor epoxide was lower, at 1.918 ±0.978 μgL^{-1} in fish ponds sediment in the wet season. Heptachlor and heptachlor epoxide residue in river water downstream within River Kuja watershed was between 0.233 to 1.244 ±0.031 μL^{-1} in river water. Therefore, this cyclodiene pesticide residue varied consistently over the study period.

These concentrations in fish ponds sediment were above the WHO and NEMA recommended value of 0.03 μgL^{-1} for both heptachlor and heptachlor oxide. The presence of heptachlor and its degradation product is an indication that heptachlor has been used in the area in recent times and is still currently in use. The higher concentration of heptachlor oxide than heptachlor in other matrices and study shows that the rate of application was higher in the past than it is currently (Abong'o, 2018). Heptachlor residues were detected probably due to its application as a household insecticide, termite control agent as well as an herbicide, in agricultural settings whereby it ended up being transported downstream as run-off. These levels should be of

concern since heptachlor and heptachlor oxide have been reported by ATSDR to accumulate in fish, livestock and the body fat of humans and could still be detected up to three years after exposure (ATSDR, 2002). These concentrations were well above the WHO recommended limit of 0.6 μgL^{-1} for drinking water more so for the sediments. There is need to ensure continuous monitoring since endrin can persist in the soil for more than a decade, and exposure to it causes severe harmful health effects such as central nervous system injury and death (ATSDR, 1996; Shepherd et al., 2000).

According to Abongo *et al*. (2014), the main sources of organochlorine pesticide residues in Lake Victoria Basin catchments are mainly due to agricultural activities and public health vector control. The study revealed that high levels of pesticide residues detected in the sediments during the period under assessment occurred during the wet season and this was attributed to, probably, runoffs from farms where the pesticides were previously applied. In addition, the study revealed no organophosphates detected in any of the water and sediment samples (Shepherd et al., 2000), except for *p,p'*- DDD which was identified at all sampling stations over the five-year span. DDTs results showed a markedly higher concentration followed by cyclodienes and the least was HCHs.

Endosulfan sulfate residues in analysed fish ponds was (0.178 ±0.002 μgL^{-1}), followed by (8.715 ±2.817 μgKg^{-1}) residue level in sediment sample (0.186 ±0.051 μgKg^{-1}) in river fish and (1.063 ±0.978 μgKg^{-1}) in wastewater fish. Overall, endosulfan sulfate was lower in the water samples and fish but higher in the sediment samples within the study period. WHO and NEMA have no guideline value for endosulfan sulfate since its occurrence in drinking water is usually at concentrations that don't arouse health concerns. However, its environmental impact on other organisms should be taken into consideration. Studies have shown endosulfan sulfate to be persistent and toxic to non-targeted organisms such as fish and should therefore be of environmental concern.

The results from this study indicate that higher Organochlorine pesticide (OC) residual values were recorded in bottom sediments than in the water samples, likely due to the hydrophobic nature of the pesticides, hence end up accumulating in the fatty tissues of existing biota such as fish, as well as in bottom sediments (Ndunda et al., 2018). The current study shows that HCH isomers such as lindane (γ-HCH) residue levels analysed recorded lower values in both wet and dry seasons (0.571 ±0.737). These results are lower than those obtained by Getenga et al. (2004) who recorded a slightly higher residue level of 1.294 μgL^{-1} in natural (river) water but results by Osoro et al. (2016) indicated a slightly lower value of 0.52 ±0.01 μgL^{-1}, especially by lindane HCH isomer in natural water.

Although there occurs disparities in both results, the organochlorine residue levels are lower than exisiting WHO/FAO maximum acceptable limits in natural water of 2.0 μgL^{-1} (IUPAC, 2003; Kristensen et al., 2018) and the benchmark set by NEMA (GoK, 2006) hence not toxic or harzadous to both humans and environment. In river water sediment samples, the concentrations of *α*-HCH and *δ*-HCH were generally higher compared to that of β and *γ*-HCH isomers, when both wet and dry seasons results were compared. Hydrophilic pesticides tend to be pushed out of water to the sediments making their concentrations decrease rapidly in water column, hence, sediments act as sinks for these pollutants and do release to water the same pesticides back in order to keep the equilibrium balance (Linde, 1994; Abong'o et al., 2014).

Previous studies have shown that concentrations of these compounds are of great concern especially if exposure is over a long period (FAO/WHO, 2006; Njogu et al., 2010; Osoro et al., 2016). This study show OCPs residue concentrations in water samples estimated at 0.002 to 0.332 ±0.073 and 0.009 to 0.032 ±0.0009 μgL^{-1}, respectively,. These results are lower than what WHO/FAO as prescribed as benchmarking for the drinking water (IUPAC, 2003; Kristensen et al., 2018). The result configures with Madadi et al. (2005) who obtained lower results than the World Health Organisation recommended in drinking water.

The average pesticide residual levels obtained during the dry season in the month of (January-March) and in the rainy season in (August-October) indicate strong variability and distribution in the two seasons than those reported in other areas like in the marine set up (Wandiga et al., 2005) and those carried out by Getenga et al. (2004) along river Nzoia basin whose results indicated that OCPs identified in water samples during the period of short rain season, usually in the month of October-November, ranged from BDL to 4.08±0.00 μgL^{-1}. The study by the latter attributed the observed variations to seasonality and probably, recent use of pesiticides in the study area, in an effort to control pests in existing sugarcane farms (Mogere, 2000; Shepherd et al., 2000). In addition, this study indicates that DDTs have approximately higher mean concentrations followed by that of cyclodienes and least, that of the HCHs in the sequence DDTs > cyclodienes > HCHs, respectively. These results show seasonal similarity to that of Wandiga et al. (2002) in the estuarine waters of River Athi and those of Abong'o et al. (2014) which discussed OC levels in dry and short rain seasons' results from the Kavirondo Gulf of Lake Victoria. However, studies by Abong'o et al. (2014) indicates that among DDT metabolites, only *p,p'*-DDD mean results were lower than WHO benchmark whereas those of *p,p'*-DDT and *p,p'*-DDE were above WHO and NEMA maximum acceptable standards in water (BDL to 3.97±0.258 and BDL to 7.16±0.012 μgL^{-1}), respectively. The above maximum acceptable standards results were attributed to previous use of pesticides in the lake basin area to control pests, additionally, due to availability of cheaper herbicides and fungicides in the local market. Overall, these concentrations are fairly low in river waters. These low levels of DDT and its metabolites in some sampling stations could be due to its restricted use by the government for its use only in public health sector.

Mean DDT level concentrations were in the decreasing order: *p,p'*-DDD > *p,p'*-DDT > *p,p'*-DDE, for water samples collected during this study with an overall mean of 0.05 μgL^{-1}. The high overall mean concentration of *p,p'*-DDT observed (1.9 ±0.42) μgKg^{-1} in sediments from

upstream River Kuja catchment compared to the other DDT metabolites suggests an indication of recent usage of DDT in the study area and possibility of sediments acting as pollutant sinks. According to Linde (1994) pesticides that are non-polar are slowly released into available conditions such as sediments hence, are easily observable in such aquatic environments as organic pollutant sinks for release into immediate surroundings once a natural vacuum occurs. As long as more pollutants enter the aquatic system, continuous accumulation may occur hence polluting such natural environment needing immediate attention.

The other probable reason could be that the lipophilic power of pesticides is enhanced in dry season and residue dilution balance from biota and bed sediments in natural water ecosystems could trigger the observed concentration differences in both seasons in the study area. The high mean concentrations at various sampled stations show that there is probably recent application of the compounds in the area due to probably active agricultural or other anthropogenic activities in River Kuja watershed.

Results obtained for sediments in this study are lower than WHO/FAO of 5.2 μgKg^{-1} maximum acceptable thresholds when compared with those of Musa et al. (2011) in River Yala/Nzoia catchment showing residual values of 0.05 to 59.01 μgKg^{-1} and BDL-24.54 μgKg^{-1} in wet and dry seasons, respectively. Some of the Organochlorine pesticides detected in the sediments, such as heptachlor, DDT, DDE, and endosulfan are known to have endocrine and estrogenic disrupting properties (Howard, 2001; Aktar et al., 2009), which may greatly impact on the biodiversity of the fragile aquatic ecosystem. The presence of DDT and some of its degradation residues in investigated matrices and in HCH isomers such as lindane (γ-HCH) can be traced in Kenya and in the region as they have previously been in use for Public Health concerns such as in eradication of tse-tse fly, malaria and control of termites in construction industry before their banning in 1986 (PCPB, 2009; NCLR, 2013). The hydrophobic and hydrophilic nature of the OCPs enable their slow and easy accumulation in the environment, hence making them

easy to be dissolved by the surface water down into water sources downstream (Klumpp et al., 2002; LVBC, 2011; Nyaundi et al., 2019).

Most of these chemical compounds have been banned (NCLR, 2013) from use, but the findings from the study shows they are still in our environment due, to probably, utilisation in River Kuja catchment (Mbabazi, 1998; Ndunda et al., 2018). The cyclodiene compounds detected like endosulfan has an environmental importance as it persist and remain toxic to many non-target creatures like fish (Getenga et al., 2004; Omwenga et al., 2016) on the other hand heptachlor is an insecticide that is commonly used to kill termites in homes. The results indicated that, the concentrations of most of the organochlorine compounds that were analysed were below the acceptable maximum concentration of 0.1, 2.0 μgL^{-1} and 5.2 μgKg^{-1} value set by the WHO/FAO, NEMA and the European Union (IUPAC, 2003; Kristensen et al., 2018).

This study also noted that the levels of γ-HCH in Nile tilapia (*O. niloticus*) fish investigated was found to be higher during wet season than in the dry season. This could probably be due to large amounts of runoffs experienced in wet season offloading organic contaminants into the water column in the catchment at higher rates than during the dry season. Secondly, due to topographical set-up of the local area, most fish ponds in study area were located at river valleys, hence easily receive rain water from nearby coffee, tea, banana, horticultural and similar agro-chemical establishments as run-offs. Results in this study is in congruent with studies done by Ezemonye et al. (2015) whereby OCPs in riverine *Tilapia zilli* from Ogbesse river, Nigeria, were investigated and mean residues levels were between 0.02–1.73 μgKg^{-1} with β-HCH isomer having the highest mean level (1.73 μgKg^{-1}) though pesticide levels were noted to be highest in mud fish, *Clarias gariepinus* (2.3 μgKg^{-1}). The study by Ezemonye et al. (2015) also noted that average pesticide residue levels increased during the rainy season.

Over the study period, organochlorine pesticide residue were assessed on how they correlated with water quality parameters over wet and dry seasons. Results indicated both negative and

positive correlation relationships in water column and were either significantly different or insignificant, as observed over the sampling period. For instance, DDT metabolites indicated strong positive correlation towards total suspended solids (TSS) and *p,p'*-DDD also had a strong positive colleration with total phosphorus in wet season. Similarly, strong positive correlations were observed between *p,p'*-DDD metabolite and total suspended solids (TSS) and the relationship was statistically significant but showed a weak negative correlation to conductivity, temperature and total nitrogen (TN) in the dry season. The study alluded these differences to deterioration of water quality in the sampled areas, possibly due to human activities in the riparian areas which in indirectly, affect the aquatic environment downstream. A study by Kithiia & Ongwenyi (1997) looked into some problems of water quality degradation in the Nairobi river, with some special focus on land-use practices related to riparian human activities on water quality status in the river. The study further showed that excessive nutrient levels in the aquatic zone affected water conductivity, reduced dissolved oxygen (DO) levels in water, reduced pH and low redox potential but increased nutrients such as total nitrogen and total phosphorus in water. This study also indicated organochlorine pesticides showed strong positive correlations towards dissolved oxygen and pH and negatively correlated to other measured water quality parameters in both seasons within the study perod. This study therefore drew conclusions that nutrient levels in water could affect organic pollutant absorption in water, which may indirectly induce metabolic processes in the trophic levels of aquatic organisms hence different bioaccumulation quantities, hence harmful effect to human and environmental health. All negative correlations of the measured DDT metabolites with physico-chemical parameters were not statistically significant. Strong positive correlations were observed between HCH isomers against water quality parameters. The relationship between δ-HCH against total phosphorus was significantly different, at $p < 0.05$. In addition, HCH isomers depicted negative correlations.

For instance, δ-HCH was negatively correlated with temperature (r =-0.889; p =0.002) and the relationship was significantly different ($p < 0.05$); α-HCH was negatively correlated with dissolved oxygen whereas α-HCH depicted a negative correlation with conductivity and dissolved oxygen.

During the dry season, all positive correlations of the DDT metabolites with physico-chemical parameters were not significant (Table 4.7), this was contrary to the wet season when all the three metabolites had strong positive correlations with physico-chemical parameters. *p,p'*-DDD and *p,p'*-DDT metabolites showed strong negative correlation with total phosphorus (TP) (r = -0. 722; p = 0.043) and total nitrogen (TN) (r = -0.932; p = 0.001) and the relationship was statistically significant ($p < 0.05$). The positive correlation value of 0.422 was highest followed by 0.476 (station B) and the lowest positive coreration value was 0.001.

Strong positive correlations (Table 4.10) was obtained for cyclodiene pesticides concentrations against water quality parameters at various sampling stations during wet season. Endosulfan II compound was strongly positively correlated to turbidity (r = 0.915; p = 0.03), total phosphorus (r = 0.782; p = 0.025), total suspended solids (0.655; p = 0.044) in wet months and was noted to be statistically significant as well. In addition, endosulfan sulfate indicated a strong positive correlation with pH levels in the wet season and was statistically significant (r = 0.883; p = 0.032). Though relationships were statistically significant ($p < 0.05$), heptachlor compound showed a negative correlation with all measured water quality parameters. This correlation was observed to be with temperature and TSS in wet season only (r = -0 .738, p = 0.03; r = -0.905, p = 0.034), respectively. In dry season, heptachlor was positively correlated towards TSS (r = 0.655, p = 0.022), TP (r = 0.782, p = 0.033) and towards turbidity (r = 0.915, p = 0.03) and the relationship was statistically significant. Heptachlor epoxide and endrin aldehyde were positively correlated with pH (r = 0.883, p = 0.05) and (r = 0.806, p = 0.016) and attachment stastically significant, in the dry season respectively (Table 4.10). In comparison, heptachlor

epoxide was negatively correlated against temperature ($r = -0.257$, $p = 0.539$) and towards conductivity ($r = -0.059$, $p = 0.889$) while endrin aldehyde was noted as negatively correlated towards turbidity and dissolved oxygen (DO), ($r = -0.199$, $p = 0.637$) in the dry season.

CHAPTER SIX

CONCLUSIONS

The spatial distribution of the concentrations of OCPs residual values in Upper River Kuja watershed during wet and dry seasons indicated some noticeable trends which led to the following conclusions:

1) The study demonstrates that OCPs are found in water, fish and the other sediment in the sampled area of study. The metabolite with the widest distribution range during the wet season was *p,p'*-DDT, while the metabolite with the narrowest distribution range was *p,p'*-DDD. The spatial distribution of the concentrations of the DDT metabolites was much wider and had higher concentrations in the season of lower rainfall (dry season) than during the season that receives more/high rains. Occurrence of these organochlorine pesticides indicates recent use of these pollutants in River Kuja and its catchment area.
2) Values of DDTs, HCHs and those of cyclodienes in sediment samples, detected during the study period were below the World Health Organization (WHO)/FAO maximum recommended thresholds of 5.28 and 2.37 μgKg^{-1}.
3) Though the residue concentrations of the metabolites was fairly well distributed, the mean levels in dry season, especially of the metabolite *p,p'*-DDT were slightly higher in dry season than those recorded in the wet season, this could be due to reduced water levels and its reduced mixing strengths.
4) Overall, the concentrations of all the DDT metabolites were below WHO maximum acceptable standards of 2.0 μgL^{-1} and below NEMA locally maximum acceptable thresholds in natural drinking water (1.5 μgL^{-1}). However, some sampling stations recorded scores above EPA (0.2 μgL^{-1}) and WHO maximum acceptable standards (IUPAC, 2003; Kristensen et al., 2018).

5) In addition, existing semi-intensive agricultural practices in the study area could be a major source of the metabolite residues noted. This study therefore reveals that although organochlorine pesticides were banned several decades now, save for public health purposes, they actually exist in our local natural environment.
6) However, results implore the fact that pesticide contamination in water and sediments exist in River Kuja drainage basin, indicating that anthropogenic activities such as urbanization, industrial and agricultural practices could be contributing to the incidences of residue levels observed in this study.
7) The positive correlations (*r*) during the wet season were not statistically significant in target sampled stations, except during the dry season which recorded higher positive correlations with water quality parameters. In addition, it was generally observed that correlations were generally stronger during the period of lower rainfall than in the period of high rainfall.

6.1 Recommendations

1) There should be heightened monitoring and surveillance to identify the sources of some banned organochlorine pesticides such as DDT, lindane and cyclodienes such as endrin and endosulfans that are currently being phased out due to its toxicity to humans and wildlife.
2) Although results obtained indicate that mean values and residual ranges found in water and fish were below the FAO/WHO and NEMA maximum acceptable benchmarks in fish and sea food, enhanced monitoring, compliance and surveillance of the pesticides is recommended to detect any variations in natural water and in biota.
3) Existing natural water require treatment before drinking such as use of reverse osmosis and charcoal filters to improve on minimizing pesticide residual revels in some sampling stations such as next to urban and active intensive farming areas where

significant levels were observed. These methds are also recommended to act as on-site treatment for domestic and industrial effluents before release into rivers and lakes.

4) Regular review of best management practices need to be in place nationally in order to keep improving wastewaters treatment before discharge into the water courses to get rid of the pesticides, organochlorine and other pollutants. This includes strict and regular monitoring, policy enforcement and combating climate change challenges. Future wastewater design and placements may need to have longer rotational tertiary section lagoons, especially in urban biological treatment systems, before discharge. Furthermore, to enhance wastewater treatments in urban areas can be improved by carrying out on-site (treatment at source) before being released to the collective lagoons which eventually empty it to rivers, lakes or into sea. Secondly, use of renewable energy should be encouraged whereby the facultative systems can be enhanced to improve on both mechanical and biological treatments.
5) Effluent and wastewater discharges points in samples town should be treated further by use of active facultative mechanisms and to allow more resident time before discharge, and be monitored regularly to determine efficiency and correction of both intake and outflow of the lagoon's outflow as a critical measure to detect compliance of correct water quality WHO/FAO and NEMA regulations.

6.2 Areas for further research

More research should be conducted on:

i) How pesticides and nutrient concentrations affect water and fish in the Lake Victoria Basin

ii) Study of toxic pollutants concentrations in fish eating birds

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APPENDICES

Appendix I: **Mean monthly rainfall readings/patterns for Kisii/Nyamira Counties over five-year period (2011 - 2015)**

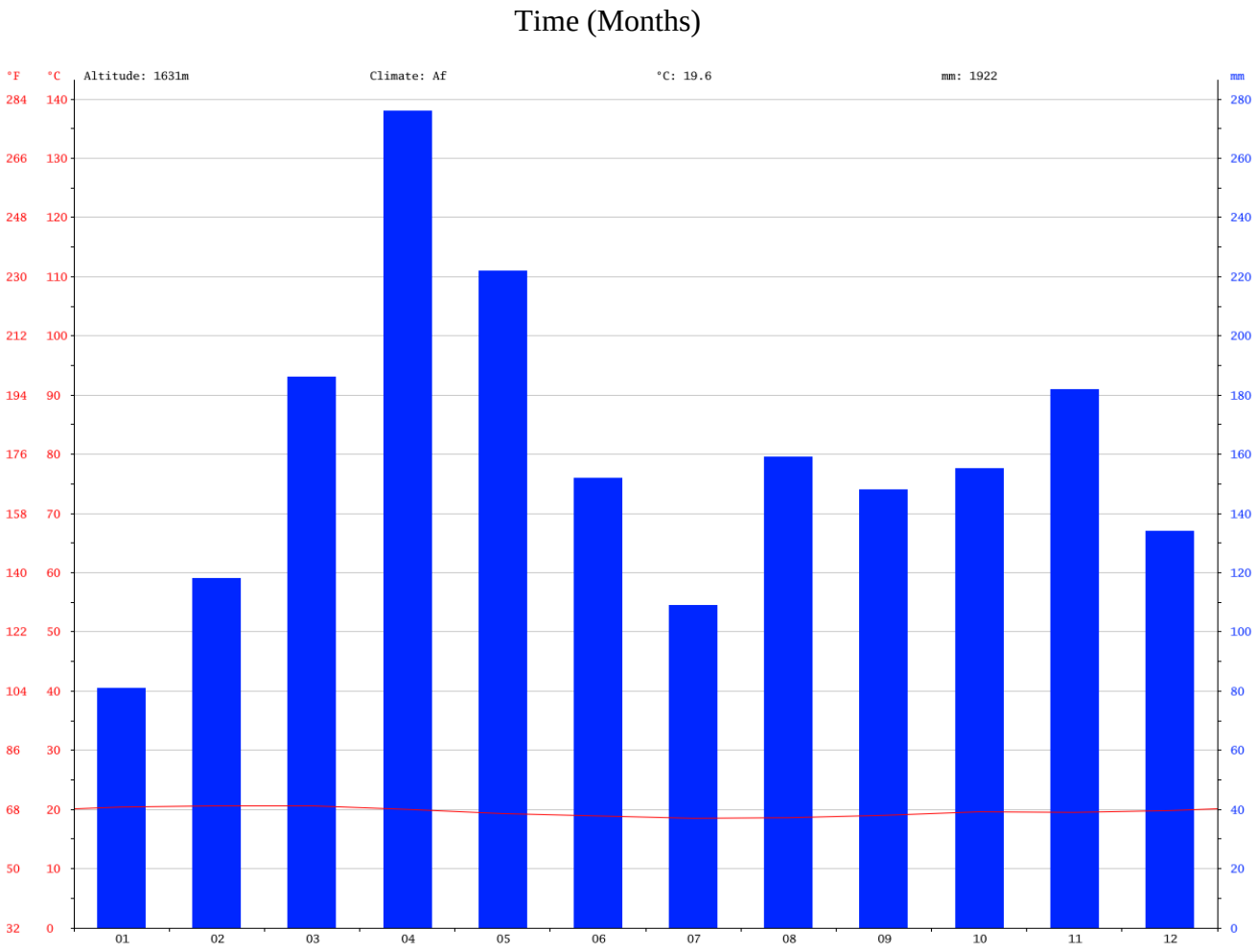

Figure: Mean monthly rainfall readings/patterns for Kisii/Nyamira Counties over five-year period (2011 - 2015). Source: climate-data.org

Appendix II: **Pesticide level guidelines (µg L−1) for drinking water for some organisations; FAO, US EPA and WHO maximum acceptable levels (thresholds) HCHs concentrations in drinking water.**

Pesticide	WHO	EPA	Australia
Aldrin	0.03	NC	0.01
Dieldrin	0.03	NC	NC
DDT	2	0.2	0.06
Lindane	2	0.2	0.05
Methoxychlor	20	40	0.02
Endrin	NC	2	NC
Heptachlor	0.03	0.4	0.05
Heptachlor Epoxide	0.03	0.2	0.05
Endosulfan	NC	NC	0.05

Source: IUPAC 2003, NC = Not classified.

Appendix III: **Banned and Restricted Pesticides in Kenya**.

Source: Pests Control & Products Board (PCPB, Version I, 2014)

Common Name	**Former Use**
All isomers of HCH	Insecticide
Chlordane	Insecticide
Parathion	Insecticide
Heptachlor	Insecticide
Dibromochloropropene (DBCP)	Soil fumigant
Ethylene dibromide (EDB)	Soil fumigant
Phenoxy Herbicide	Herbicide
Toxaphene	Acaricide
Captafol	Fungicide
Chlordeform	Acaricide/Insecticide
Heptachlor	Insecticide

Source: Pests Control & Products Board (PCPB, 2012).

Appendix IV: **Quantities of imported pesticides into Kenya (Tonnes)**.

Year	Insecticides/ Acaricides	Herbicides	Fungicides	Others	Total
2009/2010	3.181	1.84	2.415	1.396	8.832
2008/9	2.995	2.933	2.34	1.413	9.681
2007/8	2.887	2.29	2.65	1.33	9.157
2006	2.48	1.86	3.19	1.23	8.749
2005	2.84	1.31	2.36	1.19	7.709
2004	2.89	1.54	2.031	597	7.049
2003	2.67	1.39	1.68	421	6.44
2002	2.75	1.51	2.14	723	6.83
2001	2.32	1.396	1.779	434	361
2000	1.76	633	1.665.9	154	565
1999	2.189	593	2.29	1.116	4.431.9
1998	1.841.4	1.407.8	4.225.4	370	6.179
1997	2.077.8	703	2.39	1.59	7.606
1996	1.876.2	649.5	732.1	656	5.827.5
1995	1.413	997.7	3469	602	6.946.4

Source: Pests Control & Products Board (PCPB, 2012).

Appendix V: **Volume and value of Pesticides imported into Kenya for Agricultural or other Public Health Use, from 2007 – 2010**.

Figure: Volume and value of Pesticides imported from 2006/2007 to 2009/2010 in Kenya
(Source: PCPB Annual report 2009/2010)

Source: Pests Control & Products Board (PCPB, 2012).

Appendix VI: **Volume and value of Pesticides imported into Kenya for Agricultural or other Public Health Uses, from 2007 – 2012**.

Pesticides Use	**2006/2007**	**2007/2008**	**2008/2009**	**2009/2012**
Insecticides Quantity (Tons)	2.475	2.887	2.995	3.181
Insecticides value (Ksh m)	1.181	3.909	2.079	2.493
Fungicides Quantity (Tons)	3.19	2.651	2.34	2.415
Fungicides value (Ksh m)	1.251	0.602	3.153	3.874
Herbicides Quantity (Tons)	1.859	2.289	2.933	1.84
Herbicides value (Ksh m)	0.324	0.206	0.944	0.939
Others Quantity (Tons)	1.225	1.33	1.413	1.396
Others value (Ksh m)	0.362	0.191	1.167	0.918
Total Quantity (Tons)	8.749	9.157	9.681	8.832
Total value (Ksh m)	3.443	4.908	7.343	8.232

Source: Pests Control & Products Board (PCPB, 2012).

Appendix VII: **General levels of Pesticide usage in Kisii/Nyamira Counties.**

Need/Enterprise	**% Coverage**	**Annual Pesticides usage, weight (kg)**		
		Fungicides	**Acaricides/Insecti**	**Herbicides**
Tea	60	Ridomil, Dithane Marshall, Copper spray, M45,	Chlorpyrifos, Karate, Diazinon	Roundup
French Beans	45	Hexythiazox/ Azoxystrobin		
Coffee	70	Triadimefon/ Copper Oxychloride		Metribuzin
Maize	50	Azoxystrobin	Chlorpyrifos/ Imidacloprid	
Fruits	70		Abamectin 20	
Beans	80	Hexaconazole		Fluroxypyr
Passion	60		Buprofezin	
Horticultural cr	75	Propineb 70% / Mancozeb	Diazinon/Doom	Roundup
Bananas	45	Milraz	Karate	Roundup
Cattle	70		Triatix, Delnav	
Tomatoes	80	Dimethoate		Metribuzin
Vegetables	65	Triadimefon		

Source: Pests Control & Products Board (PCPB, Version I, 2014).

Appendix VIII: **Mean ± physico-chemical parameters from sampled stations (A – H), River Kuja watershed**.

TABLE: Mean ± SE physico - chemical parameters Apr-15

Site/Param	Temp (°C)	Cond (µScm^{-1})	TSS (µgL^{-1})	DO (µgL^{-1})	pH	Turb (NTU)	TP (µgL^{-1})	TN (µgL^{-1})
A.	27.10± 1.09	139.3± 4.12	76.35 ± 1.23	7.65 ± 0.12	7.83± 0.01	125.67± 3.89	0.207±0.02	3.653±0.012
B.	28.13 ± 1.34	77.70 ± 2.45	32.00 ± 1.78	7.01 ± 0.07	7.94± 0.78	61.97± 1.690	0.083±0.01	3.444± .004
C.	28.06 ± 1.81	96.07 ± 1.76	76.54 t 1.93	7.21 ± 0.32	8.08± 0.94	61.90 ± 1.230	0.11±0.011	2.714±0.020
D.	27.73± 0.97	111.23± 1.8	62.67± 1.23	8.24 ± 0.37	8.01± 0.02	79.47± 1.340	0.156±0.06	3.81 ± 0.001
E.	28.07 ± 2.09	103.4± 1.76	61.67± 1.45	7.36± 0.39	8.02± 0.01	102.67 ± 2.39	0.127±0.002	2.922 ± 0.04
F.	27.67 ± 1.45	76.40 ± 1.98	125.50±1.45	7.15 ± 0.78	7.88± 0.09	133.33 ± 2.19	0.146±0.004	2.153 ± 0.01
G.	27.33 ± 1.17	93.57 ± 2.78	193.00±4.35	7.62 ± 0.02	7.93± 0.13	148.67 ± 2.39	0.183±0.003	3.118 ± 0.02
H.	27.3 ± 0.120	81.13 ± 3.65	166.50± 3.21	7.24 -1. 0.02	9.80± 0.32	133.33 ± 1.34	0.225±0.007	2.707±0.004

Key: Temp = Temprature; Cond = Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; pH = Power of Hydrogen; Turb = Turbidity; TP = Total Phosphates; TN = Total Nitrogen

TABLE: Mean ± SE physico - chemical parameters

Jul-15 (b)

Site/Param	Temp (°C)	Cond (μScm^{-1})	TSS (μgL^{-1})	DO (μgL^{-1})	pH	Turb (NTU)	TP (μgL^{-1})	TN (μgL^{-1})
A.	27.73 ±0.99	124.67 ±2.89	240.00 ±1.95	7.13 ±0.01	8.15 ±0.01	160.00 ±0.09	0.21 ±0.01	2.61 ±0.06
B.	27.03 ±0.43	130.37 ±1.78	205.50 ±2.87	6.98 ±0.03	7.94 ±0.01	156.33 ±2.67	0.48 ±0.07	5.03 ±0.05
C.	27.37 ±0.38	126.37 ±1.39	330.50 ±1.56	7.37 ±0.04	7.57 ±0.01	263.33 ±3.12	0.49 ±0.01	5.00 ±0.05
D.	27.21 ±0.21	127.28 ±1.24	334.30 ±2.21	7.21 ±0.03	7.49 ±0.03	268.37 ±1.89	0.50 ±0.06	4.97 ±0.01
E.	26.07 ±0.45	47.40 ±1.43	137.38 ±2.12	7.69 ±0.01	7.41 ±0.01	122.00 ±2.34	0.23 ±0.01	5.00 ±0.01
F.	26.77 ±0.65	110.43 ±1.34	43.00 ±1.98	6.77 ±0.01	7.21 ±0.01	189.40 ±1.78	0.29 ±0.02	3.09 ±0.04
G.	26.87 ±0.45	107.57 ±0.07	214.00 ±1.34	6.24 ±0.02	7.42 ±0.01	187.67 ±1.22	0.33 ±0.04	1.38 ±0.04
H.	27.27 ±0.63	157.40 ±0.95	70.32 ±1.00	7.85 ±0.02	7.69 ±0.03	77.30 ±1.34	0.20 ±0.05	1.92 ±0.02

Key: Temp = Temprature; Cond = Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; pH = Power of Hydrogen; Turb = Turbidity; TP = Total Phosphates; TN = Total Nitrogen

TABLE: Mean ± SE physico chemical parameters May-16 (c)

Site/Param	Temp (°C)	Cond (μScm^{-1})	TSS (μgL^{-1})	DO (μgL^{-1})	pH	Turb (NTU)	TP (μgL^{-1})	TN (μgL^{-1})
A.	27.10 ±0.01	139.30 ±0.01	76.35 ±0.98	7.65 1-0.01	7.83 ±0.02	125.67 ± 2.45	0.21 ±0.01	3.65 ±0.01
B.	28.13 ±0.09	77.70 ±0.016	32.00 ±0.06	7.01 ±0.04	7.94 ±0.06	61.97 ±1.24	0.08 ±0.01	3.44 1-0.01
C.	28.06±0.01	96.07 ±0.01	76.54 ±0.98	7.21 ±0.05	8.08 ±0.07	61.90 ±1.11	0.11 ±0.02	2.71 ±0.03
D.	27.73±0.01	111.23 ±0.01	62.67 ±0.99	8.24 ±0.09	8.45 ±0.02	79.47 ±1.32	0.16 ±0.01	3.81±0.02
E.	28.07 ±0.02	103.40 ±0.01	61.67 ±0.99	7.36 ±0.01	8.02 ±0.02	102.67 ±0.91	0.13 ±0.02	2.92 ±0.01
F.	27.33 ±0.01	76.40 ±0.01	125.50 ±1.54	7.15 ±0.10	7.88 ±0.01	133.33 ±1.78	0.15 ±0.01	2.15 ±0.03
G.	27.30 ±0.01	93.57 ±0.01	193.00 ±2.45	7.62 ±0.04	7.93 ±0.03	148.67 ±2.14	0.18 ±0.01	3.19 ±0.01
H.	27.30 ±0.02	81.13 ±0.02	166.50 ±2.45	7.24 ±0.02	9.80 ±0.02	133.33 ±1.34	0.23 ±0.01	2.71 ±0.01

Key: Temp = Temprature; Cond = Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; pH = Power of Hydrogen; Turb = Turbidity; TP = Total Phosphates; TN = Total Nitrogen

TABLE: Mean ± SE physico - chemical parameters Jul-16 (d)

Site/Param	Temp (°C)	Cond (µScm^{-1})	TSS (mg/I)	DO (µgL^{-1})	pH	Turb (NTU)	TP(µgL^{-1})	TN (µgL^{-1})
A.	27.03±0.07	130.37±1.9	205.50±3.45	6.98±0.02	7.94±0.03	156.33±4.12	0.48±0.03	5.03±0.01
B.	27.37±0.01	126.37±2.56	330.50±4.83	7.37±0.06	7.57±0.02	263.33±4.17	0.49±0.02	5.00±0.012
C.	27.21±0.01	127.28±1.93	334.30±2.89	7.21±0.03	7.49±0.01	268.37±2.91	0.50±0.01	4.97±0.03
D.	26.07±0.02	47.40±1.45	137.38±3.62	7.69±0.02	7.41±0.09	122.00±1.93	0.23±0.03	5.00±0.012
E.	26.77±0.03	110.43±2.42	43.00±1.01	6.77±0.09	7.21±0.02	189.40±4.17	0.29±0.03	3.09±0.06
F.	26.87±0.01	107.57±3.19	214.00±2.01	6.24±0.06	7.42±0.01	187.67±2.91	0.33±0.01	1.38±0.01
G.	27.27±0.02	157.40±3.18	70.32±1.07	7.85±0.01	7.69±0.01	77.30±2.56	0.20±0.01	1.92±0.02
H.	27.07±0.01	160.13±1.23	59.34±1.12	7.77±0.06	7.70±0.01	48.63±2.13	0.15±0.01	2.34±0.02

Key: Temp = Temprature; Cond = Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; pH = Power of Hydrogen; Turb = Turbidity; TP = Total Phosphates; TN = Total Nitrogen

TABLE: Mean ± SE physico - chemical parameters Nov-17 (e)

Site/Param	Temp (°C)	Cond (µScm^{-1})	TSS (µgL^{-1})	DO (µgL^{-1})	pH	Turb (NTU)	TP (µgL^{-1})	TN (µgL^{-1})
A.	26.33±0.03	59.80±1.98	498.00±3.20	8.95±0.02	7.05±0.01	368.00±1.45	0.245±0.001	4.179±0.211
B.	25.90-10.04	66.00±1.26	270.00±4.71	7.49±0.04	6.76±0.02	152.33-11.44	0.188±0.002	4.846±0.012
C.	22.87±0.05	57.87±1.38	132.00±3.21	8.23±0.01	6.83±0.009	189.67±1.12	0.290±0.012	3.813±0.092
D.	26.40±0.03	57.63±2.09	411.50±3.31	7.67±0.03	7.13±0.03	343.33±2.91	0.343±0.031	3.291±0.062
E.	26.83±0.07	67.13±3.12	431.00±2.12	6.62±0.03	7.13±0.04	270.67±2.13	0.307±0.046	3.464±0.042
F.	26.17±0.01	200.77±5.01	11.46±1.32	8.36±0.07	7.93±0.03	32.63±1.22	0.170±0.041	3.262±0.062
G.	26.10±0.01	68.53±2.91	421.00±2.78	8.35±0.09	7.10±0.01	278.67±2.33	0.366±0.061	3.511±0.032
H.	26.47±0.03	89.80±1.22	16.00±2.34	7.87±0.02	7.59±0.008	83.50±1.98	0.219±0.051	3.279±0.051

Key: Temp = Temprature; Cond = Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; pH = Power of Hydrogen; Turb = Turbidity; TP = Total Phosphates; TN = Total Nitrogen

TABLE: Mean ± SE physico - chemical parameters Oct-17 (f)

Site/Param	Temp (°C)	Cond (µScm^{-1})	TSS (µgL^{-1})	DO (µgL^{-1})	pH	Turb (NTU)	TP (µgL^{-1})	TN (µgL^{-1})
A.	26.50±0.01	117.1011.94	227.00-11.03	7.82E1.01	7.38±0.01	89.63±1.88	0.34±0.02	3.96±1.01
B.	27.33±10.03	101.90±1.94	335.0011.12	6.54±0.02	7.20E1.01	160.0012.92	0.46E1.02	3.78±0.03
C.	26.67±1.04	125.63±1.45	342.50±1.01	7.85E1.04	7.47±0.04	189.3312.89	0.49±0.02	3.34±0.21
D.	26.20±0.15	48.10±2.34	104.50-11.03	8.45±0.03	7.0410.03	92.40±3.09	0.27±0.01	2.59±0.34
E.	27.30±0.02	115.80/3.12	242.00±2.12	7.68±0.01	7.66±0.04	103.53±2.98	0.4610.02	3.2510.01
F.	26.20±0.11	179.07±2.92	78.50±3.21	7.07±0.02	7.87E1.02	67.03±2.12	0.13±0.01	2.21±0.03
G.	25.6710.04	119.27±3.17	290.50±4.12	7.24±0.03	7.98±0.03	99.60±1.33	0.19±0.02	3.56±0.04
H.	25.40±0.08	245.67±5.12	44.00±11.23	8.56±1.01	8.1410.06	33.35±3.33	0.15E1.02	2.36±0.04

Key: Temp = Temprature; Cond = Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; pH = Power of Hydrogen; Turb = Turbidity; TP = Total Phosphates; TN = Total Nitrogen

TABLE: Mean±SE physico - chemical parameters Sep-15 (g)

Site/Param	Temp (°C)	Cond (μScm^{-1})	TSS (μgL^{-1})	DO (μgL^{-1})	pH	Turb (NTU)	TP(μgL^{-1})	TN (μgL^{-1})
A.	15.40±0.01	148.30±2.09	27.50±0.09	5.59±0.2	7.28±0.01	73.00±1.90	0.15±0.01	1.41±0.02
B.	18.40±0.02	126.80±1.34	78.67±2.32	6.44±0.34	6.93±0.03	75.00±0.972	0.08±0.003	2.18±0.04
C.	18.40±0.03	127.80±1.98	53.00±1.01	6.44±0.98	7.11±0.04	89.00±1.93	0.08±0.008	2.30±0.03
D.	17.50±0.03	138.70±3.22	31.40±0.98	7.38±0.65	7.45±0.06	93.00±1.87	0.07±0.002	1.57±0.04
E.	12.10±0.04	134.80±1.34	28.80±0.45	4.81±0.11	7.54±0.05	84.00±2.43	0.11±0.05	1.72±0.04
F.	15.40±0.01	308.00±2.92	52.80±01.23	4.45±0.12	7.80±0.05	30.00±2.65	0.21±0.04	1.39±0.06
G.	15.90±0.04	163.50±2.11	62.00±0.17	7.43±0.34	7.42±0.04	81.00±2.33	0.14±0.01	1.58±0.04
H.	19.80±0.05	169.00±3.82	30.80±0.96	4.48±0.44	7.50±0.04	35.00±3.12	0.19±0.05	1.55±0.01

Key: Temp = Temprature; Cond = Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; pH = Power of Hydrogen; Turb = Turbidity; TP = Total Phosphates; TN = Total Nitrogen

TABLE: Mean ± SE physico - chemical parameters Jul-17 (h)

Site/Param	Temp (°C)	Cond (µScm^{-1})	TSS (µgL^{-1})	DO (µgL^{-1})	pH	Turb (NTU)	TP (µgL^{-1})	TN (µgL^{-1})
A.	16.30±0.01	206.00±1.92	813.50±2.89	5.14±0.02	7.51±0.01	383.00±2.91	0.485±0.012	5.835±0.008
B.	19.50±0.03	214.00±1.32	874.00±1.92	5.94±0.04	7.58±0.02	305.00±1.23	0.412±0.030	S.67±0.034
C.	19.10±0.04	220.00±2.82	879.00±2.12	6.00±0.03	7.42±0.01	313.00±1.94	0.318±0.032	5.392±0.041
D.	20.10±0.05	104.00±3.41	830.00±2.45	5.60±0.02	7.35±0.05	265.00±2.12	0.151±0.021	3.212±0.037
E.	14.90±0.02	197.914.12	381.00±1.72	6.30±0.05	7.98±0.03	126.00±1.67	0.163±0.011	5.435±0.021
F.	13.00±0.03	185.70±3.15	177.00±1.32	7.50±0.01	7.73±0.21	105.00±1.23	0.141±0.009	0.504±0.011
G.	15.70±0.03	254.00±1.95	129.50±1.34	4.30±0.09	7.83±0.03	61.00±1.01	0.169±0.003	0.918±0.027
H.	15.40±0.03	246.00±3.98	123.50±3.96	5.80±0.02	7.86±0.01	44.00±0.98	0.102±0.002	1.130±0.018

Key: Temp = Temprature; Cond = Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; pH = Power of Hydrogen; Turb = Turbidity; TP = Total Phosphates; TN = Total Nitrogen

TABLE: Mean± SEphysico - chemical Apr-15 (i)
parameters

Site/Param	Temp (°C)	Cond (µScm^{-1})	TSS (µgL^{-1})	DO (µgL^{-1})	pH	Turb (NTU)	TP (µgL^{-1})	TN (µgL^{-1})
A.	27.10± 1.09	139.3± 4.12	76.35 ± 1.23	7.65 ± 0.12	7.83± 0.01	125.67± 3.89	0.207±0.02	3.653±0.012
B.	28.13 ± 1.34	77.70 ± 2.45	32.00 ± 1.78	7.01 ± 0.07	7.94± 0.78	61.97± 1.690	0.083±0.01	3.444± .004
C.	28.06 ± 1.81	96.07 ± 1.76	76.54 t 1.93	7.21 ± 0.32	8.08± 0.94	61.90 ± 1.230	0.11±0.011	2.714±0.020
D.	27.73± 0.97	111.23± 1.8	62.67± 1.23	8.24 ± 0.37	8.01± 0.02	79.47± 1.340	0.156±0.06	3.81 ± 0.001
E.	28.07 ± 2.09	103.4± 1.76	61.67± 1.45	7.36± 0.39	8.02± 0.01	102.67 ± 2.39	0.127±0.002	2.922 ± 0.04
F.	27.67 ± 1.45	76.40 ± 1.98	125.50±1.45	7.15 ± 0.78	7.88± 0.09	133.33 ± 2.19	0.146±0.004	2.153 ± 0.01
G.	27.33 ± 1.17	93.57 ± 2.78	193.00±4.35	7.62 ± 0.02	7.93± 0.13	148.67 ± 2.39	0.183±0.003	3.118 ± 0.02
H.	27.3 ± 0.120	81.13 ± 3.65	166.50± 3.21	7.24 -1. 0.02	9.80± 0.32	133.33 ± 1.34	0.225±0.007	2.707±0.004

Key: Temp = Temprature; Cond = Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; pH = Power of Hydrogen; Turb = Turbidity; TP = Total Phosphates; TN = Total Nitrogen

TABLE: Mean±SE physico - chemical Apr-15 (i) parameters

Site/Param	Temp (°C)	Cond (µScm^{-1})	TSS (µgL^{-1})	DO (µgL^{-1})	pH	Turb (NTU)	TP (µgL^{-1})	TN (µgL^{-1})
A.	27.10± 1.09	139.3± 4.12	76.35 ± 1.23	7.65 ± 0.12	7.83± 0.01	125.67± 3.89	0.207±0.02	3.653±0.012
B.	28.13 ± 1.34	77.70 ± 2.45	32.00 ± 1.78	7.01 ± 0.07	7.94± 0.78	61.97± 1.690	0.083±0.01	3.444± .004
C.	28.06 ± 1.81	96.07 ± 1.76	76.54 t 1.93	7.21 ± 0.32	8.08± 0.94	61.90 ± 1.230	0.11±0.011	2.714±0.020
D.	27.73± 0.97	111.23± 1.8	62.67± 1.23	8.24 ± 0.37	8.01± 0.02	79.47± 1.340	0.156±0.06	3.81 ± 0.001
E.	28.07 ± 2.09	103.4± 1.76	61.67± 1.45	7.36± 0.39	8.02± 0.01	102.67 ± 2.39	0.127±0.002	2.922 ± 0.04
F.	27.67 ± 1.45	76.40 ± 1.98	125.50±1.45	7.15 ± 0.78	7.88± 0.09	133.33 ± 2.19	0.146±0.004	2.153 ± 0.01
G.	27.33 ± 1.17	93.57 ± 2.78	193.00±4.35	7.62 ± 0.02	7.93± 0.13	148.67 ± 2.39	0.183±0.003	3.118 ± 0.02
H.	27.3 ± 0.120	81.13 ± 3.65	166.50± 3.21	7.24 -1. 0.02	9.80± 0.32	133.33 ± 1.34	0.225±0.007	2.707±0.004

Key: Temp = Temprature; Cond = Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; pH = Power of Hydrogen; Turb = Turbidity; TP = Total Phosphates; TN = Total Nitrogen

Appendix IX: **Mean ±SE spatial distribution of hexachlorocyclohexane isomers in river water samples during wet and dry seasons**.

Site	**α-HCH wet**	**α-HCH dry**	**β-HCH wet**	**β -HCH dry**	**γ-HCH wet**	**γ -HCH dry**	**δ -HCH wet**	**δ-HCH dry**
A	1.214±0.030	1.775±0.04	0.011±0.01	0.985±0.04	0.0371±0.01	0.162±0.01	0.096±0.02	0.289±0.01
B	1.303±0.01	2.361±0.78	0.020±0.04	0.681±0.04	0.033±0.01	1.244±0.78	0.004±0.01	0.035±0.04
C	0.018±0.04	0.019±0.02	0.003±0.02	0.847±0.04	0.003±0.02	0.000	0.000	0.029±0.01
D	1.21± 0.78	1.985±0.78	0.030±0.04	0.617±0.04	0.004±0.01	0.781±0.04	0.015±0.02	0.046±0.02
E	0.028±0.04	1.324±0.78	0.527±0.02	0.991±0.02	0.000	0.041±0.01	0.008±0.04	0.026±0.01
F	0.099±0.04	0.085±0.04	0.965±0.04	0.984±0.04	0.0271±0.0	0.682±0.01	0.049±0.01	0.245±0.01
G	0.023±0.02	2.356±0.78	0.938±0.02	1.118±0.78	0.027±0.01	2.192±0.78	0.046±0.01	0.031±0.01
H	0.27±0.015	2.145±0.78	0.982±0.04	0.042±0.01	0.054±0.04	0.289±0.01	0.022±0.01	0.1104±0.01

Appendix X: **Mean ±SE spatial distribution of the concentrations of cyclodiene pesticide compounds in the fish ponds during wet season**.

Site	**Hept.**	**Ald.**	**HE**	**Ends. I**	**Endr.**	**Dield.**	**Ends. II**	**EA**	**ES**	**Met.**
A	0.137±0.01	0.009±0.04	0.164±0.02	0.009±0.01	0.009±0.04	0.018±0.01	0.0000	0.0000	0.0000	0.239±0.01
B	0.078±0.042	0.002±0.01	0.024±0.01	0.107±0.01	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C	0.0000	0.0000	0.0000	0.006±0.004	0.0000	0.0000	0.007±0.01	0.055±0.01	0.063±0.04	0.307±0.01
D	0.141±0.014	0.214±0.01	0.413±0.01	0.093±0.02	0.0000	0.0000	0.0000	0.0000	0.0000	0.268±0.01
E	0.019±0.01	0.003	0.0000	0.099±0.02	0.414±0.04	0.0000	0.0000	0.036±0.01	0.134±0.01	0.0000
F	0.060±0.01	0.0000	0.467±0.01	0.023±0.01	0.471±0.02	0.0000	0.026±0.01	0.279±0.01	0.437±0.03	0.151±0.04
G	0.117±0.04	0.059±0.04	0.463±0.04	0.1142±0.01	0.506±0.04	0.0000	0.018±0.01	0.206±0.04	0.358±0.04	0.166±0.02
H	0.113±0.04±0.04	0.065±0.04	0.068±0.01	0.113±0.01	0.097±0.03	0.0000	0.021±0.01	0.248±0.04	0.430±0.02	0.165±0.01

Key: Hept.-Heptachlor
Ald-Aldrin
HE-Heptachlor epoxide
Ends I-Endosulfan I
Endr-Endrin
Dield-Dieldrin
Ends II-Endosulfan II
EA-Endrin aldehyde
ES-Endosulfan sulfate
Met-Methoxychlor

Appendix XI: **Mean ±SE spatial distribution of the concentrations of cyclodiene pesticide compounds in the fish ponds during dry season**.

Site	**Hept.**	**Ald.**	**HE.**	**Ends. I**	**Endr.**	**Dield.**	**Ends. II**	**EA.**	**ES.**	**Met.**
A	0.037±0.01	0.001±0.01	0.006±0.02	0.001±0.01	0.002±0.01	0.001±0.01	0.004±0.01	0.002±0.01	0.003±0.01	0.0131±0.01
B	0.009±0.04	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.002±0.01
C	0.004±0.01	0.0000	0.0000	0.0000	0.0000	0.0008±0.03	0.001	0.006±0.02	0.001±0.01	0.008±0.012
D	0.085±0.03	0.010±0.01	0.012±0.01	0.0000	0.009±0.03	0.052±0.01	0.0000	0.001	0.0000	0.017±0.01
E	0.005±0.01	0.004±0.01	0.0000	0.0000	0.005±0.02	0.037±0.01	0.0000	0.004±0.02	0.003±0.01	0.001±0.01
F	0.069±0.04	0.0000	0.005±0.02	0.004	0.0000	0.047±0.02	0.002±0.01	0.024±0.02	0.009±0.3	0.009±0.04
G	0.065±0.04	0.009±0.02	0.006±0.02	0.0000	0.0000	0.044±0.01	0.004±0.01	0.018±0.01	0.005±0.01	0.036±0.01
H	0.075±0.02	0.009±0.03	0.006±0.02	0.0000	0.002±0.01	0.046±0.02	0.002±0.01	0.021±0.01	0.007±0.02	0.037±0.01

Key: Hept.-Heptachlor Ald-Aldrin

HE-Heptachlor epoxide Ends I-Endosulfan I

Endr-Endrin Dield-Dieldrin

Ends II-Endosulfan II EA-Endrin aldehyde

ES-Endosulfan sulfate Met-Methoxychlor;

Appendix XII: **Spatial distribution of cyclodienes pesticides in fish pond sediment in river waters during wet season**.

Site	Hept	Ald.	HE	Ends. I	Endr	Dield.	Ends. II	EA	ES	Met.
A	15.9	0.23	0.26	2.32	23.49	8.56	1.66	1.39	2.91	42.78
B	1.54	25.62	0.58	3.02	32.17	7.21	1.00	0.00	0.74	0.00
C	1.81	27.61	0.00	0.00	6.21	0.00	1.84	0.00	6.21	0.05
D	2.91	8.36	0.11	2.87	0.61	0.00	0.47	0.75	1.08	0.21
E	2.06	46.70	0.39	0.07	19.07	54.67	7.36	3.84	21.25	0.24
F	1.60	4.34	0.00	0.06	5.76	0.53	0.29	0.47	6.05	1.82
G	1.76	12.24	0.36	0.18	12.12	0.27	2.03	0.65	12.56	0.10
H	1.89	22.65	0.13	0.00	13.93	47.12	6.64	7.42	18.88	0.22

Key: Hept.-Heptachlor Ald-Aldrin

HE-Heptachlor epoxide Ends I-Endosulfan I

Endr-Endrin Dield-Dieldrin

Ends II-Endosulfan II EA-Endrin aldehyde

ES-Endosulfan sulfate Met-Methoxychlor;

Appendix XIII: **Analyses of Variance (ANOVA).**

Table Analyzed	**PondFish_HCH_wet**
Data sets analyzed	A-D
ANOVA summary	
F	0.4594
P value	0.7256
P value summary	ns
Significant diff. among means (P < 0.05)?	No
R squared	0.2562
Brown-Forsythe test	
F (DFn, DFd)	6.487e+030 (3, 4)
P value	<0.0001
P value summary	****
Are SDs significantly different (P < 0.05)?	Yes
Bartlett's test	
Bartlett's statistic (corrected)	
P value	
P value summary	
Are SDs significantly different (P < 0.05)?	

ANOVA table	SS	DF	MS	F (DFn, DFd)	P value
Treatment (between columns)	0.007734	3	0.002578	F (3, 4) = 0.4594	P=0.7256
Residual (within columns)	0.02245	4	0.005612		
Total	0.03018	7			

Data summary

Number of treatments (columns)	4
Number of values (total)	8

Table Analyzed	**PondFish_HCH_dry**

Data sets analyzed	A-D

ANOVA summary	
F	4.312
P value	0.0960
P value summary	ns
Significant diff. among means (P < 0.05)?	No
R squared	0.7638

Brown-Forsythe test	
F (DFn, DFd)	+infinity (3, 4)
P value	<0.0001
P value summary	****
Are SDs significantly different (P < 0.05)?	Yes

Bartlett's test	
Bartlett's statistic (corrected)	
P value	
P value summary	
Are SDs significantly different (P < 0.05)?	

ANOVA table	SS	DF	MS	F (DFn, DFd)	P value
Treatment (between columns)	0.5831	3	0.1944	F (3, 4) = 4.312	P=0.0960
Residual (within columns)	0.1803	4	0.04508		
Total	0.7634	7			

Data summary

Number of treatments (columns)	4
Number of values (total)	8

ddt_wet (Earthen pond Fish)

Number of families	1
Number of comparisons per family	3
Alpha	0.05

Tukey's multiple comparisons test	Mean Diff.	95.00% CI of diff.	Significant?	Summary	Adjusted P Value	
pp-DDE vs. pp-DDD	0.02506	-0.4443 to 0.4944	No	ns	0.9732	A-B
pp-DDE vs. pp-DDT	-0.4231	-0.8925 to 0.04622	No	ns	0.0651	A-C
pp-DDD vs. pp-DDT	-0.4482	-0.9176 to 0.02117	No	ns	0.0563	B-C

Test details	Mean 1	Mean 2	Mean Diff.	SE of diff.	n1	n2	q	DF
pp-DDE vs. pp-DDD	0.2555	0.2305	0.02506	0.1123	2	2	0.3155	3
pp-DDE vs. pp-DDT	0.2555	0.6787	-0.4231	0.1123	2	2	5.328	3
pp-DDD vs. pp-DDT	0.2305	0.6787	-0.4482	0.1123	2	2	5.643	3

Table Analyzed	**Fish_ddt_dry**
Data sets analyzed	A-C
ANOVA summary	
F	4.901
P value	0.1134
P value summary	ns
Significant diff. among means (P < 0.05)?	No
R squared	0.7657
Brown-Forsythe test	
F (DFn, DFd)	+infinity (2, 3)
P value	<0.0001
P value summary	****
Are SDs significantly different (P < 0.05)?	Yes
Bartlett's test	
Bartlett's statistic (corrected)	
P value	
P value summary	
Are SDs significantly different (P < 0.05)?	

ANOVA table	SS	DF	MS	F (DFn, DFd)	P value
Treatment (between columns)	0.5157	2	0.2579	F (2, 3) = 4.901	P=0.1134
Residual (within columns)	0.1579	3	0.05262		
Total	0.6736	5			

Data summary	
Number of treatments (columns)	3
Number of values (total)	6

Two-Way ANOVA of Fish_ddt_dry

Number of families	1
Number of comparisons per family	45
Alpha	0.05

Tukey's multiple comparisons test	Mean Diff.	95.00% CI of diff.	Significant?	Summary	Adjusted P Value	
Heptachlor vs. Aldrin	0.2261	-0.1003 to 0.5526	No	ns	0.2713	A-B
Heptachlor vs. Heptachlor Epoxide	0.3318	0.005350 to 0.6583	Yes	*	0.0456	A-C
Heptachlor vs. Endosulphan I	0.2022	-0.1243 to 0.5287	No	ns	0.3867	A-D
Heptachlor vs. Endrin	0.2539	-0.07259 to 0.5804	No	ns	0.1737	A-E
Heptachlor vs. Dieldrin	0.2809	-0.04557 to 0.6074	No	ns	0.1101	A-F
Heptachlor vs. Endosulphan II	0.2853	-0.04114 to 0.6118	No	ns	0.1021	A-G
Heptachlor vs. Endrin Aldehyde	0.2618	-0.06471 to 0.5883	No	ns	0.1523	A-H
Heptachlor vs. Endosulphan sulphate	0.2897	-0.03678 to 0.6162	No	ns	0.0947	A-I
Heptachlor vs. Methoxychlor	0.2366	-0.08990 to 0.5631	No	ns	0.2302	A-J
Aldrin vs. Heptachlor Epoxide	0.1057	-0.2208 to 0.4322	No	ns	0.9373	B-C
Aldrin vs. Endosulphan I	-0.02392	-0.3504 to 0.3026	No	ns	>0.9999	B-D
Aldrin vs. Endrin	0.02775	-0.2987 to 0.3542	No	ns	>0.9999	B-E

Aldrin vs. Dieldrin	0.05478	-0.2717 to 0.3813	No	ns	0.9992	B-F
Aldrin vs. Endosulphan II	0.05920	-0.2673 to 0.3857	No	ns	0.9985	B-G
Aldrin vs. Endrin Aldehyde	0.03564	-0.2908 to 0.3621	No	ns	>0.9999	B-H
Aldrin vs. Endosulphan sulphate	0.06356	-0.2629 to 0.3900	No	ns	0.9975	B-I
Aldrin vs. Methoxychlor	0.01044	-0.3160 to 0.3369	No	ns	>0.9999	B-J
Heptachlor Epoxide vs. Endosulphan I	-0.1296	-0.4561 to 0.1969	No	ns	0.8355	C-D
Heptachlor Epoxide vs. Endrin	-0.07794	-0.4044 to 0.2485	No	ns	0.9898	C-E
Heptachlor Epoxide vs. Dieldrin	-0.05092	-0.3774 to 0.2756	No	ns	0.9995	C-F
Heptachlor Epoxide vs. Endosulphan II	-0.04649	-0.3730 to 0.2800	No	ns	0.9998	C-G
Heptachlor Epoxide vs. Endrin Aldehyde	-0.07006	-0.3965 to 0.2564	No	ns	0.9951	C-H
Two-Way ANOVA of Fish_ddt_dry						
Heptachlor Epoxide vs. Endosulphan sulphate	-0.04213	-0.3686 to 0.2844	No	ns	0.9999	C-I
Heptachlor Epoxide vs. Methoxychlor	-0.09525	-0.4217 to 0.2312	No	ns	0.9647	C-J
Endosulphan I vs. Endrin	0.05167	-0.2748 to 0.3782	No	ns	0.9995	D-E
Endosulphan I vs. Dieldrin	0.07870	-0.2478 to 0.4052	No	ns	0.9892	D-F
Endosulphan I vs. Endosulphan II	0.08312	-0.2434 to 0.4096	No	ns	0.9846	D-G
Endosulphan I vs. Endrin Aldehyde	0.05956	-0.2669 to 0.3860	No	ns	0.9985	D-H

Endosulphan I vs. Endosulphan sulphate	0.08748	-0.2390 to 0.4140	No	ns	0.9787	D-I
Endosulphan I vs. Methoxychlor	0.03436	-0.2921 to 0.3608	No	ns	>0.9999	D-J
Endrin vs. Dieldrin	0.02703	-0.2995 to 0.3535	No	ns	>0.9999	E-F
Endrin vs. Endosulphan II	0.03145	-0.2950 to 0.3579	No	ns	>0.9999	E-G
Endrin vs. Endrin Aldehyde	0.007889	-0.3186 to 0.3344	No	ns	>0.9999	E-H
Endrin vs. Endosulphan sulphate	0.03581	-0.2907 to 0.3623	No	ns	>0.9999	E-I
Endrin vs. Methoxychlor	-0.01731	-0.3438 to 0.3092	No	ns	>0.9999	E-J
Dieldrin vs. Endosulphan II	0.004422	-0.3221 to 0.3309	No	ns	>0.9999	F-G
Dieldrin vs. Endrin Aldehyde	-0.01914	-0.3456 to 0.3073	No	ns	>0.9999	F-H
Dieldrin vs. Endosulphan sulphate	0.008783	-0.3177 to 0.3353	No	ns	>0.9999	F-I
Dieldrin vs. Methoxychlor	-0.04433	-0.3708 to 0.2821	No	ns	0.9998	F-J
Endosulphan II vs. Endrin Aldehyde	-0.02356	-0.3500 to 0.3029	No	ns	>0.9999	G-H
Endosulphan II vs. Endosulphan sulphate	0.004361	-0.3221 to 0.3308	No	ns	>0.9999	G-I
Endosulphan II vs. Methoxychlor	-0.04876	-0.3752 to 0.2777	No	ns	0.9997	G-J
Endrin Aldehyde vs. Endosulphan sulphate	0.02792	-0.2986 to 0.3544	No	ns	>0.9999	H-I
Endrin Aldehyde vs. Methoxychlor	-0.02520	-0.3517 to 0.3013	No	ns	>0.9999	H-J

Endosulphan sulphate vs. Methoxychlor	-0.05312	-0.3796 to 0.2734	No	ns	0.9994	I-J		

Test details	Mean 1	Mean 2	Mean Diff.	SE of diff.	n1	n2	q	DF
Heptachlor vs. Aldrin	0.4391	0.2130	0.2261	0.08247	2	2	3.878	10
Heptachlor vs. Heptachlor Epoxide	0.4391	0.1073	0.3318	0.08247	2	2	5.690	10
Heptachlor vs. Endosulphan I	0.4391	0.2369	0.2022	0.08247	2	2	3.468	10
Heptachlor vs. Endrin	0.4391	0.1853	0.2539	0.08247	2	2	4.354	10
Heptachlor vs. Dieldrin	0.4391	0.1582	0.2809	0.08247	2	2	4.817	10
Heptachlor vs. Endosulphan II	0.4391	0.1538	0.2853	0.08247	2	2	4.893	10
Heptachlor vs. Endrin Aldehyde	0.4391	0.1774	0.2618	0.08247	2	2	4.489	10
Heptachlor vs. Endosulphan sulphate	0.4391	0.1494	0.2897	0.08247	2	2	4.968	10
Heptachlor vs. Methoxychlor	0.4391	0.2026	0.2366	0.08247	2	2	4.057	10
Aldrin vs. Heptachlor Epoxide	0.2130	0.1073	0.1057	0.08247	2	2	1.812	10
Two-Way ANOVA of Fish_ddt_dry								
Aldrin vs. Endosulphan I	0.2130	0.2369	-0.02392	0.08247	2	2	0.4101	10
Aldrin vs. Endrin	0.2130	0.1853	0.02775	0.08247	2	2	0.4758	10
Aldrin vs. Dieldrin	0.2130	0.1582	0.05478	0.08247	2	2	0.9393	10
Aldrin vs. Endosulphan II	0.2130	0.1538	0.05920	0.08247	2	2	1.015	10
Aldrin vs. Endrin Aldehyde	0.2130	0.1774	0.03564	0.08247	2	2	0.6111	10
Aldrin vs. Endosulphan sulphate	0.2130	0.1494	0.06356	0.08247	2	2	1.090	10
Aldrin vs. Methoxychlor	0.2130	0.2026	0.01044	0.08247	2	2	0.1791	10
Heptachlor Epoxide vs. Endosulphan I	0.1073	0.2369	-0.1296	0.08247	2	2	2.223	10
Heptachlor Epoxide vs. Endrin	0.1073	0.1853	-0.07794	0.08247	2	2	1.337	10
Heptachlor Epoxide vs. Dieldrin	0.1073	0.1582	-0.05092	0.08247	2	2	0.8731	10
Heptachlor Epoxide vs. Endosulphan II	0.1073	0.1538	-0.04649	0.08247	2	2	0.7973	10
Heptachlor Epoxide vs. Endrin Aldehyde	0.1073	0.1774	-0.07006	0.08247	2	2	1.201	10
Heptachlor Epoxide vs. Endosulphan sulphate	0.1073	0.1494	-0.04213	0.08247	2	2	0.7225	10
Heptachlor Epoxide vs. Methoxychlor	0.1073	0.2026	-0.09525	0.08247	2	2	1.633	10

Endosulphan I vs. Endrin	0.2369	0.1853	0.05167	0.08247	2	2	0.8860	10
Endosulphan I vs. Dieldrin	0.2369	0.1582	0.07870	0.08247	2	2	1.349	10
Endosulphan I vs. Endosulphan II	0.2369	0.1538	0.08312	0.08247	2	2	1.425	10
Endosulphan I vs. Endrin Aldehyde	0.2369	0.1774	0.05956	0.08247	2	2	1.021	10
Endosulphan I vs. Endosulphan sulphate	0.2369	0.1494	0.08748	0.08247	2	2	1.500	10
Endosulphan I vs. Methoxychlor	0.2369	0.2026	0.03436	0.08247	2	2	0.5892	10
Endrin vs. Dieldrin	0.1853	0.1582	0.02703	0.08247	2	2	0.4635	10
Endrin vs. Endosulphan II	0.1853	0.1538	0.03145	0.08247	2	2	0.5393	10
Endrin vs. Endrin Aldehyde	0.1853	0.1774	0.007889	0.08247	2	2	0.1353	10
Endrin vs. Endosulphan sulphate	0.1853	0.1494	0.03581	0.08247	2	2	0.6141	10
Endrin vs. Methoxychlor	0.1853	0.2026	-0.01731	0.08247	2	2	0.2968	10
Dieldrin vs. Endosulphan II	0.1582	0.1538	0.004422	0.08247	2	2	0.07583	10
Dieldrin vs. Endrin Aldehyde	0.1582	0.1774	-0.01914	0.08247	2	2	0.3282	10
Dieldrin vs. Endosulphan sulphate	0.1582	0.1494	0.008783	0.08247	2	2	0.1506	10
Dieldrin vs. Methoxychlor	0.1582	0.2026	-0.04433	0.08247	2	2	0.7602	10
Endosulphan II vs. Endrin Aldehyde	0.1538	0.1774	-0.02356	0.08247	2	2	0.4040	10
Endosulphan II vs. Endosulphan sulphate	0.1538	0.1494	0.004361	0.08247	2	2	0.07478	10
Endosulphan II vs. Methoxychlor	0.1538	0.2026	-0.04876	0.08247	2	2	0.8360	10
Endrin Aldehyde vs. Endosulphan sulphate	0.1774	0.1494	0.02792	0.08247	2	2	0.4788	10

Table Analyzed	**WW_Fish_HCH_wet**
Data sets analyzed	A-D
ANOVA summary	
F	5.138
P value	0.0739
P value summary	ns
Significant diff. among means (P < 0.05)?	No
R squared	0.7940
Brown-Forsythe test	
F (DFn, DFd)	1.928e+031 (3, 4)
P value	<0.0001
P value summary	****
Are SDs significantly different (P < 0.05)?	Yes
Bartlett's test	
Bartlett's statistic (corrected)	
P value	
P value summary	
Are SDs significantly different (P < 0.05)?	

ANOVA table	SS	DF	MS	F (DFn, DFd)
Treatment (between columns)	36.43	3	12.14	F (3, 4) = 5.138
Residual (within columns)	9.454	4	2.363	
Total	45.88	7		

Data summary	
Number of treatments (columns)	4
Number of values (total)	8

Table Analyzed	**WW_Fish_HCH_dry**
Data sets analyzed	A-D
ANOVA summary	
F	3.071
P value	0.1534
P value summary	ns
Significant diff. among means (P < 0.05)?	No
R squared	0.6972
Brown-Forsythe test	
F (DFn, DFd)	6.939e+030 (3, 4)
P value	<0.0001
P value summary	****
Are SDs significantly different (P < 0.05)?	Yes
Bartlett's test	
Bartlett's statistic (corrected)	
P value	
P value summary	
Are SDs significantly different (P < 0.05)?	

ANOVA table	SS	DF	MS	F (DFn, DFd)
Treatment (between columns)	18.28	3	6.094	F (3, 4) = 3.071
Residual (within columns)	7.938	4	1.985	
Total	26.22	7		

Data summary	
Number of treatments (columns)	4
Number of values (total)	8

Table Analyzed	**WW-ddt_wet**
Data sets analyzed	A-C
ANOVA summary	
F	0.8040
P value	0.5253
P value summary	ns
Significant diff. among means (P < 0.05)?	No
R squared	0.3490
Brown-Forsythe test	
F (DFn, DFd)	2.205e+030 (2, 3)
P value	<0.0001
P value summary	****
Are SDs significantly different (P < 0.05)?	Yes
Bartlett's test	
Bartlett's statistic (corrected)	
P value	
P value summary	
Are SDs significantly different (P < 0.05)?	

ANOVA table	SS	DF	MS	F (DFn, DFd)	P value
Treatment (between columns)	0.8671	2	0.4335	F (2, 3) =0.8040	P=0.5253
Residual (within columns)	1.618	3	0.5392		
Total	2.485	5			

Data summary	
Number of treatments (columns)	3
Number of values (total)	6

HCH_dry_Receivingwater_Fish	1				
Number of families					
Number of comparisons per family	6				
Alpha	0.05				
Tukey's multiple comparisons test	Mean Diff.	95.00% CI of diff.	Significant?	Summary	Adjusted P Value
a-HCH vs. ß-HCH	0.05402	-0.3823 to 0.4904	No	ns	0.9864
a-HCH vs. g-HCH	-0.4533	-0.8896 to -0.01693	Yes	*	0.0395
a-HCH vs. d-HCH	-0.04871	-0.4851 to 0.3876	No	ns	0.9900
ß-HCH vs. g-HCH	-0.5073	-0.9437 to -0.07096	Yes	*	0.0180
ß-HCH vs. d-HCH	-0.1027	-0.5391 to 0.3336	No	ns	0.9172
g-HCH vs. d-HCH	0.4046	-0.03177 to 0.8409	No	ns	0.0766
Test details	Mean 1	Mean 2	Mean Diff.	SE of diff.	n1
a-HCH vs. ß-HCH	0.2101	0.1561	0.05402	0.1598	8
a-HCH vs. g-HCH	0.2101	0.6634	-0.4533	0.1598	8
a-HCH vs. d-HCH	0.2101	0.2588	-0.04871	0.1598	8
ß-HCH vs. g-HCH	0.1561	0.6634	-0.5073	0.1598	8
ß-HCH vs. d-HCH	0.1561	0.2588	-0.1027	0.1598	8
g-HCH vs. d-HCH	0.6634	0.2588	0.4046	0.1598	8

Table Analyzed	**Fish_ddt_wet**
River waters	
Data sets analyzed	A-C
ANOVA summary	
F	8.602
P value	0.0019
P value summary	**
Significant diff. among means (P < 0.05)?	Yes
R squared	0.4503
Brown-Forsythe test	
F (DFn, DFd)	2.156 (2, 21)
P value	0.1408
P value summary	ns
Are SDs significantly different (P < 0.05)?	No
Bartlett's test	
Bartlett's statistic (corrected)	7.458
P value	0.0240
P value summary	*
Are SDs significantly different (P < 0.05)?	Yes

ANOVA table	SS	DF	MS	F (DFn, DFd)	P value
Treatment (between columns)	0.6721	2	0.3361	F (2, 21) = 8.602	P=0.0019
Residual (within columns)	0.8204	21	0.03907		
Total	1.493	23			

Data summary	
Number of treatments (columns)	3
Number of values (total)	24

Table Analyzed	**Fish_ddt_dry**
River waters	
Data sets analyzed	A-C
ANOVA summary	
F	7.139
P value	0.0043
P value summary	**
Significant diff. among means (P < 0.05)?	Yes
R squared	0.4047
Brown-Forsythe test	
F (DFn, DFd)	3.607 (2, 21)
P value	0.0450
P value summary	*
Are SDs significantly different (P < 0.05)?	Yes
Bartlett's test	
Bartlett's statistic (corrected)	14.69
P value	0.0006
P value summary	***
Are SDs significantly different (P < 0.05)?	Yes

ANOVA table	SS	DF	MS	F (DFn, DFd)	P value
Treatment (between columns)	1.981	2	0.9906	F (2, 21) = 7.139	P=0.0043
Residual (within columns)	2.914	21	0.1388		
Total	4.895	23			

Data summary	
Number of treatments (columns)	3
Number of values (total)	24

Appendix XIV: **Picture gallery (a – n) showing sampling stations and related activities**.

(a) On-farm earthen fish pond for aquaculture practices:

(b) Ice-box having water & fish samples for laboratory analyses:

(c) PhD student carrying out field data collection:

(d) Electro-fischer machine fish sampling:

(e) Wastewater lagoons, Kisii Urban Centre:

(f) Gas chromatography (GC) machine with MS computer equipment:

(g) Artisanal fishers at WW tertiary lagoons:

(h) Water sampler & the Ekman, bottom grab equipments:

(i) Functional coffee bulberry/factory:

(j) Research assistants using Electro-fischer equipment:

(k) Sampling at existing fish ponds:

(l) River/stream within upstream catchment:

(m) Cattle dip for livestock spray:

(n) Earthen fish ponds for fish culture practices:

Appendix XV: **Copy of National Research Fund research permit.**

REPUBLIC OF KENYA

NATIONAL COMMISSION FOR SCIENCE,TECHNOLOGY & INNOVATION

Ref No: **592378**

Date of Issue: **02/March/2021**

RESEARCH LICENSE

This is to Certify that Mr.. Joseph Kiyuka Nyaundi of Kisii University, has been licensed to conduct research in Kisii on the topic: PESTICIDE LEVELS IN CULTURED AND WASTEWATER RAISED FISH, FISH POND EFFLUENT AND RECEIVING WATERS IN HIGH DENSITY POPULATED AREAS OF SOUTH WESTERN KENYA for the period ending : 02/March/2022.

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Appendix XVI: **Copy of Research Introductory letter.**

Telephone: 057 250 3197
Email: postgraduate *a* kisiiuniversity.ac.ke

KISII UNIVERSITY

P. O. Box 408-40200
KISII, KENYA.
www.kisiiuniversity.ac.ke

OFFICE OF POSTGRADUATE STUDIES

KSU/SPGS/NACOSTI/02 8th December, 2014

The Secretary
NACOSTI
P.O Box 30623
NAIROBI

Dear Sir,

RE: JOSEPH KIYUKA NYAUNDI (DAS/6004/14)

I wish to confirm that Mr. Joseph Kiyuka Nyaundi is our bonafide PhD. Student enrolled in the Faculty of Agriculture Natural Resource Management in the Department of Applied Aquatic Sciences and is pursuing the Phd. of Limnology Science. He has completed his coursework and written a proposal for his thesis. The proposal has been approved and is ready for data collection, analysis and finally write the thesis.

The office of the Postgraduate Studies, is highly recommending him for the research grant he has applied for from your organization to enable him carry out the research work, write and defend his thesis and be ready to serve the country. Any assistance that will be given to this student will be appreciated.

Thank you so much

Yours sincerely,

KISII UNIVERSITY DIRECTOR 08 DEC 2014 P.O. Box 408-40200,KISII SCHOOL OF POSTGRADUATE STUDIES

Prof. B.A. Ondigi, **PhD, MKIM**
DIRECTOR SCHOOL OF POSTGRADUATE STUDIES.

cc. **VC -to note in file**
DVC (ASA)
DVC (A&F)
Dean FARNM

Appendix XVII: **Copy of plagiarism report.**

ASSESSMENT OF PESTICIDE RESIDUE LEVELS IN WATER, WASTEWATER LAGOONS, FISH PONDS AND FARMED FISH IN THE CATCHMENT OF RIVER KUJA, KENYA

ORIGINALITY REPORT

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