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ECOLOGICAL AND HUMAN HEALTH IMPLICATIONS OF CONTAMINANTS LINKED WITH CAGE AQUACULTURE IN THE VOLTA BASIN OF GHANA

BY

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DECLARATION

I, Emmanuel Kaboja Magna, declare that the materials contained in this thesis are my original work conducted at the Institute for Environment and Sanitation Studies, University of Ghana, Legon, under the joint supervision of Prof. Christopher Gordon, Prof. Augustine Donkor and Dr Samuel Senyo Koranteng. Except where acknowledged, no part of this study has been discussed for some other degree in the past.

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ABSTRACT

The presence of persistent organic pollutants (POPs) and heavy metals in farmed fish raises a global concern. There is the need for comprehensive monitoring of these pollutants, which present risk to the aquatic ecosystem as well as to humans through the dietary consumption of farmed fish. The levels of selected indicators: polychlorinated biphenyls, organochlorine pesticides and heavy metals in water, sediment, cage tilapia and fish feed samples from four cage aquaculture farms on the Volta Basin were investigated. The organochlorine pesticides (OCPs) were quantified using the Gas Chromatography equipped with Electron Capture Detector (GC-ECD); the polychlorinated biphenyls (PCBs) with GC/MS and the heavy metals, the Atomic Absorption Spectrometer (AAS). Hexane was used as a solvent for the water extraction for pesticides. At the same time, sediment, cage tilapia and fish feed were sonicated in an ultrasonic bath using an acetone/hexane (2:1v/v) solvent mixture. After the clean-up, the eluates were condensed in a rotary vacuum evaporator and collected in 2 ml ethyl acetate vial for GC analysis. A mixture of $HNO_3/HCl/H_2O_2$ was used to digest fish, fish feed, sediment, and water samples for heavy metals. The concentrations of OCPs in water range, <LOD – 0.799 µg/l (fish farm A), <LOD – 0.520 µg/l (fish farm B), <LOD – 1.173 µg/l (fish farm C), <LOD – 0.280 µg/l (fish farm D) and <LOD – 0.037µg/l (Control). The predominant OCPs in water were methoxychlor, *o,p'*-DDD, *α*-endosulfan, methoxychlor, and δ-HCH in fish farms A, B, C, D, and control, respectively. The sediment OCPs levels range; <LOD – 8.253 µg/kg (fish farm A), ND – 6.00 µg/kg (fish farm B), ND – 2.362 µg/kg (fish farm C), ND – 13.861 µg/kg (fish farm D) and ND – 0.503µg/kg (control). *δ*-HCH, *o,p'*-DDD, α—endosulfan, *o,p'*-DDD and heptachlor were the predominantly detected OCPs in sediment sampled from fish farms A, B, C, D and control respectively. For the fish feed, the levels of the OCPs

range ND – 2.21 µg/kg, ND – 4.02 µg/kg, ND- 7.87 µg/kg in fish farms A, B and D, respectively. Similarly, for the fish, the ranges were; ND – 2.310 µg/kg (fish farm A), <LOD – 4.260 µg/kg (fish farm B), <LOD – 6.109 µg/kg (fish farm D) and ND – 0.878 µg/kg (control). The highest concentration of 6.109 µg/kg was encountered for δ-HCH in the tilapia for fish farm D, whiles *p,p'*-DDE recorded the lowest in farm A. PCBs in water recorded a range of ND – 0.508 ng/l in fish farm A, ND – 0.528 ng/l in farm B, ND – 0.815 ng/l in farm C, ND – 0.594 ng/l in fish farm D and ND – 0.173 ng/l in control. In the sediment, the mean ranges of the PCBs were ND – 0.492 ng/g, ND – 0.475 ng/g, ND – 0.394 ng/g, ND – 3.328 ng/g and ND – 0.113ng/g in fish farms A, B, C, D and control respectively. For the heavy metals, Pb, Zn, Fe, Mn, Ni and Cr were detected in the water, sediment, fish feed and fish samples. The concentrations of OCPs, PCBs, and heavy metals in water, sediment, fish feed and fish were below the EU/WHO/USEPA MRL except for heptachlor in water from fish farms A, B, D, and endrin in the fish farm C. Pb in water and Mn in fish reported levels above the MRL. The study revealed that the pesticides in the sediment were from anthropogenic sources such as agricultural, industrial and municipal waste. Evaluating the ecotoxicological risk of the pesticides in the surface sediment using the sediment quality guidelines, it was evident that only ∑HCH could pose a health risk to the benthic organisms. It was also observed that the heavy metals detected in the sediment originated from both anthropogenic and lithogenic sources. There was a low potential ecological risk of the heavy metals to the organisms in the sediment during the period of observation. There was no health health risk associated with the consumption of caged tilapia, except tilapia from farms B and D contaminated with endrin, Cr, Ni, and As that could pose cancer risk to consumers. Further Laboratory-based research should be conducted on other contaminants and a detailed potential health risk assessment estimated for the sustainability of the aquaculture industry

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
ADI	Average Daily Intake
ARDEC	Aquaculture Research and Development Centre
ASV	Average Shale Value
ATSDR	Agency for Toxic Substances and Disease Registry
AWPL	Aquatic life water permissible limits
BCF	Bio-concentration factor
BOD	Biochemical Oxygen Demand
CCME	Canadian Council of Ministers of the Environment
CFCs	Chlorofluorocarbons
CLRTAP	Convention on long-range transboundary air pollution protocol
COD	Chemical Oxygen Demand
CSF	Cancer Slope Factor
DGDs	Decision Guidance Documents
EDI	Estimated Daily Intake
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
EU	European Commission
FAO	Food and Agriculture Organisation
FDA	Ghana Food and Drugs Authority
FMC	Food Machinery Corporation
FSCBP	Fisheries Sector Capacity Building Project
GC/MS	Gas Chromatography equipped with Mass Spectrometer
GC-ECD	Gas Chromatography equipped with Electron Capture Detector
GDP	Gross Domestic Product
GFEA-U	German Federal Environment Agency–Umweltbundesamt
GHSCLC	Globally Harmonized System of Classification and Labelling of Chemicals
GPS	Geographical Positioning System
GSA	Ghana Standards Authority

HI	Hazard Index
HM	Heavy Metals
HPLC	High-Performance Liquid Chromatography
ILO	International Labour Organisation
IPCS	International Programme on Safety Chemicals
K_{ow}	Octanol-water partitioning coefficient
LC_{50}	Lethal concentration
LD_{50}	Lethal dose
MoFAD	Ministry of Fishery and Aquaculture Development
NOAA	National Oceanographic and Atmospheric Administration
OCP	Organochlorine pesticides
PBDEs	Polybrominated biphenyl ethers
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
PIC	Prior informed consent
PICT	Pollution-induced Community Tolerance
PLI	Pollution Load Index
POC	Particulate Organic Carbon
PON	Particulate Organic Nitrogen
POPs	Persistent organic pollutants
PTFE	Polytetrafluoroethylene
PTWI	Provisional Tolerable Weekly Intake
RFD	Reference dose
SAICM	Strategic Approach to International Chemicals Management
SDGs	Sustainable Development Goals
SQGs	Sediment Quality Guidelines
TBM	Transboundary Movements
THQ	The Hazard Quotient
TWQR	Target Water Quality Ranges (TWQR)

UNECE	United Nations Economic Commission for Europe
UNEP	United Nation for Environment Programme
USEPA	United States Environmental Protection Agency
USSR	Union of Soviet Socialist Republic
WHO	World Health Organisation
WRI	Water Research Institute

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

World fish production is estimated at approximately 179 million tons in 2018, with an overall first-sale value expected at USD 401 billion, of which 82 million tons were generated from the aquaculture industry, estimated at USD 250 billion (FAO 2020). Aquaculture alone accounted for about 46 percent of the total production and about 52 percent of fish for human consumption. Globally, food intake rates are increasing rapidly compared to population expansion, owing to the knowledge of the health benefits associated with fish consumption, increased incomes, enhanced foreign fish trade, and increased relative preference for fish protein (Chan *et al.*, 2017).

Over the past years, aquaculture has developed to become the fastest growing food-producing sector in the world. For instance, during the last fifty years, aquaculture has tremendously grown from the production of less than a million tonnes to about 80 million tonnes by 2016, amounting to about US$232 billion in revenue (FAO 2018). Aquaculture contribution has expanded significantly, with an estimated potential of 3.5 million tonnes per year in Africa (Shaheen *et al.*, 2013). The aquaculture sector is a food industry that has rapidly grown worldwide by providing economic income and high-quality food products and employing many skilled and unskilled workers (Manage, 2018). Despite the undeniable benefits of aquaculture, its operations mainly have some environmental impacts, and so it is mostly criticized worldwide.

The African catfish (*Clarias gariepinus*), Nile tilapia (*Oreochromis niloticus*), and the African Arowana (*Heterotis niloticus*) are the frequently cultured fish species in Ghana currently (Rurangwa *et al.*, 2015). Ghana presently does not practice marine culture, primarily because of lack of technology, non-existence of sound policies, inadequate expertise and certain related cultural limitations such as the land tenure systems (Amenyogbe *et al.*, 2018). Nonetheless, the aquaculture sector provides income and employment opportunities, reduces poverty and improve food and nutrition security in developing countries, including Ghana (Chan *et al.*, 2017). The aquaculture and inland fisheries contribute about 30% of the total fish production in Ghana. It is also projected that the Ghanaian fisheries contribute about 1.5 percent to the GDP yearly with a GDP growth rate of 5 percent (Asiedu et al., 2017). Around 80 percent of total domestic fish production is locally consumed, constituting almost 60 percent of the total animal protein intake (Asiedu et al., 2017). According to the Fisheries Commission of Ghana, Ghana's annual fish protein demand is about 960,000 metric tons (Ayisi, 2017). Despite this huge demand, the nation can produce about half of the quantity demanded locally from freshwater, brackish water, and marine water, promoting aquaculture in Ghana.

Significant sources of aquaculture production in Ghana are cages, ponds, tanks, dugouts, and small reservoirs (Rurangwa *et al.*, 2015). The cage system of culturing fish in Ghana accounts for 2% of the farms by number with a higher by-catch output (Amenyogbe *et al.*, 2018). Most of the cage aquaculture farms are located around the Kpong Dam and the Akosombo Dam. The medium-sized and small cage farms are also found in Akuse in Lower Manya Krobo District, Akrusu in Upper Manya Krobo District of Eastern Region, and Kpeve in South Dayi District of the Volta Region. Several cage aquaculture systems are run by large-scale commercial farmers on Lake Volta, with very few farmers practising aquaculture in earthen ponds. Tilapia (*Oreochromis niloticus*) is the most cultured species preferred by the consumers (FAO, 2016).

The small-scale aquaculture farmers use a variety of feeds, including cereals such as; rice bran, maize bran, and wheat bran. On the other hand, the large commercial farmers obtained their feed from Rannan and beacon hills produced in Ghana. Others are imported from the USA, Netherlands, Denmark, Brazil, and Vietnam (Karikari, 2017). Even though aquaculture reduces fisheries pressure over natural resources and creates a large volume of businesses worldwide, it faces many challenges, partly relating to environmental issues and fish product quality (Ginés *et al.*, 2018).

In recent times POPs have negatively impacted the environment, drawing most scientific and public attention. POPs are hazardous substances characterized by substantial environmental persistence, bioaccumulation and biomagnification along the food chain and negatively affect human health and the environment (UNEP, 2001; Yohannes, 2014). POPs are chlorinated compounds with carbon-chlorine bonds, which are difficult to break. They are semi-volatile, thereby favouring their long-range transport. Owing to their persistence, as well as lipophilic in nature, they accumulate in biological matrices. For these reasons, many organochlorines made the Stockholm Convention’s “dirty dozen” list for POPs of global concern. Because of their harmful nature, United Nations Environment Program (UNEP) and the Stockholm Convention on POPs aim to eliminate or restrict the use and emission of some of the compounds. Thus, the POPs include PBDEs, OCPs, PCBs, PCDFs, PCDDs, PAHs, and degradation products. Exposure to persistent organic compounds has been linked to a wide range of conditions, for example, reproductive toxicity, immunotoxicity, hepatoxicity, neurotoxicity, necrosis, and endocrine abnormalities (Buah-Kwofie *et al.*, 2010).

Fish meal and fish oil constitute about 50–70% of all material in fish feed. Typically, the fat content of the fish meal is 2–20%, and the dry matter content is about 90%

(Suominen *et al.*, 2011). In aquaculture, dioxins or PCBs and organochlorine pesticides are the persistent organic pollutants present in aquafeed manufactured with fish oil and fish meal (Easton *et al.*, 2002; Antunes and Gil, 2004; Hites *et al.*, 2004; Navas *et al.*, 2005; Bordajandi *et al.*, 2006; Maule *et al.*, 2007; Kelly *et al.*, 2007; McKee *et al.*, 2008; Serrano *et al.*, 2008; Shaw *et al.*, 2008; Botaro *et al.*, 2011; Perugini *et al.*, 2013). For example, in the Atlantic salmon diet, concentrations of DDT, PCBs and PBDEs were measured to be 36, 66 and 10.9 ng g $^{-1}$, respectively (Grigorakis & Rigos, 2011). These undesirable contaminants in the farmed high energy Atlantic salmon were due to the fish oils from pelagic fish species used as a feed ingredient in the salmonid feeds (Berntssen *et al.*, 2016).

Amlund *et al.* (2012) similarly found that in farmed rainbow trout, the dietary retention of sum chlordane (*cis-trans* and oxy-chlordane) and sum toxaphene in the edible part of market-size fish was approximately 33 and 27%, respectively. McKee *et al.* (2008) established low levels of Chlordane, DDT, dieldrin, Lindane, heptachlor and HCB in trout (*Oncorhynchus mykiss*) muscle and feed samples. Botaro *et al.* (2011) also revealed that chlordane-related compounds might be transferred to farmed fish through the feed.

Other POPs sources in animal feeds include feed additives such as anti-caking substances, minerals, vitamin mixtures and supplements (Kim *et al.*, 2007). These feed additives can also give incidental high PCDD/Fs and *dl*-PCBs animal feed contamination that exceeds normal background levels (Berntssen *et al.*, 2016).

Furthermore, the global expansion in the aquaculture industry and the public health risk associated with the dietary consumption of the farmed fish, the development of farmed fish feed with fish oils and fish meals are currently replaced with vegetable oil and meal in most of the developed countries (Ytrestoyl *et al.*, 2015). Inadequate information exists in literature with regards to the aquaculture feed imported into Ghana.

Ghana's main farmed fish species are the *Clarias gariepinus, Heterotis niloticus,* and *Oreochromis niloticus* in freshwater. Whereas few studies on POPs and heavy metals have been documented in freshwater and marine fishes in Ghana (Kuranchie-Mensah *et al.*, 2012; Ntow, 2005; Gbeddy *et al.*, 2015; Adu-Kumi *et al.*, 2010; Asante *et al.*, 2013; Elegbede *et al.*, 2015; Gbeddy *et al.*, 2012; Karikari, 2017), little or no studies have been carried out on POPs, and heavy metals in cage farmed fish in Ghana. Therefore, it is imperative to examine the impact of these contaminants in Ghana as they can create severe economic and health problems.

1.2 Problem Statement

In 2016, aquaculture production in Africa increased by 18% (FAO, 2018). However, there has been a growing concern about pollution of the aquatic environments with contaminants such as pesticides and heavy metals by intensive aquaculture systems. Trace metal contaminants enter the environment around fish farms from various sources. According to Russell *et al.* (2011), fish farms cages and structures are prone to biofouling, and to reduce the effects of biofouling, antifoulants are applied to the structures. These antifoulants have copper and little zinc as their active ingredient, which leaches gradually into the water. Due to the continued expansion of aquaculture to meet the demand for aquatic food products, the use of copper-based antifoulants is likely to increase, and there is concern about the accumulation of copper in the farmed fish, water and sediments below fish farms and its potential toxicity to benthic organisms (Russel *et al.*, 2011).

Studies have shown that persistent organic pollutants and heavy metals tend to bioaccumulate in fish via direct uptake of these compounds present in water, sediment and fish diet (Botaro *et al.,* 2011). Polybrominated biphenyl ethers (PBDEs), organochlorine pesticides, polychlorinated biphenyl and dioxins are recognized contaminants of the fish oil components of the feeds (Maule *et al.*, 2007; Russel *et al.,* 2011). Fishmeal and fish oil form as much as 65% of the fish feed used in the aquaculture industry (Russel *et al.*, 2011).

Studies demonstrated that fish meal derived from trash fish generally contains some heavy metals with high concentrations as mercury (Hg), Cadmium (Cd), and Lead (Pb), and this contains these heavy metals more than fish meal derived from fish oil where levels are low, most often below the limit of quantification (Cd = 0.07–0.40µg/g dry weight; Pb = 0.12–2.05µg/g dry weight) (Amlund *et al.*, 2012; Sabbir *et al.*, 2018; Mo *et al.*, 2019). Plant oil, such as rapeseed oil, used by some fish feed manufacturers, has been investigated to contain arsenic and lead where levels up to 0.5 and 1.1 mg/kg, respectively (Amlund *et al.*, 2012). Heavy metals such as zinc (Zn), iron (Fe), manganese (Mn), arsenic (As), cobalt (Co), copper (Cu), and selenium (Se) are combined with fish feeds to fulfil the mineral requirements (Grigorakis & Rigos, 2011).

According to Sapkota *et al.*, 2008, fish feeds formulated with metals to meet the nutritional requirements are responsible for sediment contamination and the water column underneath fish cages. In the light of this assertion, some heavy metals such as Pb, Ni, Zn, Cu, Fe and Cd have been analysed in the eastern Mediterranean in the water column and sediment beneath cages (Basaran *et al.*, 2010). These heavy metals can bioaccumulate in fish and biomagnify in the food chain, resulting in deleterious effects on humans, such as renal system disorders, neurological, and cardiovascular (Ahmed *et al.*, 2016; Mwakalapa *et al.*, 2019).

Some studies have also shown that levels of POPs in fish oils depend on the fish species and geographic location. For example, fish oil from Pacific fish species has been shown to have lower levels of dioxins and dl-PCB than oil from fish species in the North Sea (Lundebye *et al.*, 2017). The presence of residues of these environmental contaminants in foods of aquatic origin has led to more significant calls for information on the presence of these compounds in products entering overseas markets (European Food Safety Authority, 2006). These contaminants (POPs and heavy metals), as indicated earlier, can bioaccumulate in the fish. So, feeding fishery products and by-products to farmed fish can potentially raise the levels of these pollutants in the farmed fish. These then biomagnify as they move up the food chain to their final consumers, humans.

There have been drastic expansions in the cage aquaculture system in Ghana, with several small, medium and large commercial cage farms situated on the Volta Basin. In 2013, the Ghanaian aquaculture production increased from 32,500 mt/yr to about 52,000 mt/yr in 2016. It is even predicted to reach 72,000 mt in the next 3-5 years (Amenyogbe *et al.*, 2018). Out of the total aquaculture production, cage production alone constitutes about 74% (Karikari, 2017). Even though aquaculture is fast growing in Ghana and contributes immensely to the country’s economy, there is a concern about the pollution of aquatic environments by chemical contaminants. Several contaminants from wastes, bush burns, oil fields, and agricultural fields, made up of pesticides, fertilizers and agrochemicals, drain into the lake through runoffs after rainfall. Such pollutants negatively affect the lake's water quality and affect the aquatic ecosystem and, ultimately, the fish population (Ntow, 2005).

Again, some aquafeeds are manufactured within the country while others are imported, particularly from the Asian countries where aquaculture is practised. The feeds are manufactured with cereals, fish oil, vegetable oil, and trash pelagic fish from different sources through some processes. These processes require comprehensive safety controls to monitor the presence of heavy metals and POPs, which present a risk for human health through animals fed with contaminated feeds. The research questions that readily arise following the above challenges are:

1.3 Research questions

1. Is the Volta Basin cage aquaculture farms polluted with POPs and heavy metals?
2. Does the level of POPs and heavy metals in the farms pose a significant threat to the aquatic organism?
3. Is the population exposed to any health risk through the consumption of the cage tilapia from the Volta Basin?
4. Is the fish feed from the farms safe of the POPs and heavy metals for the cage tilapia?

1.4 Objectives of the Study

The study's main objective was to investigate the levels of persistent organic pollutants (organochlorine pesticides and polychlorinated biphenyl) and heavy metals residues in the Nile tilapia (*Oreochromis niloticus*) cultured on the Volta basin and their potential toxicological risk assessment on humans through the dietary consumption of the tilapia.

The specific objectives are to:

1. Investigate the levels of heavy metals, OCPs, and PCBs in sediment, water, fish feed and the cage cultured Tilapia (*Oreochromis niloticus)* on the Volta Basin
2. Assess the sources and ecological risk of OCPs as well as heavy metals pollution in the surface sediments from the Volta Basin
3. To determine the potential human health risks associated with the dietary intake of cage-fish (Nile tilapia) in terms of POPs and heavy metals pollution

CHAPTER TWO

LITERATURE REVIEW

2.1 Persistent Organic Pollutants (POPs)

POPs are mostly halogenated and are often characterised by their high lipid and low water solubility. POPs are resistant to degradation, mobile, and widespread over large areas, even in areas where they have never been used or produced. They are present in biota and soil sediments in quantities of parts per billion or million and water samples in quantities of parts per trillion. Therefore, efficient, exact and accurate analytical techniques are needed to detect their traces and ultra-trace in many matrices (Osibanjo and Ayejuyo, 1994). POPs include PCBs, furans, OCPs and dioxins. This study focuses on POPs such as organochlorine pesticides and PCBs.

2.1.1 Organochlorine Pesticides (OCPs)

Organochlorine is an organic compound containing hydrogen, carbon, chlorine and sometimes oxygen and sulphur, whose electron pairs share with more or one chlorine atom to form a covalent bond. According to the following, organochlorine pesticides (OCPs) are synthetic, non-polar, poisonous and environmentally persistent dichlorodiphenylethanes, cyclodienes, or chlorinated benzenes used for pest control Ogunfowokan *et al.* (2012). They are also known by other names: chlorinated hydrocarbons, chlorinated organic substances, chlorinated insecticides, and chlorinated plastics. Most industrial chemicals such as polychlorinated dibenzodioxins (PCDDs) or dioxins, polychlorinated biphenyls (PCBs) and chlorofluorocarbons (CFCs) are therefore classified as organochlorine.

They were widely used in agriculture and for mosquito control from the 1940s to the 1960s. Farmers use oCPs to control weeds, weevils, vectors such as tsetse flies and mosquitoes. The full use of pesticides worldwide, particularly in developing countries to maximise crop yields, has led to widespread contamination worldwide.

The OCPs exhibit properties that contribute to their persistence and accumulation in the environmental matrices due to the C-Cl bonds. OCPs are stable during hydrolysis because of C-Cl bonds, and their stability increases as the number of chlorine atoms increases. This persistence gives it the value of pest control, such as termites around homes (Ogunfowokan *et al.*, 2012). OCPs have a greater degree of halogenation, resulting in high lipid solubility and low solubility in water (Koranteng, 2015). This causes them to easily pass through the phospholipid structure of the biological membrane and accumulate in fat deposits. OCPs have a strong affinity for suspended particulate matter. They are subsequently deposited into the river and marine sediments or wetland soils due to their low water solubility and high hydrophobicity (Yang *et al.*, 2005). They can also be carried by water and air in trace quantities worldwide (Alle *et al.*, 2009). Heptachlor, mirex, toxaphene, aldrin, dichlorodiphenyltrichloroethane (DDT), Chlordane, dieldrin, endrin, and hexachlorobenzene are among the "dirty dozen" of the Twelfth Stockholm Convention on Persistent Organic Pollutants (Li *et al.*, 2014; UNEP, 2004). Li *et al.* (2014) further reported that six OCPs were included in the list of POPs contaminants at the fourth meeting of the Stockholm Conference of the Parties held in 2009. Organochlorine pesticides can be classified into three categories, according to Agbeve (2014):

1. Dichlorodiphenylethanes such as DDT, DDE, DDD or TDE, methoxychlor, perthane and dicofol (kelthane)
2. Chlorinated cyclodienes such as aldrin, dieldrin, endrin, heptachlor, Chlordane, and endosulfan
3. Chlorinated benzenes and cyclohexanes such as HCHs, toxaphene, mirex, HCB, and chlordecone

2.1.1.1 Dichlorodiphenyltrichloroethane and its Metabolites

Muller reported the insecticidal capacity of DDT in controlling moths on the cloths at a research facility in 1939, which started the use of organochlorine pesticides for pest management (Matsumura, 1975). DDT is the most widely used and known insecticide worldwide. It was used as an insecticide and to control malaria and typhoid disease vectors during World War II. DDT usage against malaria vector control is believed to have saved millions of lives. Therefore, it was described as a beautiful, miraculous chemical by Sir Winston Churchill in 1945 because of its use in the war front and its effectiveness against body lice that transmit typhus against plague-carrying fleas and mosquitoes that carry malaria yellow fever.

As of 1945 in the US, DDT was made common for public sale. The government promoted industrial use, agricultural and household application. However, opposition to its use was realized by the 1962 publication of Rachel Carson’s book Silent Spring book. The document drew the general public's attention to the adverse effects of DDT released into the atmosphere. It challenged the rationale of broadcasting potentially poisonous chemicals without advancing their effects on the environment and health. Carson’s research pointed out that the chemical has adverse effects on organisms, such as bald birds. She, therefore, described DDT as the ‘elixir of death’ (Carson, 1962). Carson’s work attracted outrage from the pesticide industries and other social groups. Despite her fact-finding about the adverse effect of DDT, her credibility as a scientist was attacked and vilified. Due to the high toxicity of DDT, its usage was prohibited in most countries in the 1970s. The toxicity of the substance also brought about its restriction to disease vector control under the Stockholm Conventions on POPs. Between the 1970s and 1980s, global bans and prohibitions were implemented, but due to their cheap cost and versatility in pest control, some developing nations still use OCPs for agricultural practices and public health (Xue *et al.*, 2006; Williams, 2013). Their use may result from a lack of sufficient regulatory oversight and implementation of these chemicals' production, as well as their trade and use (Williams, 2013).

It is well assumed that OCPs cause the thinning of eggshells in bird species, cause reproductive failure (UNEP, 2004), and have possible endocrine-disrupting adverse effects and cancer risk in humans (Eskenazi et al. 2009; Snedeker, 2001). Dichlorodiphenyltrichloroethane (DDT) breaks down to dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE) in the body or the environment. DDE is produced by the removal of hydrogen chloride (HCl), and dichlorodiphenyldichloroethane (DDD) is formed by reductive dechlorination (Baird & Cann, 2005). During sample analysis, the addition of all DDT congeners is often grouped as total DDT. Dichlorodiphenyldichloroethane was also produced as an insecticide, but to a much lower degree than DDT (Koranteng, 2015). During DDT production, some reach the air, water, and soil, thereby reaching where it was not applied (Farooq & Harris, 2002). DDT is found in many dumping grounds; and, therefore, tend to pollute the environment.

Most DDT in the environment presently results from its current and past use in different geographical locations. DDD and DDE are present only in the environment due to the pollution or degradation of DDT. Also, DDT sprayed to control mosquitoes, insects in crops, and forests may be released into the air, water and soil; these are transported in the air over a long distance away from their source. When they evaporate from polluted soil and water, they travel to a far distance where they were not used, making them available within the air. These contaminants have indeed been detected in the Arctic and Antarctic regions in bogs, snow, and wildlife, beyond where they have never been used (Farooq & Harris, 2002). DDT, DDE and DDD in the vapour form have a half-life of approximately 1.5-3 days, which may break down in the environment due to reactions from the sun rays (Farooq & Harris, 2002). These chemicals last longer in the soil, while in the soil, DDT breaks down into DDE and DDD by the activity of the microorganisms. They bind strongly to the soil until they are washed into rivers and lakes during runoff. Few of the DDT, DDE and DDD seep into the ground polluting the groundwater. In surface water, DDT binds with other particulates matter, thereby depositing in the sediment. DDT may also be absorbed by fish and other small organisms in the water. In invertebrates (like whales and seals) and fish, this persistent chemical accumulates at elevated amounts, thereby reaching thousands of times higher levels than in the water. The highest levels/deposits of DDT in their fatty tissue are found in animals. DDT in the soil can also be uptaken by some plants and animals or people who eat those crops. Figure 2.1 indicates the degradation pathways of DDT and its metabolites.

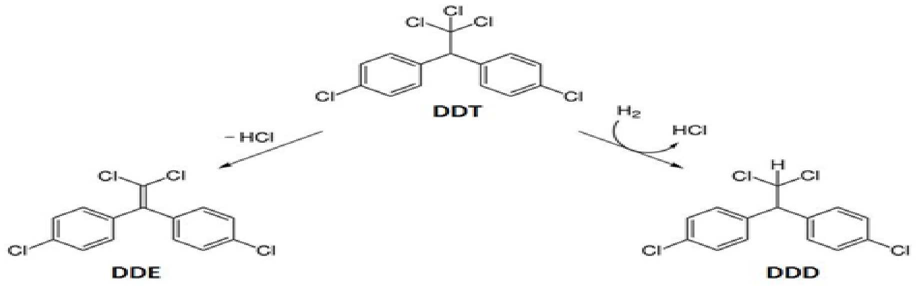


Figure 2.1: Degradation of DDT to form DDE and DDD

2.1.1.2 Chlorinated Cyclodienes

Chlorinated cyclodienes consist of aldrin, Chlordane, dieldrin, endosulfan, endrin and heptachlor. They are produced from the Diels-Alder dienes reaction. Dieldrin and aldrin were produced during the war in Europe. They were used in sheep baths and as a seed dressing in the United Kingdom and were even used to control tropical diseases caused by mosquitoes and locusts (Jefferies & Hanson, 2000). Jefferies & Hanson

(2000) went on to say that sloe, for example, has been used as a foliar insecticide on a wide variety of crops. It acts as an avicide and rodenticide. Endrin is a stereoisomer of dieldrin and is structurally similar to aldrin and heptachlor epoxide. Endrin can be absorbed in the sediment and persists in the environment for some time. It has the ability to adsorb in the subcutaneous fat of marine animals and is highly toxic to aquatic species. Endrin has a half-life of about ten years. Exposure of humans to endrin is through inhalation of dust or vapour, skin absorption, and affects the nervous system when it enters the body.

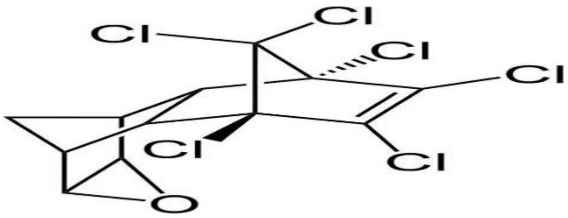


Figure 2.2: Molecular structure of Endrin

Heptachlor has a molecular name, (1, 4, 5, 6, 7, 8, 8-heptachloro-3a, 4, 7, 7a-tetrahydro-4, 7-methanoindene). It is a whitish powder with an insecticide property (Rashid, 2011). Heptachlor technical grade contains 28% of other related compounds and 72% heptachlor

Heptachlor acts as an endocrine disruptor, therefore altering the body’s hormonal system. It is primarily used to control insects and pests in cotton and corn. It is also used in combatting malaria. Heptachlor shows several properties; it is not soluble in water and binds strongly to aquatic sediments and bio-concentrate in the fatty tissues of organisms. Heptachlor evaporates readily into the air. It persists for a long time in the soil and breaks down into a more toxic compound, heptachlor epoxide (Rashid, 2011). The product, heptachlor epoxide, residue in the soil, has levels more than the parent compound because of its rapid degradation compared to heptachlor. Heptachlor epoxide dissolves in water easily and therefore gets absorbed into soil particles and persists in soil and water for a long time.

Their environmental persistence makes them available in breast milk, dairy products, fish and drinking water through the food chain until being absorbed by the human. Humans may also inhale them from disposal sites or when they get into contact with the contaminated soil. During the 1970s, its usage in the United States slowed. In 1988, the U.S. Environmental Protection Agency banned the selling of all its products and prohibited the use of heptachlor to combat fire ants in power transformers.

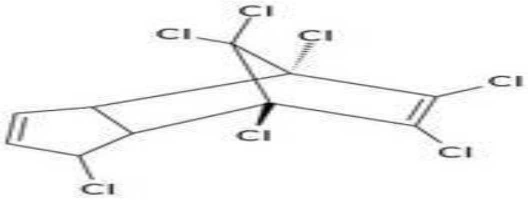


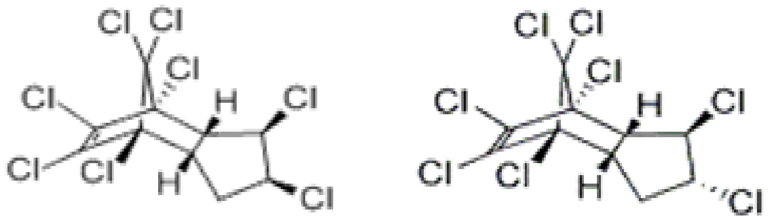
Figure 2.3: molecular structure of heptachlor

Aldrin and dieldrin are synthetic organochlorine insecticides that were used widely in agriculture in every part of the world to control insects in the soil and to promote public health through the control of mosquitoes, tsetse flies, as well as the vectors that cause malaria (Baird, 1997; Nollet, 2000). The technical-grade formulations contain no less than 85.5% of either chemical. It was named after a German Kurt Alder. Usually, Dieldrin, and endrin stereoisomer, is formed by epoxidation of aldrin with peracetic or perbenzoic acid. Both aldrin and dieldrin are made of clear-to-white crystals with densities higher than water in their "pure" formulations and low volatility and aqueous solubility. Both are relatively stable in the presence of organic and inorganic alkalis and mild acids, slightly corrosive to metals upon storage, and compatible with most fertilizers and pesticides.

The EPA eliminated the use of aldrin and dieldrin to control crop pests in 1974, and the use for termite eradication was voluntarily withdrawn by the producer in 1987. Aldrin is manufactured by adding norbornadiene together with hexachlorocyclopentadiene in a Diel-Alder reaction. Aldrin is transformed into Dieldrin upon entry into the human body or the natural environment. Aldrin's transformation into Dieldrin is by the activity of bacteria and the sun.

Aldrin has names such as Aldric, Aldrex, Drinox, Octalene, seedrin and compound 118. Aldrin and dieldrin enter the atmosphere primarily through crop treatment and soil volatilisation or directly during application. Aldrin and its reaction product dieldrin are absorbed in soil with high organic matter content.

Dieldrin binds closely to the soil and eventually disintegrates into the air. Some of these products seep into the ground polluting the groundwater. The transport of these compounds is through soil erosion and sediment transport. Dieldrin possesses the long-range distance property whiles in the environment and is blown by the wind as they are firmly attached to dust particles (ATSDR, 2002). Dieldrin and aldrin are not water-soluble but quickly attached to sediment and hardly seeped in deeper soil and groundwater layers. For that matter, their concentration in the water environment is low and less than 5ng/L. However, concentrations in the water may rise in areas of high agricultural activities with pronounced soil erosion and massive sediment transport. These compounds are less persistent in tropical areas as compared to temperate regions. These compounds bioconcentrate and biomagnify through the terrestrial and aquatic food chains.



Cis-chlordane

Trans-chlordane

Figure 2.4: cis-chlordane and trans-chlordane

Chlordane is a cyclodiene pesticide used between 1948 to 1988 on corn and citrus on lawns and domestic gardens to control termites (Robert, 2002). It has a chemical formula, $C_{10}H_6Cl_8$ (Octachloro-4,7-methanohydroindane). The technical grade chlordane consists of *cis*-chlordane ($\propto -$Chlordane), *trans*-chlordane (β-chlordane and γ-chlordane), *trans*-nonachlor and heptachlor, which degrades to heptachlor epoxide (Dearth & Hites, 1991). Chlordane is highly hydrophobic and binds strongly to the surface of the soil for about 20 years. It does not readily dissolve in water, and its effect on groundwater is negligible. Chlordane can persist in the ecosystem and eventually breaks down in the soil. In the soil, cis-chlordane residue levels are less than trans-chlordane due to the differences in their degradation rate (Rashid, 2011). The grades of Chlordane leave the soil's surface by evaporation process contaminating the air and its molecules dispersing to areas where they not applied. They evaporate slower from heavy soils as compared to the lighter and sandy soils. Some of the Chlordane bonds itself tightly to sediment particles in the water column and others are released into the air by evaporation. By reaction to light and some chemicals in the atmosphere, Chlordane decomposes (ATSDR, 1994).

Human exposure to Chlordane is mainly due to the intake of chlordane-contaminated soil-grown crops, the inhalation of chlordane-contaminated air mainly from landfill sources, and the ingestion of fish, dairy products and high-fat meat. The level of

Chlordane entering the body is dependent on the quantity of water, air, or food, in the body and the length of time an individual is exposed to it. Much of the Chlordane that reaches the body disappears after some days, mainly through faeces and other smaller quantities expelled through the urine. Large amounts of Chlordane taken by mouth can cause convulsions and death in people (Ware, 1988). Due to worries about cancer risk, it has documented evidence of human exposure and body fat deposition, persistence in the environment, and wildlife risk. It discontinued other above-ground applications for the next five years until it was eliminated for use by US EPA in 1988 (ATSDR, 1994).

Endosulfan is a chlorinated insecticide and acaricide that is chemically similar to DDT. In the 1950s, endosulfan was first developed by Farbwerke Hoechst and was manufactured by FMC in the USA. First registered in the United States in 1954, more than 1 million lbs of endosulfan were being used annually in commercial agricultural settings on a wide range of vegetables, fruits, cereals, and cotton, as well as ornamental shrubs, trees, vines, and ornamental herbaceous plants (US EPA, 2002). It emerged as a leading chemical used against a broad spectrum of insects and mites in agriculture and allied sectors.

The technical grade for endosulfan is a diastereomeric mixture of two biologically active isomers $\propto$-endosulfan and β-endosulfan along with certain impurities, and in a ratio of 7:3 (GFEA-U, 2007; Wan *et al.*, 2005). The β-endosulfan is converted to $\propto$-endosulfan but not vice versa (Schmidt *et al.*, 2001). Due to its acute toxicity, the potential for bioaccumulation, and its critical function as an endocrine disruptor. It has been commonly used to control insect pests such as whiteflies, aphids, potato beetles, and cabbage worms in agriculture. In the global atmosphere, it is one of the most abundant OCPs. It can be transported to remote areas, such as the Arctic regions, over an extended range of distances (Weber *et al.*, 2010) via wind and water currents. Because of this, many birds, marine mammals, and fish populations accumulate the residues in their fat cells, contaminating the traditional fish consumers'.

Endosulfan is believed to act directly on the central nervous system of fish, which can lead to detrimental effects such as convulsions, hyperactivity and, in severe cases, mortality (Rehman *et al.,* 2016). Endosulfan persists for an extended period in the soil, evaporating into the air and breaking very slowly (Afful, 2015). Endosulfan metabolizes into endosulfan diol and endosulfate, which are structurally similar to the parent compound.

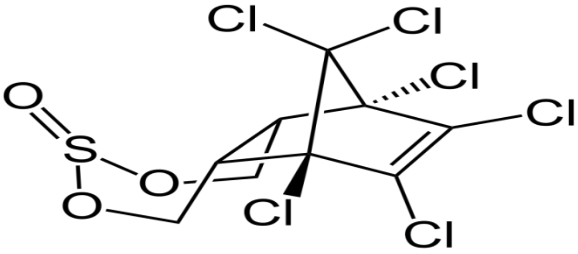


Figure 2.5: Molecular structure of Endosulfan

2.1.1.3 Hexachlorocyclohexane (HCH) and Hexachlorobenzene (HCB)

Hexachlorocyclohexane (HCH) has the IUPAC name 1, 2, 3, 4, 5, 6-hexachlorocyclohexane and molecular formula $C_6H_6Cl_6$. HCH has eight isomers (Afful, 2015). However, only four of the isomers ($\alpha - \mathrm{HCH}, \beta - \mathrm{HCH}, \gamma - \mathrm{HCH}, \delta - \mathrm{HCH}$) are of commercial significance. The $\gamma - HCH$, also known as the Lindane shown in figure 2.6, is the only isomer with the insecticidal property. The Lindane is used in many products to control lice and mites (scabies) in humans. Lindane has been used to treat food crops, forest products, soil treatment, and the treatment of livestock and pets, seeds and seedlings (Afful, 2015). During the production of technical lindane, isomers such as α-HCH and β-HCH are produced (Rashid, 2011).

These products are highly toxic than the parent compound lindane. However, they lack insecticidal properties. Lindane was initially synthesized in 1825 and later named after the Dutch chemist Teunis van der Linden (1884–1965), the first to isolate and describe γ-hexachlorocyclohexane in 1912. It is projected that global lindane usage from 1950 to 2000 for agricultural, livestock, forestry, human health, and other purposes amounts to around 600 000 tons (Sandu & Virsta, 2015). The products used for agricultural purposes were from Europe, Asia, the US, Africa, and Oceania (Vijgen, 2006). Even though all HCH isomers, including Lindane, are toxic, carcinogenic, endocrine disrupters and are known to exert damaging effects on the reproductive and nervous systems in mammals, it is ubiquitously used in tropical countries to increase agricultural yields because of its low production cost and significant pesticide properties (Salam & Das, 2012).

Lindane is predominantly high in the marine environment and the soils, with higher concentrations in cold regions. Like any other OCP, Lindane exhibits long-range transport within the atmospheres' most notably in the European territories (WHO, 2003). Onogbosele and Scrimshaw (2014) discovered α-HCH in the soils has half-lives of 161 days (Doelman *et al.*, 1990) and 55 days (Singh *et al.*, 1991), 100-184 days for β-HCH (Singh *et al.*, 1991), and 88 to 1146 days (aerobic conditions) and 12 to 174 days (anaerobic conditions) for γ-HCH (Slooff and Matthijsen, 1988). Through the application of lindane to control mosquitoes, agricultural and forestry applications, and contamination from waste plants, lindane enters into the water. The primary source of Lindane in drinking water is runoff and leaching/leachate from insecticide used on cattle, lumber, gardens (Humphreys *et al.*, 2007). Lindane has also been found in the surface and groundwater, especially in areas closer to dump sites, but the compound is not often found in drinking water supplies (ATSDR, 1998). Lindane is biodegraded in aquatic systems, and the estimated degradation half-lives of Lindane in rivers and lakes range from three to 300 days (Sang *et al.*, 1999). In surface waters, Lindane evaporates into a long-distance where it was not applied or manufactured. Lindane is categorized as “moderately hazardous” by WHO, and its production and use banned worldwide under the Stockholm Convention on persistent organic pollutants (Rashid, 2011)

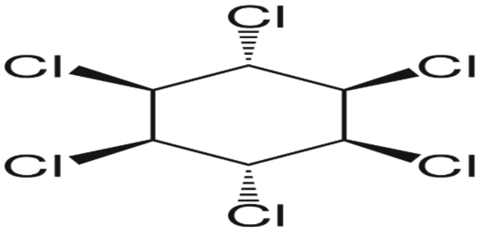


Figure 2.6: Molecular structure of α-HCH (Lindane)

Hexachlorobenzene was used as a seed dressing for crops pesticide to prevent fungi and as a chemical intermediate in the manufacture of dyes, synthesis of organic chemicals, rubber and wood preservation. It has a chemical formula C_6Cl_6 and an IUPAC name 1,2,3,4,5,6-hexachlorobenzene. It belongs to the class of chlorobenzenes that is benzene, in which chlorines replace all of the hydrogens. Commercial grade HCB comprises approximately 1.8 per cent pentachlorobenzene, 98 per cent HCB, and 0.2 per cent 1,2,4,5-tetrachlorobenzene (WHO-IPCS, 1997). Other industrial-grade contaminants of HCB include octa- and heptachlorodibenzofurans, decachlorobiphenyl and octachlorodibenzo-p-dioxin (EFSA, 2006).

The commercial production of HCB started in 1933, and the chemical is a white crystalline substance, insoluble in water and denser than water. Worldwide production of HCB as pesticides was estimated to be 10,000 tonnes/year from 1978-1981. The use of HCB in agricultural applications has been discontinued in many countries since the 80s. However, HCB is released unintentionally through the anthropogenic and non-anthropogenic processes. HCB is a by-product of industrial chemicals including carbon, tetrachloride, perchlorethylene, trichloroethylene and pentachlorbenzene. HCB is also released during the combustion of coal, waste incineration and specific metal processes.

The World Health Organization (WHO) has categorized Hexachlorobenzene as an “extremely hazardous” substance because victims exposed to HCB as a result of intake of treated seeds or food experienced symptoms such as photosensitive skin lesions, porphyrinuria and debilitation, colic, hyperpigmentation, and severe weakness, Breastfeeding children whose mothers consume contaminated food, died from a condition called “Pembe Yara” or “pink sore,” as a result of high doses of HCB in the breast milk.

HCB is neither rapidly degraded by biotic or abiotic processes nor by biotic or abiotic procedures but is readily dissoluble in organic compounds. It is relatively non-stable and volatilises easily. It is also resistant to the types of hydrolysis processes that may destroy other organochlorines or organophosphorus substances and is not subject to photolytic decomposition (Mill and Hague, 1986). The half-life of HCB is projected to be 2.7-5.7 years in surface waters and 5.3-11.4 years in groundwater (EFSA, 2006). Volatilisation from the water column is moderately rapid. However, strong adsorption of the compound with particles and organic substances in the water can result in the long-term preservation of the sediment material (EFSA, 2006). It is highly resistant to degradation and has a high partition coefficient (K_{OW}=3.03-6.42), and it is known to bio-concentrate in the fat of living organisms (Amuzu, 2012).

Hexachlorobenzene tends to remain in the environment for a long time and is a highly persistent compound; even in less concentration, these are toxic to birds, fish, and animals.

The high persistence combined with its high partition coefficient provides a suitable condition to bioconcentrate in the organisms. HCB half-lives for aerobics and anaerobic degradation range from 2.7 to 22.9 years (Ritter *et al.*, 1995; Chandra & Chaundhary, 2013). HCB's chemical properties, such as low water solubility, high stability and semi-volatility, are favourable for its long-range transport and are thus found in Arctic air, water and organisms (Amuzu, 2012). HCB is widespread in the atmosphere and is found in biological and environmental samples worldwide. HCB is included in the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution Protocol (CLRTAP-POP) and the Stockholm Convention on Persistent Organic Pollutants (POPs) (EFSA, 2006)

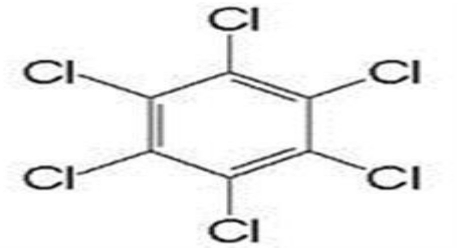


Figure 2.7: Molecular structure of Hexachlorobenzene (HCB)

2.1.2 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are the synthetic organic compounds produced from biphenyls by replacing hydrogen with chlorine atoms. PCBs are oily liquids or solids; clear to yellow in colour, no smell or taste. They are either manufactured as industrial chemicals for commercial reasons or generated accidentally during burning processes, particularly during incineration of waste. PCBs are among the first chemicals that are listed for restriction and elimination by the Stockholm Convention. They are therefore described as “dirty-dozen’’. There are 209 theoretically possible PCB congeners based on the number of chlorine atoms that can be substituted on the biphenyl rings (Antolin-Rodriguez *et al.*, 2016). Commercially, they are attractive because they are chemically inert liquids and are difficult to burn. They have low vapour pressures and are excellent electrical insulators. Polychlorinated biphenyls are often used as lubricating oils and refrigerants in condensers, electrical appliances and transformers. PCBs are also used for casting wax, hydraulic fluids, heat transfer devices, carbon paper, compressors, plasticizers, dyes, adhesives, fluorescent light ballasts and liquid-cooled electric motors (Reddy *et al.*, 2018). The estimated world production of PCBs is 1.5 million metric tons, of which about 10% is still in the atmosphere today (Wolska *et al.,* 2012; Reddy *et al.*, 2018).

PCBs are synthetic organic compounds called chlorinated hydrocarbons. Generally, they have the chemical formula $C_{12}H_{(10-n)}Cl_n$, where n is the number of chlorine atoms and ranges between 1 and 10. The two rings of a PCB molecule can rotate around the link that connects them. Repulsion between neighbouring chlorine atoms often affects the form. The rings of a given PCB are roughly in the same plane (called coplanar) or in a separate, more perpendicular (called non-planar) plane. Coplanar PCBs are "dioxin-like" and more toxic.

Technically, based on the various chlorination ability of the carbon atoms, there are 209 PCB (mono-to deca) congeners. PCBs' commercial production began in 1929, but their use has been prohibited or heavily limited in many regions since the 1970s and 1980s due to threats to public health and the environment. PCB products have been produced under the trade names viz., in the Kanechlor (Japan), Fenclor (Italy), Pyroclor (United Kingdom), Phenoclor (France), Aroclor (United States), Delor (former Czechoslovakia), Clophen (Germany), and Sovol for former USSR (USEPA, 2004; Reddy *et al.*, 2018). Twelve non-ortho and mono-ortho substituted PCB congeners such as dl-PCBs have shown similar toxicity as in polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) due to their specific chlorine substitution in positions that allow a planar conformation (Reddy *et al.*, 2018).

Due to the chemical stability of PCBs, both in biotic and abiotic environments, PCBs are persistent and sustained for years without substantial biodegradation, oxidation or reduction (Zeng *et al.*, 2013). The high solubility of lipid PCBs makes it possible to bind to lipid segments in animal tissues and concentrate on livestock through the food chain (Reddy *et al.*, 2018). Therefore, human exposure to PCBs is through diet, primarily from meat, fish and dairy products. PCB compounds often show a wide variety of toxicological reactions. These include reproductive deficits, tumour promotion, immunotoxicity, teratogenicity, carcinogenicity, and endocrine toxicity.

2.2 General characteristics of Persistent Organochlorine Compounds

It is established that about 40% of the pesticides used to belong to the OCPs compounds because of their low cost and efficient action against several pests in the agricultural industry (Gupta, 2004; Jayaraj *et al.*, 2016). Pollution of these pesticides in air, water and soil has increased due to their elevated application in agricultural fields.

2.2.1 Persistence

The tendency of a toxicant to remain unchanged and active over extended periods is known as persistence. In the environment, OCPs are detected via contaminated waste disposed of in landfills, aerial spraying of pesticides and other discharges from industrial units. OCPs are volatile and stable, allowing them to bind to the soil and air, increasing their likelihood of persistence in the different environmental matrices. The persistence of OCP compounds varies from moderate persistence with a half-life of approximately 60 days to high persistence with a half-life up to 10–15 years (Augustijn-Beckers *et al.*, 1994; Jayaraj *et al.*, 2016). The most frequently applied pesticide in agricultural practice is the DDT, which is highly persistent and has a half-life of 2–15 years (Jayaraj *et al.*, 2016). Pesticide's persistence allows long-range environmental transport and subsequent deposition and accumulation in the soil, sediments and living systems.

Certain physical factors may influence the persistence of organochlorine pesticides, including pH, light, moisture and temperature. However, some microorganisms may break down organochlorine compounds in the environment as well as in living tissues.

2.2.2 Toxicity

The toxicity of a substance is the capacity of that substance to cause injury/harm to a living organism. The toxicity of a compound depends on several factors, including the dose time. The dose is the amount or quantity of a chemical that a surface plant or animal is exposed. The dose-time categorizes toxicity into acute and chronic. Acute toxicity refers to how harmful a pesticide is to an organism after a specific short-term exposure. When a pesticide is applied, non-target organisms may be exposed to it, experiencing the acute and short-term toxic effects. The acute effect usually occurs immediately or within a 24-hour exposure period. After a period of exposure, the organisms begin to experience decreasing levels of exposure as the pesticide gradually disappears through decomposition and other dissipation pathways.

However, after a short application, the organism can also uptake the residues directly from plants, soil, and water in the agricultural fields and their surroundings. When a pesticide persists in the environment, its residues are expected to build up in a different situation. All chronically exposed species (chronic toxicity) are at risk of toxicity accumulation in their tissues in such conditions. The internal doses may be sufficient over time to cause sublethal or lethal effects (Peakall, 1993). Baird (1997), therefore, defined chronic toxicity of a compound as continuous exposure to a toxin over an extended period, often expressed in months or years, which eventually can cause irreversible side effects. So, therefore, the toxicity of organochlorine pesticides can either have an acute or chronic effect on insect pests, wildlife and human, resulting in death or damage to the body (Afful, 2015). The inherent toxicity cannot be changed, but one can limit the possibility of poisoning by preventing or limiting the exposure. Toxicity of OCPs can be expressed in terms of lethal dose (LD_{50}) and lethal concentration (LC_{50}) values.

The lethal dose (LD_{50}) is the quantity of pesticide (lethal dose), killing half of the organisms studied. The pesticide is routed via the skin (dermal) or the mouth (oral). The smaller the LD_{50} value, the more poisonous the chemical is because less of it affects the organisms (Baird, 1997). Also, the LC_{50} value measures the toxicity of a pesticide when test animals inhale air mixed with pesticide dust, vapours or spray mist. The LC_{50} is the level of a lethal pesticide to 50% of the observed population and is mainly determined for a specific exposure period (e.g. inhalation for 4 hours). The length of exposure is essential because shorter exposure periods generally require higher pesticide concentrations to produce toxic effects.

The LC_{50} values for pesticides in the air are expressed as the ratio of chemical to air, in parts per million (ppm) or parts per billion (ppb). For fish and aquatic organisms, LC_{50} values are also determined based on the pesticide concentration in the water. There are different routes that pesticides may enter the body of an organism. These include; ingestion, inhalation during aerial spraying or dust particles and absorption through the skin. Animals die as a consequence of direct pesticide spray deposition in their habitat (Sánchez-Bayo, 2011).

Ingestion of pesticide may be through direct intake of contaminated plants, fruits, granules coated seeds, as well as fatty foods including dairy products, poultry, meat, and fish (Rusiecki *et al.,* 2008). Toxicity by ingestion can also occur by drinking polluted water from irrigation channels, drains, farm ponds, puddles, streams, rivers and lakes, which may contain elevated levels of residues of pesticides, especially in or near agricultural fields that serve as water sources (Sánchez-Bayo, 2011). Jayaraj *et al.* (2016) quipped that many of the organochlorine molecules, apart from being carcinogenic or neurotoxic, their exposure may also lead to neuromuscular disorders, stimulation of drugs and steroid metabolism. It has been found that long-term exposure to trace concentrations of OCPs causes cancer, liver damage, immunotoxicity and congenital disabilities. Exposure to estrogenic compounds has also been correlated with the increased occurrence of testicular and breast cancers. This estrogenic effect is thought to be responsible for the weakening of birds' eggshells by DDT. Wolff *et al.* (1993) also examined that the risk of hormone-related cancers, including breast, prostate, stomach and lung cancer, was increased by organochlorine pesticides. Evidence has emerged that the organochlorines interact with endocrine receptors, particularly estrogen and androgen receptors. Studies on animals suggest that organochlorines may alter the function of the endocrine system by these interactions (Vonier *et al.*, 1996). OCPs have carcinogenic effects, resulting in current regulatory action limiting their use or removing registration for multiple organochlorines.

2.2.3 Bioaccumulation

Bioaccumulation is defined as the accumulation of contaminants through any route in the tissue of organisms, namely respiration, ingestion or direct contact with polluted water, sediment, and pore water. With this phenomenon, the concentration of the chemical or pollutant is increased from the environment to the first organism in the food chain. Bioaccumulation depends on the uptake of chemicals by the organism, the storage capacity of the organism, hydrophobicity, age, sex and the type of organism involved. The organism that has these contaminants in the body has a higher concentration than the surrounding environment. The level of contaminants in the aquatic organisms relative to these contaminants in the water is called bioconcentration. The bioconcentration factor (BCF) is the equilibrium ratio of the level of a particular compound in a fish (Co) relative to the concentration dissolved in the surrounding water (Cw) (Baird,1997). BCF is mainly used as an indicator of a compound's propensity to bioconcentrate in aquatic organisms.

$$\mathrm{BCF}=\frac{concentration\ of\ chemical\ pollutant\ in\ organism\ (C_o)}{concentration\ of\ chemical\ pollutant\ in\ water\ (C_w)} \quad \text{……………(Equation 2.1)}$$

Due to variations in the ability of different fish to metabolize a given chemical, the BCF values vary not only from chemical to chemical but also to some extent from one type of fish to another (Afful, 2015). Various predictive models have been proposed to estimate BCFs for organic compounds based on their hydrophobicity using their n-octanol/water partition coefficient (K_{ow}). The degree of adsorption to soil or suspended sediments, the partition coefficient, is given by adsorption isotherms which can either be measured or calculated from the partition of individual compounds between water and octanol, K_{ow}. In that regard, the partition coefficient, K_{ow} for a chemical, is defined as:

$$K_{ow}=\frac{concentration\ of\ chemical\ in\ Octanol}{concentration\ of\ chemical\ in\ water} \quad \text{……………………………(Equation 2.2)}$$

The higher the octanol-water partition coefficient K_{ow}, the more likely a chemical is bound to the organic matter in soil and sediment (Afful, 2015).

OCPs tend to bioaccumulate in living tissues in water and sediments, particularly in fish, plants, birds, terrestrial animals, farm animals, and domestic animals. Their levels increase in the order of magnitude as they ascend through the food web, especially as they enter higher species. Other health problems of OCPs bioaccumulation at higher concentration includes; vomiting, dizziness, headache, muscle tremors, liver damage, nausea, convulsions and death (Dachs *et al.*, 2002). On exposure to soil, these pollutants bind to the soil particles and persist there until they are removed during erosion and uptake by plants or microorganisms.

2.2.4 Long-Range Transport

Long-range transmission of OCPs originates from water, animal migration, air transport, and other anthropogenic pathways (Zhang *et al.*, 2007). The OCPs, for example, may travel through the air during aerial spraying and ultimately end up in other parts of the ecosystem, such as plant leaves, soil or water. In addition, directly applied OCPs may be

washed off into the surrounding surface water sources or seep into the lower soil layers and groundwater. In drainage systems, dam reservoirs and lakes, OCPs and many other chemical pollutants from agricultural fields have been identified as contaminants likely to threaten the quality of water bodies that support fishery industry, irrigation, industrial, domestic and human consumption (Shinggu *et al.*, 2014). Some of the OCPs are persistent, and their persistence and semi-volatility make them capable of long-range atmospheric transport, leading to their presence and accumulation in remote areas (Huang *et al.*, 2019).

OCPs released in tropical and subtropical regions may disperse to polar and high mountain areas due to long-range atmospheric transport (LRAT) and global condensation, where temperatures are cold enough to absorb OCPs (Pokhre *et al.*, 2018). Chakraborty *et al.* (2010) and Devi *et al.* (2011) have observed elevated levels of OCPs in the atmosphere in some Indian cities and even from high altitude ambient air. Atmospheric OCP levels can approach 4000pgm^{-3} in some agricultural regions of India, which is among the highest values recorded in the literature (Pozo *et al.*, 2011; Pokhre *et al.*, 2018). Virtually all living organisms in any part of the globe have detectable amounts of POPs in their tissue (Schafer & Kegley, 2001). In this context, global concern has been raised about POP pollution from low-latitude countries (tropical and sub-tropical environments).

2.3 Previous Studies on OCPs in Fish Harvested in Ghana

Fish is an important protein source in Ghana, eaten mainly by all people who live in rural poor and the urban rich (BoG, 2008). Fish sustains considerable biomass, including breeding birds, crocodile population and other carnivorous aquatic animals (Buah-Kwofie *et al.*, 2018). Fish is used for environmental pollution management because they can concentrate contaminants from their diet and water, thereby evaluating the transfer of contaminants through the food web (Akoto *et al.*, 2016). However, the importance of this biota is gradually threatened due to organic pollutants. Various investigations have been conducted in Ghana to understand the state of OCPs and PCBs contamination in foodstuffs, including fish and its exposure to humans.

Otchere (2005) investigated the contamination levels of coastal lagoons in Ghana by OCPs and determined their Spatio-temporal variations in molluscs. The results of Otchere found that in the wet season, Mussels reported elevated levels due to increased runoff from the land. There was a high DDT/DDE ratio in the wet season, depicting more recent contamination from agricultural fields and the public health interventions. Similarly, Darko *et al.* (2008) also observed the presence of lindane, endosulfan, aldrin, dieldrin, *p,p*' -DDE and *p,p*-DDT in fish (*Tilapia zilli*) in Lake Bosumtwi. They revealed the DDT detection rate of about 78% of the fish samples. Their results reported a range of 070 – 4.65ngg^{-1} of all the OCPs studied. Residues of OCPs analysed in all matrices may have resulted from runoff from agricultural application, vector management techniques and diffuse sources via atmospheric deposition. Essumang *et al.* (2009), in a separate development, investigated the presence of four OCPs (DDE, DDD, DDT and propiconazol) in the lagoon tilapia from four lagoons in Ghana. All the OCPs analysed were detected in Etsii and the Fosu lagoons but at lesser concentrations than the water samples analysed from the same lagoons. However, the total OCPs residues for the fish samples analysed showed higher bioaccumulation of OC pesticides in the Fosu lagoon than Etsii lagoon. The total OCP residue levels for Etsii and Fosu were 0.0155 mg/kg and 0.0088 mg/kg, respectively. The overall OCPs concentration detected ranges between ND – 0.0098 mg/kg. In all the OCPs analysed, propiconazol was higher in the fish samples, followed by DDE, a metabolite of DDT.

Adu-Kumi *et al.* (2010) reported the presence of OCPs and other organic pollutants in edible fish from the Weija Lake, Lake Volta, and Lake Bosumtwi. In their investigations, the levels of OCPs obtained were generally low, with the highest concentrations measured from DDT and its derivatives followed by Chlordane compounds, HCB and gamma-hexachlorocyclohexane. The tilapia concentrations of the OCPs showed that freshwater in Lake Bosumtwi is relatively polluted compared to Lake Volta and Lake Weija. Similarly, apart from the chlordane compounds, there were more OCPs in catfish from Lake Volta and Weija Lake than in tilapia from the same lakes. The catfish is a carnivore with higher lipid content than the tilapia and probably bioaccumulate more OCPs. There was a relatively low metabolite/parent compound ratio of DDT in the tilapia and the catfish indicating recent contamination, though, a banned on the DDT trade. Afful *et al.* (2010) detected fourteen individual OCPs namely, *p,p'*-DDT *p,p'*-DDE, α-endosulfan, dieldrin, aldrin, endrin, endrin-aldehyde, endosulfan sulphate, endrin ketone, endrin aldehyde, γ-HCH, δ-HCH, heptachlor, and γ-chlordane in the six fish species sampled from Nsawam and Weija village of the Densu Basin. Their research showed that freshwater fish's organochlorine concentrations were below the Australian Maximum Residue Limits (MRL) of 50 µg/kg to 1000 µg/kg.

Kwablah Anim *et al.* (2010) conducted a similar study to investigate the burden of total chlorine and OCPs in fish from the Densu Basin using neutron activation analysis. Extractable organochlorine and the total chlorine concentrations ranged from 150.00 mg/kg to 350.40 mg/kg and 77.70 mg/kg to 1123.59 mg/kg, respectively. Another investigation by Kuranchie-Mensah *et al.* (2012) ascertained the levels of 15 OCPs, and essential EU recommended 7 PCBs in four fish species, including; *Chrysichthys nigrodigitatus*, *Clarias gariepinus*, *Oreochromis niloticus* and *Tilapia zilli*. The mean concentration of the HCHs, Drins, DDTs CHLs, HCB and PCBs ranged from 4.03 to 13.04 ng/g; 3.46 to 12.29 ng/g; 7.96 to 38.05 ng/g; 4.55 to 39.62 ng/g; 0.34 to 1.21 ng/g and 0.90ng/g – 7.76ng/g respectively. *Chrysichthys nigrodigitatus* and *Clarias gariepinus* recorded the highest ΣOCPs contamination over the study period among the four fish species studied. This was due to the predatory feeding behaviour of the two that placed them higher at the trophic levels with high potential bioaccumulation. PCB 28 and 52 were the predominant congeners observed among the PCBs, accounting for 58% and 60%, respectively. In all the samples analysed, PCB congener 180 was not detected. A similar work by Afful (2015) in the Weija Lake and Lake Bosomtwi detected a total of seventeen OCPs and five indicators' PCBs in each of the two study areas. Descriptive statistical analysis of the organochlorine concentrations in the fish samples showed PCB 138 and PCB 52 as OCPs with maximum concentrations in the species from Bosomtwi and Weija, respectively, with respective maximum concentrations of 18.43 µg/kg and 32.40 µg/kg. PCB 101, PCB 52, PCB 28 were the ubiquitous OCPs in the fishes from Bosomtwi, while PCB 28 were the ubiquitous OCPs in the fish samples from Weija.

The heptachlor, δ-HCH, p,p'-DDD, β-HCH, methoxychlor and endosulfan sulphate were the predominant OCP residues measured by Gbeddy *et al.* (2012). Their work focused on the OCPs in African catfish muscle, Nile tilapia muscle and gills from the middle part of the Volta Basin of Ghana. Thirteen OCPs were detected in the study area, and the frequency of occurrence ranged from 17 to 100 %. The average residue level in the muscles ranged from 0.10 to 17.35 ng/g wet weight. Asante *et al.* (2013) studied the occurrence of halogenated contaminants such as PCBs, PBDEs and HBCD in inland and coastal fish from Ghana intensively. The study detected that PCB, PBDE and HBCD in the freshwater fish, indicating that the freshwater environment in Ghana was exposed to persistent halogenated pollutants from diverse sources. PCB 153, PCB 138 and PCB 180 dominated in the analysed fish samples. The mean levels of PCBs in the tilapia fish species were 62ng/gw. Their results also showed that PCB concentrations measured in the whole specimen were below the USFDA and EU food safety guidelines. On the Volta Lake, Gbeddy *et al.* (2015) also assessed organochlorine pesticides in wild Nile tilapia and African catfish. Except for γ-HCH and endrin, 13 OCPs with levels ranging from <LOQ to 37.75 ng/g dry weight were found and quantified in catfish and tilapia.

Their findings also show a strong relationship between OCPs in the Catfish muscle tissue and the tilapia, indicating a similar source of these pollutants. Akoto *et al.* (2016) studied the presence of 16 OCPs in four species of fish harvested from the Tano reservoir. p,p^1-DDD, aldrin, and $p.p^1$-DDE have been revealed in the fish samples analysed. In *C. anguilaris, p.p*^{1}-DDE recorded the highest concentration. In contrast, aldrin recorded the lowest concentration in all the species of fish sampled. In *Marcusenius senegalensis, Sarotherodon galilaeus, Clarias anguillaris,* and *Schilbe intermedius,* respectively, the average level of OCP residues ranged from 0.097 to 0.263 µg/kg, 0.017 to 0.17 µg/kg, 0.043 to 0.30 µg/kg, and 0.027 to 0.243 µg/kg. Overall, the highest order of the total OCPs recorded in the various fish species was *C. anguillaris, M. senegalensis, S. intermedius, and S. galilaeus*. The levels of p,p^1-DDD, aldrin, and $p.p^1$-DDE residues obtained in their study were below WHO/FAO values.

Similarly, Addo *et al.* (2018) determined the levels of fifteen (15) organochlorine pesticide residues in *Tilapia guineensis, Sarotherodon melanotheron, Clarias gariepinus,* and *Tilapia zilli* collected from the Ashaiman reservoir, Ghana. At a detection limit of 0.005 mg/kg in all the fish samples, the OCPs investigated were not detected. Their concentrations were below the MRL by EU and Australia.

2.4 Previous Studies on OCPs in Water in Ghana

Quality and potable drinking water are essential for sustainable human health, quality of life, as well as the socio-economic development of humanity and, is a prerequisite for developing countries like Ghana to obtain the optimum requirement of SDG of achieving clean water as well as sanitation by 2030 (Affum *et al.*, 2018). However, groundwater and surface water bodies are compromised by pesticides through runoffs, atmospheric deposition, vector control practices and leaching due to agricultural applications (Darko *et al.*, 2008; Kuranchie-Mensah *et al.*, 2012). Nevertheless, these pesticides, such as the OCPs in the water sources, must comply with the health-based limits of WHO and water quality criteria provided in the European Union (EU) water framework Directive 200/60/EC and EU Council Directive 98/83/EC (Affum *et al.*, 2018).

Different pesticides may be found in the water columns, but the OCPs are among the notorious pesticides in water. This is because of their high toxicity, ability to bioaccumulate in the food chain, and environmental persistence (Botwe *et al.*, 2012). Ntow (2001) studied the levels of OCPs in surface water in a popular vegetable cultivation area of Akomadan in Ghana. Of the quantifiable levels of OCPs in water determined, α-endosulfan showed the highest concentration with a mean of 62.3ng/L and was detected in over 60% of all the samples analysed. Endosulfan sulphate in water with an average of 30.8ng/L was the most encountered (78%). A similar study investigated by Ntow (2005) focused on OCPs pollution on the Volta Lake. Ntow's work revealed that lindane was the most occurring chemical within the water column, with an average level of 0.008ug/L. Even though 41 samples of water out of 180 contained lindane, α-endosulfan with an average level of 0.036ug/L recorded the highest in the water. The residues from all the contaminated OCPs were believed to originate from agricultural activities. Another study conducted by Darko *et al.* (2008) to investigate the extent to which OCPs contaminated lake Bosomtwi deduced that DDE was the most ubiquitous in water (82%) with an average concentration of 0.061±0.03ng/g. They, however, noted that the lake's contamination with the DDE was probably due to past use of the OCPs. Essumang *et al.* (2009) also investigated similar contamination of four lagoons by 4 OCPs and organophosphorus pesticides. Their results revealed that the Chemu lagoon was more contaminated with OCPs than the Korle and Fosu lagoons.

The average pesticide residue in water samples from the four lagoons, Chemu, Korle, Fosu and Etsii, are 2.6384, 0.4992, 0.3045, and 1.3629mg/L, respectively. The pollution of groundwater and stream drainage vegetable plantations in the Ofinso District of Ghana was investigated by Botwe *et al.* (2012). There was no pesticide contained in the groundwater. Alpha-endosulfan, β-endosulfan, and endosulfan sulfate were detected with mean concentrations of 0.027 ± 0.015, 0.021 ± 0.010, 0.02 ± 0.010 ugL^{-1}, respectively, for surface stream water. The occurrence of endosulfan residues in the stream was due to direct overspraying, spray drift, atmospheric transport, agriculture runoff, and improper disposal of pesticide containers. Another investigation by Kuranchie-Mensah *et al.* (2012) studied the pollution of 14 OCPs in water from Weija and Nsawam. The OCPs level ranged from ND– 1.07µg/L. Abagale *et al.* (2014) investigated the levels of 21 OCPs in irrigation water in a Dam located in Tolon District of Northern Ghana. Twenty- one (21) different organochlorine residues were identified namely: *δ*-HCH (0.23 µg/g), *α*- HCH (0.094 µg/g), HCB (0.12 µg/g), *β*-HCH (0.21 µg/g), aldrin (0.25 µg/g), *γ*-HCH (0.109 µg/g), heptachlor (0.27 µg/g), cis-heptachlor epox (0.14 µg/g), trans-heptachlor epox (0.080 µg/g), trans-chlordane (0.123 µg/g), cis-chlordane (0.076 µg/g), trans-nonachlor (0.27 µg/g), dieldrin (0.17 µg/g), endrin (0.083 µg/g), *o'p*-DDE (0.15 µg/g), *p'p*-DDE (0.18 µg/g), *o'p*-DDD (0.36 µg/g), *p'p*-DDD (0.061 µg/g), o'p- DDT (0.126 µg/g). p'p-DDT obtained the highest level of 0.52 µg/g, whiles mirex recorded the least of - 0.057 µg/g. Gbeddy *et al.* (2015) also revealed 12 OCPs out of the 15 OCPs studied on the Volta Lake.

Their levels in the water ranged below LOQ to 0.699 µg/L. δ-HCH with an occurrence frequency of 14%, recorded the highest average level of 0.699µg/L. This was preceded by endosulfan sulphate, β-HCH, and heptachlor with concentrations 0.039µg/L 0.194 and 0.075µg/L, respectively. These OCPs were most likely from sources described by Ntow, 2005; Darko *et al.* 2008. Akoto *et al.* (2016) investigated 16 OCPs residues in water from the Tono reservoir. Their findings revealed that all the pesticides were below the level of detection. OCPs in soil and water supplies in Cocoa producing areas in Ghana were similarly investigated by Fosu-Mensah *et al.* (2016). Examined water samples reported the existence of endosulfan sulphate (0.01 – 0.04ug/L), *p, p'* -DDT (0.01 – 0.04ug/L), dieldrin (0.01 – 0.03ug/L), α-endosulfan (0.01 – 0.03ug/L), and lindane (0.01 – 0.03ug/L), with heptachlor the most encountered in all the water samples. Similar to other research on other surface water bodies in Ghana, Koranteng *et al.* (2016) extensively analysed and compared pesticide residue levels in the water of the Afram River at normal water levels and during flood periods. They further established the impact of drawdown farming on water quality. They found that the concentration levels of OCPs and other pesticide residues were substantially higher than the concentration of recesses in the flood regime. The difference was mainly due to the drawdown of farmlands during floods.

Their studies also indicated that β-lindane, $\delta-$lindane, aldrin, dieldrin, and endrin exceeded the WHO/EU maximum residue during the two regimes. The exposure levels and risk of pesticides to humans in an agricultural area dominated by cocoa crops in the Ankobra Basin were determined by Affum *et al.* (2018) through groundwater and surface water sources. Their findings showed that the concentrations of banned and non-banned pesticides in the surface water and groundwater varied from <LOD to 2µg/L. Some of the surface water sources were contaminated with DDTs, endrin, dieldrin, methoxychlor and HCH isomers

2.5 Previous Studies on OCPs in Sediment in Ghana

The “dirty dozen" defined under the Stockholm Convention comprises 12 OCPs, industrial chemicals and their by-products, including dioxins, PCBs, and furans. The dirty dozen OCPs includes heptachlor, dichlorodiphenyltrichloroethane (DDT), aldrin, toxaphene, dieldrin, hexachlorobenzene (HCB), endrin, mirex, and chlordane (Williams, 2013). Though most OCPs were prohibited in the 1970s and 1980s, they are still present in water, air, sediment and other environmental matrices (Essumang *et al.*, 2009; Williams, 2013; Guan *et al.,* 2009; Sarkar *et al.*, 2008). Apart from their inexpensive cost and versatility in combating different pests, some countries in the developing world still use OCPs, even for agricultural and health purposes. Because OCPs are less soluble in water, they sink to the bottom sediments (Addo *et al.*, 2018). Owing to their persistence in the atmosphere and long-range transport, heavily polluted sediments adversely influence the ecological functioning of rivers (Singh *et al.*, 2015). In Ghana, various investigations have been reported to understand the state of contamination of OCPs in sediment and their toxicity to aquatic species. In Akumadan, a well-known farming area in Ghana, Ntow (2001) investigated OCP residue levels in the water, tomato crops, sediment, and human fluids. The sediment samples showed the most considerable number of OCP compounds. All the OCPs found in sediment appeared in at least 88% of all the samples analysed. The highest mean concentration of 3.2 mg/kg was recorded in sediment for lindane, and the least mean of 0.13 mg/kg for β-endosulfan. Although lindane is commonly used in cocoa farming for capsids elimination and control of stem borers in maize (Fosu-Mensah *et* *al.*, 2016), its high concentration in the study area was probably due to non-point sources (Darko *et al.* 2008).

Detected in the sediment during their study included other organochlorine pesticide residues, such as heptachlor epoxide, DDE, and HCB. Similar work as done by Darko *et al.* (2008) on the Lake Bosomtwi realized the presence of lindane, endosulfan, aldrin, dieldrin, *p,p*-DDT, and *p,p*-DDE. The average DDT level was 4.41 ±1.54ng/g in the analyzed sediment samples. With a detection frequency of 98 per cent of the sediment samples and a mean concentration of 8,342 ± 2.96ng/g, DDE was the most experienced. The occurrence of pesticides in water and sediment in vegetation plantations in the Ofinso District of Ghana has also been reported by Botwe et al. (2012). Their work unearthed the presence of α-endosulfan, β-endosulfan, endosulfan sulphate, dieldrin, and *p,p*' DDE. The pesticide concentration levels ranged ND – 3.77ug/kg (dw), with endosulfan sulphate occurring in about 90% of all the 180 samples of sediment analysed. In contrast, in the Densu River, Kuranchie-Mensah *et al.* (2016) observed the distribution of organochlorine pesticides, their finding from the three sampling locations noted the presence of γ-HCH, *δ*-HCH, heptachlor, aldrin, dieldrin, gamma-chlordane, *α*-endosulfan, endosulfan sulphate, *p,p*'-DDT and its metabolite, *p,p'*-DDE, methoxychlor, endrin aldehyde, and endrin ketone. The mean concentration ranged from 0.030ug/kg dw to 10.98ug/kg dw.

The presence of endosulfan sulphate, β-HCH, δ-HCH, heptachlor, methoxychlor, alpha-endosulfan and dieldrin with mean concentrations of 1.39, 1.16, 1.14, 1.11, 0.90, 0.89 and 0.82 ng/g dw respectively was reported in a recent analysis by Gbeddy *et al.* (2015) on the residues of OCPs in sediment in Volta Lake. The highest occurrence frequencies varying from 83 to 100 percent were reported for endosulfan sulphate, β-HCH, δ-HCH, p,p'-DDD, and heptachlor. Another study on the Afram river of the same Volta Lake by Koranteng *et al.* (2017) revealed the presence of 15 OCPs in the sediment. γ-Chlordane recorded the highest mean concentration of 42.69µg/kg, while γ-HCH was the most encountered OCP with an incidence rate of 97%. Although most OCPs were due to past inputs and their environmental persistence, others such as endrin, endosulfan, γ-HCH, and aldrin suggest current input. Similar studies such as Akoto *et al.* (2016) in the Tono Basin discovered the presence of other OCPs such, *p,p′*-DDD, *p,p′*-DDE, and aldrin in the bottom sediment samples. Sediment OCP residue mean concentrations varied from 0.047 to 0.090 µg/g. The maximum concentration for Aldrin was reported, whilst *p,p′*-DDD was recorded at the lowest level. In Dormaa, 15 organochlorine pesticides residues in soils and drinking water around cocoa farms were evaluated by Fosu-Mensah *et al.* (2016). Four organochlorine pesticide residues occurred in the soil samples tested, namely dieldrin (0.005-0.02 mg/kg), beta HCH (<0.01-0.05 mg/kg), lindane (0.005-0.05 mg/kg), and *p,p′*-DDT (0.005-0.04 mg/kg), with dieldrin being the most frequently identified. Akoto *et al.* (2016), Gbeddy *et al.* (2015) and the findings of Fosu Mensah *et al.* (2016) revealed that the unlawful historically application of pesticides for agricultural production in Ghana was attributed to OCP residues in the various matrices analysed. Addo *et al.* (2018) researched 15 organochlorine pesticides (OCPs) to provide baseline data on the residue levels of OCP in fish and sediments in the Ashaiman reservoir. Their analysis demonstrated that the 15 OCPs assessed were below the limit of detection in the sediment samples.

2.6 International Regulations on Pesticides Use

The international and national legal framework for dealing with pesticides has evolved considerably over the last 25 years. In 1985, the FAO ratified the Universal Code of Conduct on the Distribution and Use of Pesticides. It was reviewed in 1989 and updated in 2002 to include the Prior Informed Consent (PIC) protocol. The incorporation of pesticides for public health was revised in 2013, and its name was changed to the International Pesticides Code of Conduct. The WHO also developed the Code of Conduct in 2014 as a structure for general guidelines for maintaining the protection of pesticides. Some other international organisations on pesticides came into existence. The most prominent of them is the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention), the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (Basel Convention), the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (Rotterdam Convention) and the Montreal Protocol on Substances that Deplete the Ozone Layer (Montreal Protocol) and Convention No 184 of the International Labour Organisation on Safety and Health in Agriculture (ILO Convention No 184). "Other notable developments were the adoption of a Strategic Approach to International Chemicals Management (SAICM) and the adoption of a new globally harmonised system of classification and labelling of chemicals (GHSCLC) aimed at standardising and harmonising the classification and labelling of chemicals".

In 2001, the Stockholm Convention on Prior Informed Consent for Persistent Organic Pollutants (POPs) was enacted. On 17 May 2004, it came into force in response to the urgent need for global concern on POPs (persistent chemicals that bioaccumulate in fat tissue and biomagnify across the food chain). To date, it has 173 Parties. The Stockholm Treaty restricts the import/export of POPs unless they are disposed of in an environmentally sound manner or the importing Party can use them in an exempted way.

2.7 Impact of Pesticides on Aquatic Organisms

Direct pesticide impacts have been identified at almost all biological endpoints for all classes of freshwater species. Nevertheless, most experiments have been performed in the laboratory. Despite the vast quantity of pesticides used globally and the fact that they affect biota, there is a strong potential for undesirable environmental consequences in non-target communities. Once pesticides reach freshwater habitats, they interfere with the ecosystem's biotic and abiotic components. Abiotic effects can contribute to degradation (photodecomposition by sunlight or hydrolysis by water) or the adsorption of pollutants to sediments or organic matter. Interaction with biotic components includes the uptake, metabolism and accumulation of organisms that, in effect, may cause adverse effects mainly on the freshwater biotic ecosystem.

Fish, amphibians, invertebrates, and plants make up the freshwater population. Pesticides effects on these species may have direct and indirect effects. The systemic action of a pesticide within an organism causes direct effects. However, ecological relations between species, such as competition or predation, are characterized by the biotic population and indirect effects of these encounters (Lang & Benbow, 2013). For instance, water flea mortality may lead to an increase in algal biomass through the release of grazing pressure (indirect effect) as an obvious consequence of response to a pesticide (direct effect). We will concentrate initially on the direct effects, as they are necessary for understanding the indirect effects.

The possible immediate impact of a pesticide entering a freshwater environment can be changed by certain factors coupled with the biological and physicochemical properties of the exposed ecosystem. Therefore, between ecosystems with various patterns of these influences, the results can also vary. For example, a given pesticide is more likely than an agricultural stream commonly exposed to pesticides to impact a population in a forest stream that has never received pesticide inputs. However, our understanding of the comparative relevance and differences in the patterns of these factors among natural ecosystems is minimal. It does not allow us to generalise their influence on ecosystem impacts. However, when studies are carried out within similar ecosystems (e.g., agricultural rivers) or when the factors differ only slightly between sites, the pesticide concentration (or the toxicity derived from it) should be the primary predictor of pesticide effects.

In the case of field research on the effects of pesticides on invertebrate animal populations in agricultural watercourses, the variability of the assessment parameters for the population could be explained by the pesticide content (or the derived toxicity) alone, including in biogeographical regions. The duration of exposure and the history of the communities were reasonably related in these studies. However, these determinants' intensification of pesticide action explains why field effects due to laboratory studies or artificial currents were recorded at lower levels than expected. In addition, these variables are likely to be more significant when the effects of laboratory toxicity studies are extrapolated to the real world.

2.8 Heavy Metals

Heavy metals appear to include all metals of the periodic table with an atomic number greater than 20, excluding the alkali metals and the alkali earth (Tangahu *et al.*, 2011). Heavy metals are metallic naturally occurring compounds with a very high density greater than 5g/cm^3, compared to other metals at least five times the density of water. Based on their function in the living organism, heavy metals can be divided into essential and non-essential. Some of these heavy metals, such as manganese, selenium, cobalt, chromium, copper, molybdenum, nickel, magnesium, iron, and zinc, are essential nutrients that are necessary for the body for different biochemical and physiological functions and, if not in sufficient quantities, can lead to deficiency diseases. They can, however, cause chronic or acute toxicity in high doses (Engwa *et al.*, 2019).

Organisms do not need non-essential heavy metals such as Cd, Pb, Hg, and As (Tchounwou *et al.*, 2012). Such elements have no beneficial consequences on humans, and their homeostasis mechanism is not established (Draghici *et al.*, 2011; Vieira *et al.*, 2011). The potentially harmful effects associated with exposure to them, even at trace levels, are complex and include, but are not limited to, neurotoxic and carcinogenic actions (Morais *et al.*, 2012). Heavy metals' non-biodegradable and bio-accumulative nature makes them detrimental to human and aquatic lives upon exposure to some extent. The distribution in the ecosystem of these heavy metals depends primarily on the metal's properties and other predominant environmental conditions.

Heavy metals have been widely used to measure anthropogenic contamination due to their linkage with human activities and environmental stability and persistence (Xu *et al.*, 2019). Other waste materials such as paint wastes, electronic goods, and used batteries increase the number of heavy metals found at dumpsites, and invariably, in other parts of the environment. (Cui *et al.*, 2005).

2.9 Previous studies on heavy metals in water in Ghana

Heavy metals are natural elements that may originate from the environment. They may also be released from anthropogenic sources. Anthropogenic sources include; landfill leachate, water runoff, industrial and urban storm, atmospheric sources, domestic effluents, and dumping of sewage sludge, giving rise to elevated levels of these metals relative to their average background values (Yohannes, 2014). Heavy metals are of great concern in water quality because of their environmental persistence, biogeochemical recycling, and biological risks (Armah *et al.*, 2010). Their ability to bind to suspended solids and organic material can be a source of long-term degradation and an enormous potential for bioaccumulation in food chains (Luo *et al.*, 2010). In Ghana, contamination of the surface water bodies by heavy metals has predominantly been observed by several Researchers

Fianko *et al.* (2007) investigated Sorowie and Kakum rivers to ascertain heavy metals pollution levels due to anthropogenic activities. Their research indicated the presence of metals in the pattern, Zn > Pb > Cd > Se. The level of Cd in the estuary ranged 0.011 – 0.041mg/L, Se (0.018 – 0.029 mg/L), Pb (0.020 – 0.075mg/L) and Zn (0.040 – 2.45 mg/L). Similarly, Armah *et al.* (2010) assessed the levels of eight heavy metals in the surface water and their potential origin. It was revealed that all the metals studied apart from Zn were above the permissible levels suggested by GEPA (Ghana Environmental protection Agency). The metals were identified to have originated from nature, vehicular fallout, and water carrying them from towns and mining machinery maintenance.

In the same mining area, Boamponsem *et al.* (2010) analysed the levels of Al, As, Cd, Co, Cu, Hg, Mn, Sb, Th, and V in some streams of Tarkwa using Instrumental Neutron Activation Analysis (INAA). Their studies revealed high Al, Co, Sb, Mn, As, Hg, and Cu levels in the water samples from Angonabeng and Bediabewu rivers a few miles away from some major mines' processing sites area. Similarly, the problem of gold mine tailings dams as a possible source of arsenic and heavy metal pollution was investigated by Bempah *et al.* (2013). The total mine tailing component concentrations were 1752 mg/kg As, 75.16 Wt% Fe, 1848.12 mg/kg Mn, 92.17 mg/kg

Cu and 177.56 mg/kg Zn. Their analysis showed levels of As leachate in the range of 0.04-0.56 percent.

Kpan *et al.* (2014) also studied the concentrations of Cu, Pb and Hg, Pb in water from fourteen (14) sampling sites in some illegal mining towns in Dunkwa – Offin District. It was revealed that the heavy metals in most of the sites were above the allowable limits. The concentration of Pb was 170.27mg/kg, Cu was 75.92mg/kg while Hg 211.31mg/kg. Cobbina *et al.* (2015) assessed Pb, Hg, As, Cd, and Zn pollution in portable drinking water sources from Tingah and Nangodi small-scale mining communities in northern Ghana. Their study recorded 0.031 and 0.002 (As), 0.038 and 0.064 (Hg), 0.250 and 0.031 (Pb), 0.534 and 0.023 (Cd) and 0.034 and 0.002 (Zn) for Nangodi and Tingah respectively. It was also observed that the concentrations of Pb, Zn, Cu, As and Hg in Nangodi water exceeded the limits recommended by WHO for healthy drinking water. Only Hg, Pb, and Cd were above the required limits for WHO in Tingah.

Abagale *et al.* (2013) also studied heavy metals concentrations in wastewater from car washing bays in the Tamale Metropolis of Ghana. Their study revealed the presence of Cr (0.42mg/L), Fe (4.97mg/L), Pb (0.28mg/L), and Mn (2.36mg/L) in high levels of all the samples collected. Zn, Cd, and Cu were low. It further observed that the occurrence of Fe and Mn were interrelated while Mn was also interrelated with Zn, Cu, Cd, Cr, and Pb. On the other hand, Asante et al. (2013) investigated the presence of heavy metals in the Red Volta. Their investigation showed Mn (0.239 ± 0.095mg/L), Cd (0.005 ± 0.004mg/L) and Hg (0.036 ± 0.060mg/L). All the metals studied were within the permissible levels of WHO and GRWCG (Ghana Raw water Criteria and Guidelines). In a related development about heavy metals contamination in water, Darko *et al.* (2015) investigated the impact of heavy metals pollution in the aquatic ecosystem, particularly Lake Bosomtwi. Iron (Fe), Zinc (Zn), Copper (Cu), Manganese (Mn), and Nickel (Ni) levels in the lake were within the permissible levels of WHO. However, Cadmium (Cd) and Lead (Pb) showed higher concentrations within the study period. The accumulation pattern in the study were in order Ni > Fe > Cu > Mn > Pb > Zn >Cd. The levels range from 0.003 mg/L to 0.210 mg/L, and the sources were attributed to anthropogenic activities. In a related development, research by Darko et al. (2015) on Bosomtwi Lake and the Bui Dam reported a pattern Fe (0.0058) > As (0.045 > Pb (0.026) > Mn (0.014) > Cd= Zn (0.003) > Cr (0.002). In the water samples, the concentrations of Mn, As, and Pb was above the world average drinking water levels of 0.400, 0.010, and 0.010 mg/L, respectively. The high levels were attributed to the anthropogenic activities around the lakes, such as improper disposal of lead-acid waste from artisans.

Ansah *et al.* (2018) made a similar revelation in their studies in the weija reservoir. Their results showed that Cd, Cu, Ni, Pb, and were all below the chronic freshwater quality criteria or aquatic life’s Cr and As were below the detection limit in the water during the time of their study. All other heavy metals were detected, with Ni recording the highest concentration with a range of 0.04 – 3.44mg/L. The order of accumulation of the metals in the water from Weija followed Ni > Fe = Zn > Cd > Mn > Cu > Pb > Hg.

2.10 Previous studies on heavy metals in Fish in Ghana

Fish and its products have been shown to contain varying amounts of heavy metals from water pollution. This pollution is mainly caused by industrial processes and industrial waste (Hashim *et al.,* 2014). Heavy metals in the aquatic ecosystem above the permissible levels have drawn the attention of several researchers.

The evaluation of the profile of heavy metals in fish samples from Nsawam along the Densu River was investigated by Anim *et al.* (2011). Of the heavy metals studied (Fe, Mn, Cu, Zn, Ca, Cd, Pb), Ni, Co, and Cr registered an incidence of 80, 60, and 20 percent in the fish samples, respectively. In *Hepsetus odoe*, the highest concentration of 110.56 ± 0.86 mg/kg was reported for Cu. Ni, Co, and Cr measured significantly lower concentrations, with detection limits of <0.01 mg/kg, <0.005 mg/kg and <0.001 mg/kg, respectively. The lowest concentration of Pb in *Clarias garipinus* was reported at 0.08 ± 0.01mg/kg. Cu level was beyond the maximum 30 mg/kg in all samples, while the Mn concentration detected in all fish samples exceeded the WHO limit of 0.5 mg/kg.

Asante *et al.* (2013) similarly investigated the concentration of manganese, cadmium, and mercury in the organs of *Sarotherodon galilaeus*, *Labeo senegalensis*, and *Brycinus nurse*. The gills of the *Sarotherodon galilaeus* accumulated the least concentration, whiles the gills of *Brycinus nurse* accumulated the highest concentration of Cd. *Sarotherodon galilaeus* accumulated the lowest concentration, *Labeo senegalensis* accumulated the high concentration of Hg and *Sarotherodon galilaeus* least. It was further revealed that the muscles of *Sarotherodon galilaeus* accumulated a high concentration of Mn and Hg while *Brycinus nurse* the least. Unlike Anim *et al.* 2011, Asante *et al.* (2013) concluded that the dietary consumption of fish from the Red Volta might have public health implications.

On the western coast of Ghana, two tropical fish species, *Chloroscombrus chrysurus* and *Sardinella maderensis*, sampled by Nyarko *et al.* (2013), high iron (Fe) concentrations were reported. Cu and Zn levels in the two fish species were high and could cause physiological dysfunction and even threaten their survival. Ingestion of these fish species may not result in any significant health risk since the low hazard quotient indices. However, relatively high levels of Cu were reported requiring appropriate public health concerns.

Doke & Gohlke (2014) also investigated 63 fish samples for methylmercury contamination. The results for the Hg in Ghana had a low average methylmercury level (~0.1 µg/g); however, higher mercury (Hg) levels were found in fish captured from rivers in Ghanaian gold mining regions (0.25±0.23 mg/kg ww) as compared to fish obtained from lakes/reservoirs (0.04 ±0.04 mg/kg ww) and coastal locations (0.06 ±0.04 mg/kg ww). This low Hg concentration resulted from the hazard quotient being less than 1 when using the joint FAO/WHO /PTWI but higher than one when using the USEPA reference dose.

Darko *et al.* (2015) also investigated the levels of Zn, Fe, Cu, Mn, Ni, Cd, and Pb pollution in Lake Bosomtwi. The heavy metals in tilapia were below the standards of the WHO. The bioaccumulation of metals in fish compared to water was less than the unit for all metals except Mn. Gbogbo *et al.* (2018) investigated the pollution and dangers of consuming heavy metals in *Chrysichthys nigrodigitatus* and *Brachydeuterus auritus* highly patronized in West Africa. Except for cadmium and lead, which were below detection in all samples, Cu was not found in *B. Auritus*. The rates of the other metals were well below the maximum acceptable FAO/WHO standards in the fish. They appeared in the range Se (2.97) > Zn (2.28) > Hg (0.31) > As (0.21) for *B. Auritus* and Se (3.5) > Zn (2.34) > Cu (0.59) > As (0.37) > Hg (0.19) in *C. Nigrodigitatus* Just like in *C. Nigrodigitatus,* Hg in *B. Auritus* had a target risk quotient (THQ) greater than one and therefore raising concern to consumers.

Similar to the Asante *et al.* 2013; Ansah *et al.* (2018) determined the concentrations of some heavy metals (Cu, Pb, Ni, Fe, Zn, Cr, Cd, As, Hg and Mn) in the Weija reservoir and six edible fish species (*Parachanna abscura, Clarias gariepinus, Hemichromis fasciatus, Chrysichthys nigroigitatus, Macrobrachium rosenbergii and Sarotherodon melantheron*). Their results recorded the presence of all the metals in varying concentrations except Cu and Cd. The mean concentration in the fish species ranged from 0.06mg/kg (As) in *Hemichromis fasciatus* to a maximum of 11.3mg/kg (Zn) in *Clarias batratus*. The metals levels in the six fish species were in order: *Parachanna obscura >Macrobrachium rosenbergii > Chrysicthys nigrodigitatus > Clarias batracus > Clarias gariepinus > Hemichromis faciatus > Sarotherodon melantheron*.

The levels of V, Mn, As, Hg, Cd, and Al in the muscles of *Tilapia zillii, Clarias gariepinus, Sarotherodon galilea* and *Oreochromis niloticus* using Instrumental Neutron Activation Analysis were performed on the same weija reservoir by Ameko *et al.* (2014), the metal levels in the water were positively associated with those in the fish. Their results also indicated safe arsenic, mercury, and cadmium levels and unsafe vanadium, aluminium, and manganese levels in *T. zillii*, *C. gariepinus*, *S. galilea*, and *O. niloticus* from the lake.

2.11 Previous studies on heavy metals in sediment in Ghana

As it plays an essential role in removing contaminants in the aquatic environment, sediments are considered a significant sink for pollutants released into the environment and become potential sources of these contaminants (Yohannes, 2014). These toxins, such as heavy metals, are used to assess the contamination status of aquatic ecosystems (Darko *et al.*, 2015). Aquatic sediments also play an important role in heavy metal absorption and can also be a possible source of metal contamination by releasing adsorbed metals during re-suspension episodes (Darko *et al.*, 2015; Zheng *et al.*, 2013).

The sediments also accurately represent the bedrock's geochemical composition and the anthropogenic activities in the aquatic environment. Studying heavy metals in sediment samples is critical since sediments are habitats for several benthic species, such as mudfish (Duncan *et al.,* 2018). Heavy metals presence in bed sediments, organisms, and water can bring about ecosystem changes that eventually have an adverse implication to human health (Suresh *et al.,* 2012).

Processes like precipitation, sorption and dissolution in aquatic settings negatively impact heavy metals (Abdel-Ghani and Elchaghaby, 2007). These pathways also affect temperature, pH, water disturbance, and DO level (Duncan et al., 2018). According to Duncan *et al.* (2018), heavy metals precipitate and adsorb to sediment surfaces at a higher pH. Conversely, heavy metals can also be more readily exposed to water at lower pH and higher temperatures. The accumulation of metals in the aquatic ecosystem has a direct consequence on humans and the primary function of the ecosystem. Some metals such as Zn and Se are required for metabolic activity in living organisms, but the narrow “window” between their essentiality and toxicity is crucial (Fatoki *et al.*, 2004). Others, such as Pb and Cd, demonstrate very high toxicity when even at trace quantities, requiring frequent monitoring of vulnerable aquatic ecosystems (Fianko *et al.,* 2007). Researchers have reported the presence of heavy metals in sediment in the Ghanaian rivers, lakes, coastal areas, and lagoons.

Boamponsem *et al.* (2010) investigated heavy metals levels in sediment samples from five streams in a gold mining area of Tarkwa in Ghana. The study revealed that Teberebie spring sediments were polluted with Sb, Mn, V, Al, and Cd, while mile 7 spring sediment was polluted with only Sb. The sediment pollution in the stream was heavily affected by pollution from anthropogenic and natural sources. Similarly, Duodu *et al.* (2011) observed the degree of Cu, Co, Cr, Fe, K, Mn, Ni, Pb, V, and Zn contamination in the Weija Lake and the extent to which the sediment was polluted using Energy Dispersive X-ray Fluorescence (EDXRF). Their findings indicated Cu (19.80 ± 3.77), Co (<19.80), Cr (87.62 ± 19.69), Fe (141245.5 ± 1765.39), K (25363.08 ± 3740.08), Mn (433.61 ± 60.71), Ni (58.65 ±8.81), Pb (20.03 ± 1.19), V (77.35 ± 24.02) and Zn (19.07 ±3.41) contamination in the sediment. The obtained geo-accumulation index value shows that these metals were from natural sources. The contribution from anthropogenic sources was insignificant. Within the northern territories of Ghana, Asante *et al.* (2014) also investigated the levels of manganese (Mn), Mercury (Hg), and Cadmium (Cd) in sediment from the Red Volta of Ghana. Manganese recorded the highest level of 8.87 ±10.06mg/L and mercury the least with 0.019 ±0.001 mg/L. The heavy metals concentrations in the sediment could be due to high bioaccumulation due to reduced water volume during the dry seasons. Vowotor *et al.* (2014) studied sediments from 12 separate locations within the municipality of Komenda Edina Eguafo Abrem (KEEA) for seven heavy metals. Their findings showed that Pb was the highest for heavy metals in terms of abundance. At the same time, the pollution levels of As, Cd, Hg and Pb were seen compared to the standard sediment criteria by USEPA and CBSQG.

Darko et al. (2015) found higher levels of bio-concentrations of Cd and Mn in the sediment, possibly due to contamination of heavy metal pollution in Lake Bosomtwi. In the analysis, the accumulation trend was in order Ni> Fe > Cu > Mn > Pb > Zn > Cd. Hogarh *et al.* (2016) similarly conducted a retrospective study on the contamination of heavy metals in sediment grabbed from Lake Amponsah in a mining community. Their investigation revealed a marginal decline in Hg concentration in the past decades, while the other metals (As, Cd, Cu, Pb) showed an increasing trend. This indicated greater contamination of these metals in recent times. The Hg declined because of the restriction placed in Ghana over its use. In a related development in the Weija reservoir, Ansah *et al.* (2018) observed all the ten metals studied. The concentrations of all the metals were virtually below the standard prescribed by the EU for sediment.

The source of the high levels of Cu was due to the frequent use of fertilizer and pesticides application within the location. Duncan *et al.* (2018) conducted a similar investigation by sampling sediment from twenty-seven (27) points on the Pra Basin of Ghana to determine heavy metals pollution. The sediment was rich and polluted with Cd, Cr, Pb and Ni, an indicator of human activity in the Basin. In the dry season, their study also showed higher levels than in the wet season, likely because of the low flow rate.

CHAPTER THREE

STUDY AREA

3.1 Background and Geographical Description of the study areas

The study areas comprise the Asuogyaman District in the Eastern region and the Shai Osudoku of the Greater Accra region of Ghana. Figure 3.1 is a map showing the location of the fish farms, where samples were collected. The district of Asuogyaman is situated roughly between latitudes 6^o 34^o N and 6^o 10^o N and longitudes 0^o 1^o W and 0^o14E.

The district can boast essential infrastructure, including a hydroelectricity dam, Senchi bridge, and Akosombo inland port that helps convey goods and people from southern Ghana to the northern territories. The district is endowed with tourism activities and subsistence agriculture that serve as a bedrock of employment. The district is positioned within a dry Equatorial Climate Zone, which experiences a significant amount of rainfall. This is exhibited by double maximum rainfall, which in May-July reaches its highest point, and from September to November, the minor season takes place. Usually, the rainy season begins in April, with the peak month in June and stops in November. In November and December, the dry season starts and ends in March. Average rainfall ranges from 67 mm to 1130 mm; year-round temperatures are warm with a maximum monthly average of 37.2℃ and a minimum of 21.0℃. The District of Shai-Osudoku has Dodowa as its capital. The primary activity in the district is agriculture (crop/livestock production and fisheries), supporting approximately 58.6 percent of the total population.

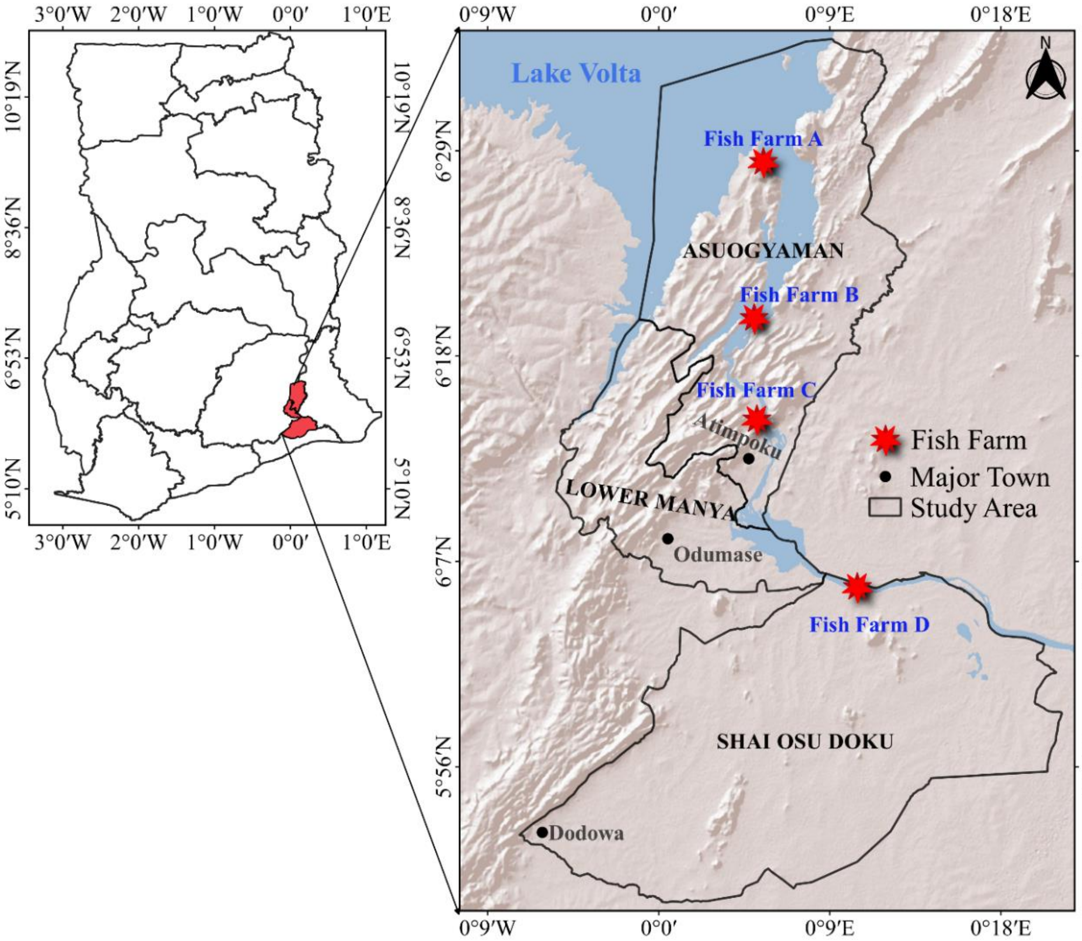


Figure 3.1: Map of the study area of the Volta Basin, Ghana

The landscape is generally gentle and hilly, a low plain with heights not exceeding 70 metres. Near the hills, in some places, big rocks and boulders are strikingly placed. The rocky hills and the large boulders offer enormous opportunities for stone extraction, which is already a significant concern in this district. Temperatures in this area are considerably high during most of the year, with the peak during the primary dry season (November - March) and the minimum during the short dry season (July - August). Rainfall is usually insufficient, with most of the very irregular rainfall occurring mainly from September to November.

CHAPTER FOUR

PESTICIDES AND HEAVY METALS LEVELS IN SEDIMENT, FISH FEED, WATER, AND CAGE CULTURED TILAPIA

4.1 Background

Due to the growing environmental stability, the tendency to magnify in the food chain, and bioaccumulation to humans and wildlife, pesticides and heavy metals are some of the biosphere pollutants of global concern (Papagiannis *et al.*, 2004). Run-off from agricultural lands is a vital source of these contaminants in the aquatic environment. Pesticides' persistence and movement in soils and their capacity to spread in the water contribute to their ability to contaminate water. Fish in aquatic habitats are exposed to these pollutants either through their gills or through their feed. Fish have become the most appropriate indicators for assessing the impact of water contamination because they concentrate contaminants in their tissues and assess pollutant transport via the trophic chain (Yohannes, 2014). As a result, pollutant bioaccumulation can be used as a measure of environmental pollution in aquatic environments. Sediments are also crucial in managing aquatic ecosystems since they act as reservoirs for pollutants (Burton, 2002). As a result, once the degree of chemical pollution gets to a point where it has an unfavourable effect on biota, sediment is declared polluted and requires remediation.

In keeping with the global interest in aquaculture product quality and controlling pollution of water bodies, this chapter assesses heavy metals and pesticide content of surface water, sediment, fish feed, and tilapia from the cage aquaculture farms in the Volta Basin. It compares it to FAO, EU, US EPA, and WHO permissible limits.

4.2 Materials and method

4.2.1 Sampling of water, sediment, fish meal and cultured tilapia samples

A sampling of the various matrices was carried out for the pesticides analyses and the other for the heavy metals analyses. Samples were collected in March, May, and July 2019. Sixty water samples were collected from four aquaculture farms, all on the Volta Basin of Ghana at an average depth of about 3 - 5m within the cages using a Kemmerer water sampler into a well-labelled acid cleaned 1L screw cap glass bottle. Each glass bottle was rinsed thrice with the water before collection. Fifteen cages were randomly selected from each farm for the sampling. Therefore, fifteen (15) water samples were obtained for organic extraction from each of the farms. Two water samples were collected at two different locations of the cage and mixed to form composite samples. This gave rise to a total of 60 water samples from the four farms. All samples were collected early in the morning between 6:00 am to 9:45 am to avoid the breakdown of specific contaminants.

At the same time, bottom sediment samples were collected where the water samples were obtained with an Ekman grab sampler. A total of 60 sediment samples for the pesticide extraction were collected and stored in a cleaned zip lock bag, labelled with an indelible pen and sealed to avoid cross-contamination. Two grabbed sediment samples were obtained at two separate locations in each of the fifteen cages from each farm and combined to form composite samples. The study also included 52 cage tilapias (*Oreochromis niloticus)* bought from three fish farms A= 19, B =16, and D =17 on the Volta Basin. The tilapia fish was not ready for harvesting in fish farm C during the period of sampling. Therefore, samples were not obtained from fish farm C. Two of the tilapia fishes were pulled together as a composite working sample. The morphometric characteristics of the two fishes were similar.

Along with the Nile tilapia, eleven (11) fish feed samples were also collected from the three fish farms for the heavy metals, OCPs and PCBs examination. For the heavy metals analyses, thirty-two (32) samples each of water and sediment (8 from each farm) collected were used. Twenty-six (26) cage tilapia samples collected from the fish farms (A =10, B = 6 and D = 10) were similarly used to analyse the heavy metal. Nine (9) fish feeds, three from each fish farm (A, B, and D), were also sampled for the heavy metals analyses.

Additionally, twenty (20) samples of each of water, sediment and wild *Oreochromis niloticus* were collected as controls from the upstream of the Volta Basin where aquaculture is not practised. All water, sediment, fish, and fish feed samples were preserved in an airtight bag at 4 °C and conveyed to the Ghana Atomic Energy Laboratory for further study.

4.2.2 Water quality parameters

All water quality analyses were established using sufficient approved, and suitable international procedures as outlined in the APHA (1998) recommended Water and Wastewater Analysis (APHA, AWWA & WEF, 2012). The Physico-chemical parameters such as temperature, pH, dissolved oxygen, electrical conductivity, and BOD were measured in situ using a thermometer, pH meter, YSI model 556, and a BOD meter, respectively. A geographical positioning system (GPS), Garmin etrex 20 model was used to record the sampling points' geographical coordinates in the fish farms.

4.2.3 Chemicals and reagents

Pesticide grade ethyl acetate, distilled water (HPLC grade), acetone, and hexane (both analytical grades) were supplied by Fisher Scientific (Loughborough, UK), silica gel and sodium sulphate were purchased from E. Merck (Germany). Disposable solid-phase florisil cartridges (500mg/6mL) were obtained from Sigma-Aldrich Chemicals USA. Certified, high purity (> 99.0 %), reference standards of α–HCH, γ–HCH, β–HCH, delta-HCH, endrin, heptachlor, aldrin, dieldrin, o,*p′*–DDT, *p,p′*–DDT, *p,p′*–DDD, *o,p′*– DDD, *p,p′*–DDE, *o,p′*–DDE, α–endosulfan, β–endosulfan and methoxychlor were obtained from Dr, Ehrenstofer GmbHm (Germany) and stored in the freezer to minimize degradation.

For the heavy metals analyses, hydrogen peroxide, hydrogen chloride (Merck, Germany) and nitric acid (Sigma-Aldrich, Germany) was used for digestion. By diluting concentrated stock solutions of 1000 mg/L in deionized water, working standards of heavy metals were prepared. Before the experimental process, the apparatus was sterilised by soaking it in dilute nitric acid (10 % v/v) for approximately 24 hours, rinsed with deionized water, and dried in an oven.

4.2.4 Sample treatment and preparation for OCPs and PCBs analysis

In the laboratory at Ghana Atomic Energy, the water samples were filtered with a 0.45 µm Whatman filter for the removal of impurities as well as other suspended solids. The samples were now kept in a freezer until further analysis

The fillets of the tilapia were removed using a stainless-steel knife. The samples were then washed with deionized water, wrapped in a pre-cleaned aluminium foil, and stored at -20℃ until extraction. After one week, the tilapia samples were taken out of the freezer and defrosted. The samples were homogenized and blended in a Kenwood blender (Plate 4.1), and the content was emptied into a dish covered with aluminium foil for the extraction process.

Plate 4.1: Blended fish in a Kenwood Blender

The sediment samples were air-dried and crushed in a mortar in the laboratory (Fritsch mortar grinder P-2) with a pestle. The content was sieved with a 250 µm mesh size sieve to remove stony particles and debris. The pelletized fish feed was also blended in a Kenwood blender and sieved 250 µm mesh into powdery for further analysis. The sieved acceptable samples (sediment and fish feed) were immediately used for the extraction.

4.2.5 Extraction of water samples for OCPs and PCBs

As reported by Solomon (2016) and Williams (2013a), liquid-liquid extraction of organochlorine pesticide residues in water samples were performed using US EPA Method 3510, with a slight modification. The samples' pH was checked to ensure that it was neutral to prevent chemical reactions from occurring with the OCPs. 50 mL of hexane was introduced into an extraction jar containing 150 mL of the water sample. The content was extracted in a Sonicator for about 30 minutes to facilitate the effective separation of the organic and aqueous phases. The organic layer was decanted into a 250 ml conical flask. The process was repeated and afterwards combined to form a whole. The extracts were concentrated in a volume of 25 ml using a rotary vacuum evaporator at a temperature of 45 °C.

4.2.6 Extraction of sediment, fish feed and fish samples for OCPs and PCBs

Solid-liquid extraction of organochlorine pesticide residues in the sediment samples was carried out using the US EPA 3550C method described by Solomon (2016) and Adeshina *et al.* (2019) with a slight modification. 10 g of the sample and 5 g of anhydrous sodium sulphate (Na_2SO_4) were weighed into an extraction jar. The mixture was thoroughly mixed with 50 ml acetone and n-hexane (2:1 v/v). The mixture was sonicated in a Bransonic 220 high-frequency ultrasonic bath (Plate 4.2) at 60 °C for 30 minutes; the organic extract was filtered through a Whatman filter paper into a well labelled 250 mL volumetric flask (Plate 4.3). The extraction process was repeated twice, and the combined extracts were concentrated to a volume of 25 ml at a temperature of 45 °C.

Plate 4.2: Extracts in a Brasonic 220 high-frequency ultrasonic bath

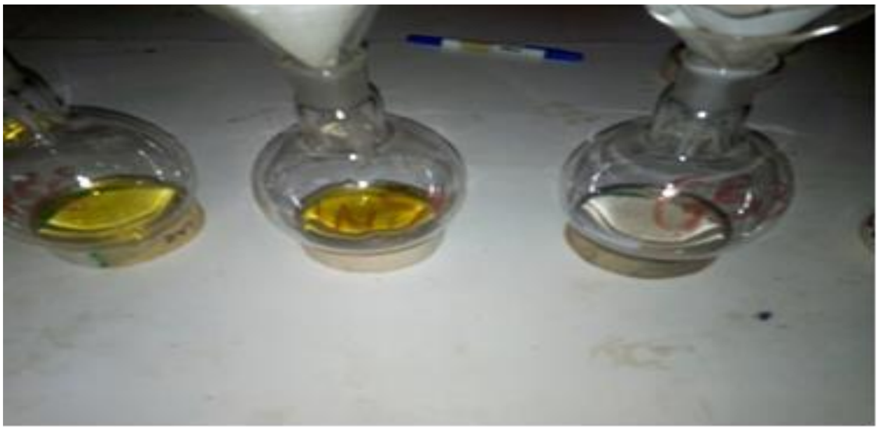


Plate 4.3: Filtered extracts of fish feed for OCPs and PCBs

4.2.7 Clean-up of water, sediment, fish feed and fish extracts for OCPs and PCBs

The clean-up procedure is required for the pesticide residues analysis in a sample in order to avoid interferences. Before the clean-up, the silica gel was activated by heating it moderately to about 150 °C in an air-tight oven. This process removes water content in the gel and increases its adsorptive capacity significantly. The glass separating column (20 cm) was packed with three layers. The agents were arranged with the activated charcoal at the top, followed by 2 g of anhydrous granulated Na_2SO_4 and the bottom packed with 4 g of activated silica gel (90 % < 45 µm). The activated charcoal removes colouration, the anhydrous Na_2SO_4 serves as a demoisturizer, and the silica gel removes co-extractants. Before clean up, the columns were conditioned with 10 mL of n-hexane. The extract was introduced into the column. The concentrate flask was rinsed with 5ml hexane and added to the column again. The eluate was concentrated to near dryness using a rotary evaporator at a temperature of 45 °C and picked in a 2 ml ethyl acetate vial for Gas Chromatography analysis

4.2.8 Determination of the OCPs residues

The final extracts were analysed using a Varian CP-3800 (Plate 4.4) gas chromatograph (Varian Association Inc. USA) equipped with a combiPAL autosampler and Ni-63 electron capture detector. The GC conditions used for the analysis were: VF-5 coated capillary column (30 m + 10 m EZ protection column × 0.25 mm inner diameter, 0.25 µm film thickness). The temperature of the injector and detector were set at 270 °C and 300 °C, respectively. The furnace temperature was programmed as follows: 70 °C held for 2 min, ramp at 25 °C/min to 180 °C, held for 1 min and finally ramp at 5 °C/min to 300 °C". In order to compensate for the relative retention times and the response behaviour, the GC conditions and the detector response were determined. Nitrogen was used as carrier gas at a 1.0 ml/min flow rate and 29 ml/min as detector additive gas. The injection volume of the analyses was 1.0 µl. The total running time for one sample was 31.4 min.

Plate 4.4: GC Varian CP-3800 for organochlorine pesticide Quantification

4.2.9 Determination of the PCBs residues

GC-MS analysis was carried out with Agilent Technologies 6890N (for GC) and 5975 (for MS) in EI mode. The interface and ion source temperatures were 280 °C and 300 °C, respectively. Chromatographic separation was conducted on a Phenomenex ZB-5MS capillary column (30 m × 0.25 mm × 0.25 µm). The gas flow of the carrier was 1.1 mL/min, the injection temperature was 265 °C, and the amount of the samples infused was 1µL. The temperatures were optimized as follows: The initial oven temperature was maintained for 1 min at 60 °C, increased to 170 °C with a 20 °C/min ramp, kept for 0.30 min and then increased by 10 °C/min to 310 °C with a maintaining time of 1.20 min. To identify each PCB holding time, a mixture of a solution of PCB 28, PC 52, PCB 101, PCB 153, PCB 138 and PCB 180, with a concentration of 10 μg/mL in isooctane, by Sigma Aldrich, was injected into the GC 2 μL. The PCBs were identified by comparing the mass spectra obtained with a library of system mass spectra (NIST, NBS).

4.2.10 Identification and quantification of OCPs and PCBs residues

Residue levels of OCPs and PCBs were quantitatively measured by reference guidelines and residence time estimations. By matching the peak heights of the samples with the respective peak heights of the reference standards for specific concentrations, the residue levels were determined by the standard external procedure. The calculation was performed within the linear range of the detector. The peak areas whose retention times correlated with the standards were extrapolated to their respective calibration curves to obtain the concentration. The LOD for OCPs and PCBs given in this work was established based on the lowest analyte level that could consistently and reliably recover 70 % or more from the enriched samples described by Koranteng (2015). Standard OCPs and PCBs mix solutions were serially diluted. The lowest concentration whose recovery from fortified samples was greater than 70 % and gave a signal to noise ratio of 1:3 was run ten times. The standard deviation of the signals was calculated. The standard deviation (SD) was multiplied by 3 to get the LOD (i.e., SD x 3 = LOD). The standard deviation for the LOD determination was multiplied by 10 to get the limit of quantification (LOQ) (i.e. SD x 10 = LOQ). The LOD and LOQ for the persistent pesticides in sediment were set as 0.12 μg/kg and 0.40 μg/kg, respectively.

4.2.11 Digestion of water samples for heavy metals

Digestion of fish water samples for heavy metals was performed using the method reported by Hadzi *et al.* (2015), with a slight modification. The water samples were digested using Sineo Jupita-A Microwave. 10 ml of the water sample was weighed into a previously acid-washed 100 ml polytetrafluoroethylene (PTFE) Teflon bomb before digestion. In a fume chamber, 6 ml of nitric acid (HNO_3) (65%), 3 ml of hydrogen chloride (35%) and 0.25 ml of hydrogen peroxide (30%) were added to the sample. On the microwave carousel, the sample was then loaded. The vessel caps were secured tightly using a wrench. The complete assembly was microwave irradiated for 40 minutes using the Sineo Jupita-A microwave digestion program.

After digestion, the Teflon bombs mounted on the microwave carousel were cooled in a water bath to reduce internal pressure and allow volatilized material to re-stabilize. The digest was made up to 20 ml with double distilled water and assayed for the presence of all the metals using the VARIAN AA 240FS- Atomic Absorption Spectrometer (Plate 3.5) in acetylene- air flame".

Plate 4.5: Varian AA 240FS- Atomic Absorption Spectrometer

4.2.12 Digestion of sediment, fish feed and fish samples for heavy metals

Digestion of the sediment samples for heavy metals was performed using the method reported by Feng *et al.* (2017), with a slight modification. Before digestion, the sediment samples were air-dried in the laboratory for about 48 hours. The dried sediment was crushed in a mortar (Fritsch mortar grinder P-2) with a pestle. The content was sieved with a 250 µm mesh size sieve to remove stony particles and debris. 0.5 g of the sieved dried sediment powder was measured into a polytetrafluoroethylene (PTFE) Teflon bomb. In each sample, 6 ml of concentrated nitric acid (HNO_3, 65 percent) and 1 mL of 30 % H_2O_2 was added. The samples were placed in the chamber of a flame. On the microwave carousel, the samples were then loaded. Using a screw, the vessel caps were fixed securely. Using the Sineo Jupita-A microwave digestion program, the whole assembly was irradiated for 50 minutes.

After the digestion, the Teflon bombs on the microwave carousel were cooled in a water bath to minimize internal pressure and stabilize the volatilized material again. The digested material was developed with double-distilled water up to 20 ml and tested for the presence of zinc (Zn), arsenic (As), copper (Cu), lead (Pb), nickel (Ni), manganese (Mn), cadmium (Cd), chromium (Cr) and iron (Fe) using the acetylene-air flame VARIAN AA 240FS- Atomic Absorption Spectrometer.

In Table 4.1, the working condition of the AAS is shown. The quantitative analysis included the measurement of final concentrations from the initial concentrations of the specified elements and their conversion into final concentrations using the equation:

$$\text{Final concentration} = \frac{\text{Initial conc (D.F) X Nominal vol}}{\text{sample weight in grams}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(Equation 4)}$$

Nominal volume was given as 20 ml, and the sample weights for water, sediment, fish and fish feed were 10 g, 0.5 g, 0.5 g and 0.5 g, respectively. Each result was expressed in mg/kg.

Table 4.1: Conditions of Atomic Absorption Spectrophotometer (AAS)

ELEMENT	WAVELENGTH nm	LAMP CURRENT nA	SLIT WIDTH Nm	FUEL	SUPPORT
Zn	213.9	5	1.0	Acetylene	Air
Pb	217.0	5	1.0	Acetylene	Air
Fe	248.3	5	0.2	Acetylene	Air
Ni	352.4	4	0.5	Acetylene	Air
Cd	228.8	4	0.5	Acetylene	Air
Cr	428.9	7	0.5	Acetylene	Air
As	193.7	10mA	0.5	Acetylene	Nitrous oxide
Mg	285.2	4mA	0.5	Acetylene	Air
Mn	279.5	5mA	0.2	Acetylene	Air

4.2.13 Quality assurance and Quality control

Quality control and quality assurance were incorporated into the analytical system. Measures were taken to guarantee the reliability of the results. All glass apparatus used for research were thoroughly rinsed with detergent and tap water. The glassware was cleaned with distilled water, carefully cleaned with analytical grade acetone, and left to dry overnight in an oven at 70 °C. They were removed from the furnace, cooled and placed in dust-free cabinets. Analyses of solvent blanks, procedural blanks and samples were performed to ensure the quality of the pesticides and heavy metals residues.

For the pesticides, the solvent used was run to verify any interfering substances within the runtime. Before sample analysis, standards for all pesticides were analysed to verify adequate system performance. Procedural recoveries were analysed concurrently with each batch of analytical extracts. Besides, recalibration curves were run with each batch of samples to check that the correlation coefficient was kept above $r^2 > 0.995$. All analyses were carried out in triplicates, and the mean concentrations were calculated based on the number of samples that tested positive for each residue. The efficiency of the OCPs and PCBs extraction method was validated by spiking samples with 0.05 mg/kg internal standard (isodrin).

Spiked samples were taken through the same extraction procedure as the samples. The isodrin was measured with good recoveries between 78 % - 115 % for OCPs and 80 % - 94 % for PCBs, indicating that the approach used is reproducible.

Additionally, the working conditions for the heavy metals were established using a serial dilution to verify the reliability of the equipment used. Precision and accuracy of procedures were verified by using Standard Reference Materials such as SLRs-4 River Water from the National Research Council Canada (NRCC), CRM 320 (fish) and IAEA-405(sediment). The calculated recoveries ranged from 86% to 115%, indicating the method was efficient.

4.2.14 Data Analyses

In order to assess the normality of the data, the Kolmogorov-Smirnov (K-S) analysis was performed, and at the p-value less than 0.05, the findings were considered statistically significant. Descriptive statistics (mean, range, SD) were computed and compared to the FAO, EU, USEPA, WHO permissible limits. One-way ANOVA was used to test the differences in the contaminants from the sampling zones, and Tukey’s post hoc test was done where significant differences existed.

4.3 Results

4.3.1 Physico-chemical parameters

In recent years, the toxicity of organics, heavy metals and metalloids in the aquatic environment has become a topical concern worldwide. This is because the contaminants in water, and sediment, at higher levels, has a potential threat to aquatic organisms because of their long persistence, toxicity, bioaccumulation, and biomagnification within the food chain (Authman *et al.*, 2015). Pollutants can decrease the fertility of most fish populations, even at low levels in the aquatic regime, contributing to a long-term decrease and eventual extinction of specific critical natural resources (Aly & Abouelfadl, 2020). The results of the analysis of water quality parameters from fish farms on Lake Volta in Ghana have been extensively discussed in the current research.

Table 4.2: Quality parameters of water samples collected from cage farms

	Water Quality Parameters				
Fish Farms	**Av.T±SD/°C**	**pH**	**DO/ mg/L**	**BOD/ mg/L**	**EC/μS cm^{-1}**
A	29.6±1.15	7.16	6.22	2.2	64.7
B	29.0±0.54	6.96	5.52	2.7	65.3
C	30.3±0.28	7.32	5.22	3.2	64.1
D	29.5±0.74	7.84	4.76	3.4	66.8

Av.T – Average temperature, SD- standard deviation

The four farms' average temperature and pH values ranged from 28.9 °C to 31 °C and 6.96 to 8.4, respectively. The highest pH value of 8.4 was detected at farm D. The average dissolved oxygen (DO) concentrations in all selected fish farms were above the optimum level of 5.0 mg/L. The mean DO concentration in farm A was 6.22 ± 0.21 mg/L. In farm B, the mean DO concentration level was 5.52 ± 0.29 mg/L. In farm C, the mean DO concentration was 5.22 ± 0.11 mg/L, and in farm D, the average DO level recorded a value of 4.76 ± 0.15 mg/L. BOD values ranged from a minimum of 2.2 mg/l in A to a maximum of 3.4 mg/l in farm D. The Volta River Authority has embarked on removing aquatic weeds downstream of the Basin. This activity is performed closer to some of the cages coupled with the discharge of unfed fish feed beneath the cages. This increases the level of BOD due to the absorption of oxygen during the oxidative decomposition of these wastes. This may account for the high BOD in fish farm D, where the practice is pronounced. High electrical conductivity (EC) may arise through natural weathering and anthropogenic sources. High conductivity may be attributed to the existence of a significant level of dissolved salts in water. The mean EC values were 64.7 µS/cm at farm A, 65.3 µS cm^{-1} at farm B, 64.1 µS cm^{-1} at farm C and 66.8 µS cm^{-1} at farm D. The average values of the E.C for all the farms were below the WHO recommended values that range from 1000 to 1500 µS/cm.

4.3.2 OCP compounds in the water samples

Table 4.3 shows the concentrations of persistent organochlorine compounds in water samples. The study revealed the presence of 7 OCPs in farm A, 11 OCPs in farm B, 10 OCPs in farm C, 10 OCPs in farm D, and 5 OCPs in control. The detected OCPs in the water samples from all the farms were δ-HCH, γ-HCH, heptachlor, α-endosulfan, β-endosulfan, endrin, *o,p′*-DDE, *p,p'*-DDE, *o,p′*-DDD, *p,p'*-DDT and methoxychlor. γ-HCH, endrin, *p,p'*-DDE and *p,p'*-DDT were not detected in fish farm A. The general concentration of OCPs in the water ranged from 0.026 µg/l (ww) *o,p′*-DDD in fish farm B to 1.541 µg/l (ww) for methoxychlor in fish farm A with occurrence frequencies of 89% and 90%, respectively. Methoxychlor recorded the highest mean concentration of 1.541 µg/l (ww) in farm A followed by endrin of 1.173 µg/l in farm C. Endrin recorded the least level in the controls with an average of 0.017 ± 0.014 µg/l.

The predominant compounds detected were methoxychlor (90%), *o,p'*-DDD (90 %), α-endosulfan (60 %) and methoxychlor (40 %) in fish farms A, B, C and D, respectively. The most encountered OCP compound in control was δ-HCH, with a detection frequency of 30%. δ-HCH contributed most significantly in fish farm A compared with γ-HCH in water from fish farms B, C and D. The organochlorine pesticides load in the water samples in terms of the farms revealed the pattern; farm C (3.210 µg/l) > farm A (1.606 µg/l) > farm B (0.986 µg/l) > farm D (0.841 µg/l) > control (0.079 µg/l).

Analyses of the organochlorine concentrations in the water compartments generally, revealed the following pattern: ΣHCHs > Σendosulfans > methoxychlor> heptachlor > ΣDDTs for fish farm A, ΣHCHs > Σendosulfans > ΣDDTs> heptachlor > methoxychlor> drins for fish farm B, drins > Σendosulfans > methoxychlor> ΣDDTs > ΣHCHs for farm C, ΣHCHs > methoxychlor> ΣDDTs> Σendosulfans> heptachlor >drins for fish farm D and ∑HCH > methoxychlor>drins for control. Whilst as many as 9 OCPs residues in water samples were below the WHO MRL in all the farms during the investigation period, only two exceeded WHO MRL during the period under review. The levels of heptachlor in farms A, B, and D, exceeded the WHO MRL for drinking water. Endrin in farm C also exceeded the required level for safe drinking water proposed by WHO

Table 4.3: Concentration (µg/L) of organochlorine pesticides in water from cage fish farms

FARM A	***γ*-HCH**	**δ-HCH**	**o,p′-DDE**	***p,p′*-DDE**	***o,p′*-DDD**	***p,p′*-DDT**	**Hept.**	**Endrin**	**Meth.**	***α*-endos.**	***β*-endos.**
Mean	ND	0.799	<LOD	ND	0.049	ND	0.062	ND	1.541	0.034	0.421
SD	-	0.058	-		0.030	-	0.023	-	0.031	0.013	-
Frequency	-	89	-		50	-	50	-	90	30	30
FARM B											
Mean	0.031	0.520	<LOD	0.041	0.026	<LOD	0.063	0.037	0.040	0.041	0.087
SD	0.001	-	-	0.038	0.018	-	0.015	0.035	0.020	0.020	0.006
Frequency	20	10	-	40	90	-	20	20	40	30	30
FARM C											
Mean	ND	0.181	0.051	<LOD	0.146	<LOD	<LOD	1.173	0.641	0.184	0.834
SD	-	0.078	0.004	-	0.041	-	-	0.161	0.084	0.077	0.058
Frequency	-	20	30	-	40	-	-	30	30	60	40
FARM D											
Mean	ND	0.280	<LOD	0.054	0.055	<LOD	0.068	0.054	0.238	0.068	0.025
SD	-	0.057	-	0.024	0.005	-	0.012	0.010	0.131	0.005	0.007
Frequency	-	20	-	30	30	-	30	30	40	30	20
CONTROL											
Mean	ND	0.037	ND	<LOD	<LOD	ND	ND	0.017	0.025	ND	ND
SD	-	0.009	-	-	-	-	-	0.014	0.008	-	-
Frequency	-	30	-	-	-	-	-	25	25	-	-
WHO/µg/L	**2.00**	**2.00**	**1.00**	**1.00**	**1.00**	**1.00**	**0.03**	**0.60**	**20.00**	**20.00**	**20.00**

LOD- Limit of Detection, Hept.- Heptachlor, Meth.- Methoxychlor, endos .-Endosulfan WHO (2011) health-based limit, SD-standard deviation

4.3.3 PCB compounds in the water samples

Table 4.4 summarizes the PCB congeners found in the water samples from the cage aquaculture farms on the Volta Basin.

Table 4.4: Mean concentrations (ng/l) of indicator PCBs in water from the cage fish farms

	FARM A	FARM B	FARM C	FARM D	CONTROL
PCBs	**Mean ±SD**	**Mean ±SD**	**Mean ±SD**	**Mean ±SD**	**Mean ±SD**
PCB 18	0.296±0.0005	0.304±0.0176	0.471±0.0762	0.297±0.0007	0.163±0.013
PCB 28	ND	ND	ND	ND	ND
PCB 52	ND	0.528±0.2420	ND	0.594±0.1448	0.172
PCB 101	ND	ND	0.815±0.2111	ND	ND
PCB 138	ND	ND	ND	0.070±0.0111	0.072
PCB 153	ND	ND	ND	ND	ND
PCB 180	0.508±0.1767	0.391±0.1590	0.436±0.2379	0.396±0.1022	0.159±0.014
ΣPCBs	**0.804±0.1772**	**1.223±0.4186**	**1.722±0.5252**	**1.357±0.2588**	**0.566±0.027**

Analysis of variance (ANOVA) revealed significant PCB differences among the farms studied at a 5 percent level ($p = 0.001$). Tukey HSD test at 5% ($p < 0.05$), also revealed that there were statistically significant differences in PCB 18 concentration in the following farms: A and C ($p=0.022$); B and C ($p=0.014$) and C and D ($p=0.001$). Farms A, B, C, and D were significantly different from the control ($p<0.001$).

Besides, two indicator congeners (CB-18 and CB-180), three (CB-18, CB-52 and CB-180), three (CB-18, CB-101 and CB-180), four (CB-18, CB-52, CB-138 and CB-180) and four indicator congeners (CB-18, CB-52, CB-138 and CB-180) were detected in water from fish farms A, B, C, D and controls respectively. However, indicator congeners PCB-28 and PCB-153 were not detected in any of the fish farms. The general concentration of PCBs in the water ranged from 0.070 ng/l to 0.815 ng/l in the fish farms. The predominant PCB indicator congers compounds detected were CB-18 and CB-180, accounting for 100% of the water samples. PCBs congener 101 recorded the highest of 0.815 ng/l in farm C and the least concentration of 0.070 ng/l in farm D. The analyses of the ∑PCB loading of all congeners in the water compartments for each farm indicated the concentrations in the order: fish farm C (1.722±0.5252 ng/l) > fish farm D (1.357±0.2588 ng/l)>fish farm B (1.223±0.4186 ng/l) > fish farm A (0.804±0.1772 ng/l) > controls (0.566ng/l). The levels of the PCBs congeners, as well as the ∑PCB, were all below the US EPA MRL for drinking water (500 ng/l)

4.3.4 Heavy metals in fish farms water

In the water column of the aquaculture cages, six heavy metals were found (i.e. Cr, Pb, Ni, Fe, Mn and Zn). The concentrations of these elements in the water samples are shown in Table 4.5 by their means and standard deviations

Concentrations of the heavy metals at the different fish farms showed no significant differences ($p > 0.05$).

Lead is highly toxic to man and other organisms since it causes brain damage, mostly to the young and induces aggressive behaviours (Ramadan, 2003). The highest mean concentration of Pb in the water was 0.542 ±0.0198 mg/L, found in farm A. Conversely, farm D recorded the lowest concentration of 0.172 ± 0.097 mg/L. The concentrations of Pb ranged 0.720 – 0.774 mg/L, 0.568 – 0.728 mg/L, 0.590 – 0.784 mg/L, 0.036 – 0.686 mg/L and 0.034 – 0.072 mg/L for fish farms A, B, C, D and controls respectively.

Table 4.5: Heavy metals concentrations (mg/L) in cage aquaculture water

FARM A	**Pb**	**Zn**	**Fe**	**Mn**	**Ni**	**Cr**
Mean ±SD.	0.542 ±0.019	ND	0.163 ±0.018	0.579±0.013	0.016 ±0.001	0.015 ±0.002
Range	0.720 – 0.774	ND	0.122– 0.182	0.562 - 0.608	0.014– 0.018	0.012 – 0.018
FARM B						
Mean ±SD	0.573±0.063	0.006±0.001	0.159±0.001	0.588±0.032	0.041±0.008	0.023±0.002
Range	0.568 – 0.728	0.004– 0.008	0.158 – 0.160	0.158– 0.760	0.039 – 0.044	0.018 – 0.024
FARM C						
Mean ±SD	0.263 ±0.060	0.002 ±0.002	0.002 ±0.001	0.589 ±0.010	0.065 ±0.003	0.012± 0.001
Range	0.130 – 0.784	0.002– 0.063	0.002 – 0.172	0.580– 0.610	0.060 – 0.068	0.002 – 0.018
FARM D						
Mean ±SD	0.172 ±0.097	0.006 ±0.002	0.213 ±0.006	0.646 ±0.016	0.041 ±0.001	0.098 ±0.021
Range	0.036 – 0.686	0.004 – 0.008	0.200 – 0.218	0.622– 0.664	0.004 – 0.042	0.060 – 0.120
CONTROL						
Mean ±SD	0.047±0.016	0.003 ±0.001	0.042 ±0.040	0.310±0.068	0.020 ± 0.002	0.012 ± 0.001
Range	0.034 – 0.072	0.004 – 0.006	0.015 -0.103	0.244 – 0.422	0.021- 0.024	0.011 -0.013
WHO	0.1	3	2	0.4	0.07	0.05
AWPL	7	30	0.3	0.027	150	2

WHO Guidelines for Drinking-Water Quality: (Javed & Usmani, 2013; WHO, 2011). Aquatic life water permissible limits (AWPL/ mg/L) (CCME, 2007).

The results of this study for all the cage aquaculture fish farms recorded Pb concentrations exceeding the threshold value established by WHO and USEPA (0.015mg/L) except levels obtained in control (Mohammadi *et al.*, 2019). Similarly, the levels of Pb in the farms were above the Ghana EPA standard of 0.1mg/L (Abagale *et al.*, 2013). However, the average level from the findings was below the aquatic life water permissible limits (CCME, 2007).

Concentrations of Zn ranged from 0.004 – 0.0080 mg/L in water for fish farm B, 0.002 – 0.0630 mg/L in water for fish farm C, 0.004 – 0.008 mg/L in fish farm D and 0.004 - 0.006 mg/l in the control samples. Zinc was not present in samples from farm A. The average zinc levels from the three fish farms, including the control, are 0.006 mg/L, 0.002 mg/L, 0.006 mg/L, and 0.003 mg/L for farms B, C, D, and controls, respectively. The concentration of Zn in water is lower than both the US-EPA limits of 5 mg/L and the target water quality ranges (TWQR) for domestic use of 3.0 mg/L (Darko *et al.*, 2015). The obtained average levels were, however, within the AWPL and WHO domestic water guidelines.

Manganese is essential for human nutrition, and high exposure beyond the expected level is correlated with harmful health effects (Landrigan *et al.*, 2004). In this analysis, the average values of Mn were 0.579 mg/L, 0.588 mg/L, 0.589 mg/L, 0.646 mg/L and 0.310 mg/L, respectively, in the water samples of fish farms A, B, C, D and control. Fish farm D recorded the highest Mn concentration, whiles the control recorded the least. The levels in the farms exceeded the health-based standards set by the World Health Organization (400 μg/L) and the European Union (50 *μ*g/L) for manganese in drinking water (WHO, 2011; Iyare, 2019). However, the level of control was below the WHO limits. The Mn concentrations in all the farms and control samples analysed surpassed the acceptable aquatic life limits (CCME, 2007).

Fe is an essential metal for most living organisms and humans and helps maintain vital organs within the body. Fe is a constituent of the proteins and enzymes, including haemoglobin and myoglobin (Yip *et al.*, 1996). As a result of its abundance on the earth, it occurs high in freshwater than any other metal (Forstner & Wittmann, 2012). The US EPA argued strongly that the intake of highly concentrated Fe water does not have any detrimental health effects because the elevated Fe levels in humans are largely due to the intake of Fe-rich foods (Edokpayi *et al.*, 2016). Fe level of 0.163, 0.159, 0.002, 0.213 and 0.042 mg/L were obtained from farm A, B, C, D and controls respectively. Fish farm D recorded the highest, and farm C recorded the least value. It was observed that Ni and Cr in all the four fish farms were relatively lower compared to the WHO and AWPL guidelines' levels.

4.3.5 OCPs and PCBs contents in sediment samples from the fish farms

Tables 4.6 and 4.7 respectively present the detected indicator polychlorinated biphenyls and organochlorine pesticides in the sediments from the fish farms in the Volta Basin. In all, a total of eleven OCPs and seven indicators PCB congeners were found in the sediments.

Generally, the OCP residues in the sediment ranged between <LOD to 33.00 µg/kg in all the studied fish farms, including the control. Endrin in fish farm D had the highest mean concentration of 13.867± 8.716 µg/kg with 83% detection frequency. However, the same compound was the least in fish farm B, with a 20% detection frequency. δ-HCH (8.154±0.414 µg/kg), α-endosulfan (6.000±1.414 µg/kg), *o,p′*-DDD (2.010±1.46 µg/kg), endrin (13.867± 8.716 µg/kg) and α-endosulfan (0.503 ±0.398) recorded the highest average levels in fish farms A, B, C, D and control respectively. The OCPs in the farms revealed the order; methoxychlor > δ-HCH> *o,p′*-DDD> *α*-endosulfan> β-HCH> *o,p′*-DDE>*β*-endosulfan>endrin(<LOD); α-endosulfan>Heptachlor> β-HCH> Methoxychlor> *p,p′*-DDE >*o,p′*-DDD >β-endosulfan > δ-HCH= *o,p′*-DDE > Endrin; Endrin > β-HCH > *o,p′*-DDD > $p,p' -$ DDT > δ-HCH > *α*-endosulfan > *p,p′*-DDE > *β*-endosulfan > *o,p′*-DDE and Endrin > *p,p′*-DDT > *o,p′*-DDD > *β*- endosulfan > β-HCH > *p,p′*-DDE > δ-HCH > *o,p′*-DDE> *α*-endosulfan > Heptachlor > methoxychlor, α-endosulfan > β-HCH > heptachlor > methoxychlor > *δ*-HCH > *o,p′*-DDE for fish farms A, B, C, D and control respectively.

The OCPs; δ-HCH (7.72-8.80 µg/kg), *o,p′*-DDD (0.52-2.12 µg/kg), *α*-endosulfan (<LOD-2.00 µg/kg), *o,p′*-DDD (1.00-28.00 µg/kg) and heptachlor (0.234 – 0.472 µg/kg) were the predominant with frequency of detection 100 %, 45 %, 68 %, 92 % and 25 % in fish farms A, B, C, D and control respectively. All the OCPs levels in the sediment from the farms were below the USEPA maximum residue levels. The levels of ∑DDT was in order:12.263 µg/kg wet weight (fish farm D) >7.185 µg/kg wet weight (farm A) >5.938 µg/kg (farm B)> 3.483 µg/kg wet weight (farm C) >0.163 µg/kg wet weight (controls).

Table 4.6: Mean concentrations (ng/g) of indicator PCBs in the sediments from the fish farm

PCBs	FARM A Mean ±SD	FARM B Mean± SD	FARM C Mean± SD	FARM D Mean± SD	CONTROLS Mean± SD
PCB 18	0.296±0.0008	0.248±0.1006	0.141±0.0516	0.296±0.0002	0.059±0.0220
PCB 28	ND	ND	ND	0.400±0.0758	ND
PCB 52	ND	ND	ND	0.066±0.0138	ND
PCB 101	ND	0.494±0.3479	0.382±0.1305	ND	ND
PCB 138	ND	ND	ND	ND	ND
PCB 153	ND	0.475±0.0799	0.394±0.0505	3.328±1.700	ND
PCB 180	0.492±0.1682	0.401±0.0999	0.354±0.0755	2.112±0.7008	0.113±0.1050
ΣPCBs	**0.788±0.1762**	**1.618±0.6283**	**1.271±0.3081**	**6.202±2.4906**	**0.172±0.127**

Table 4.7: Concentration (μg/kg) of organochlorine pesticides in sediment from cage fish farms

FARM A	**β-HCH**	**δ-HCH**	**o,p′-DDE**	***p,p′*-DDE**	***o,p′*-DDD**	***p,p′*-DDT**	**Hept.**	**Endrin**	**Meth.**	***α*-endos.**	***β*-endos.**
Mean	2.336	8.154	2.120	-	5.065	ND	3.985	<LOD	8.253	2.753	1.037
SD	0.231	0.414	1.659	-	1.796	-	1.479	-	5.252	1.262	0.701
Frequency	71	100	29	-	45	-	57	-	57	43	43
FISH FARM B											
Mean	2.152	0.710	0.710	1.480	1.293	ND	2.585	0.275	1.860	6.000	0.970
SD	0.052	0.410	0.410	0.646	0.793	-	1.639	0.092	1.612	1.414	0.415
Frequency	20	20	20	30	45	-	40	20	20	20	20
FISH FARM C											
Mean	2.362	1.793	1.012	1.113	2.010	1.803	ND	5.000	ND	1.555	1.103
SD	0.091	1.053	0.125	0.196	1.406	0.981	-	3.606	-	0.492	0.179
Frequency	33	33	67	33	56	44	-	33	-	68	33
FISH FARM D											
Mean	1.613	1.325	1.163	1.510	4.590	5.000	1.080	13.867	0.908	1.103	1.615
SD	0.321	0.148	0.142	1.010	3.735	0.505	0.505	8.716	0.271	0.714	1.186
Frequency	25	17	25	42	93	8	25	83	42	33	92
CONTROLS											
Mean	0.486	0.242	0.163	ND	ND	ND	0.301	ND	0.243	0.503	ND
SD	0.196	0.123	0.024	-	-	-	0.030	-	0.022	0.398	-
Frequency	20	15	15	-	-	-	25	-	20	15	-
USEPA MRL	**30**	**40**	**40**	**40**	**40**	**50**	**30**	**40**	**50**	**50**	**40**

LOD- Limit of Detection, Hept.- Heptachlor, Meth.- Methoxychlor, endos .-Endosulfan, USEPA (μg/kg)

Generally, the concentrations of indicator PCBs ranged from 0.042 ng/g to 5.320 ng/g wet weight. PCB congeners CB-18 and CB-180 were the predominant congeners in the observed sediment samples from the fish farms accounting for a detection frequency of 100% each. CB-153 recorded the highest concentration of about 3.328 ± 1.700 ng/g, and CB-52 was the least with level 0.059 ± 0.0220ng/g in all the studied farms. The PCB congeners concentrations were in the order; fish farm D (6.202 ±2.4906 ng/g)> fish farm B (1.618 ±0.6283 ng/g)> fish farm C (1.271 ±0.3081 ng/g) > fish farm A (0.788 ±0.1762 ng/g) > control (0.172±0.1270 ng/g). The mean levels of the congeners in the fish farms were higher than the controls. The ∑PCBs concentrations (ng/g) in the sediment ranged from 0.172 ng/g to 6.202 ng/g, where the value of ∑PCBs in fish farm D was significantly higher than the other farms.

4.3.6 Heavy metals in sediment from aquaculture farms

Results of the individual heavy metal levels in sediment from the fish farms and controls are presented in Table 4.8. Out of the nine heavy metals, six (Pb, Zn, Fe, Mn, Ni and Cr) were detected in the sediment from the study. The heavy metal Pb in the sediment from the fish farms was statistically significant at 5% ($p<0.05$). Post Hoc analysis using Tukey's HSD was conducted revealed differences in the lead concentrations between the following fish farms: fish farms A and C ($p=0.002$) and farms A and D ($p=0.015$). Fish farms A, B, C, D and control, were significant ($p<0.001$). There was, however, no statistically significant difference between fish farms A and B ($p=0.217$). The overall concentration of lead (Pb) ranged from BDL to 13.66 mg/kg. The greatest Pb level was obtained in farm C and the least in control. The mean Pb level was 13.66 ± 1.072 mg / kg in farm C, 13.64 ± 0.043 mg / kg in farm D and 0.386 ± 0.219mg/kg in the controls. The levels of Pb in farms

A and B were below the detection limit. USEPA and WHO have recommended a maximum Pb level of 10 mg/kg. However, in the present analysis, farms C and D levels were higher than the recommended target set by the USEPA/WHO. The present findings were lower than the average shale value of 20 mg/kg for Pb.

Table 4.8: Heavy metals concentration (mg/kg) of sediment samples from fish farms

Statistics		Pb	Zn	Fe	Mn	Ni	Cr
FARM A	Mean	BDL	0.495	2.771	25.215	0.920	11.565
	SD	BDL	0.064	0.564	1.509	0.021	0.646
	Max.	BDL	0.600	3.640	28.760	0.960	12.880
	Min.	BDL	0.400	1.920	23.960	0.880	10.720
FARM B	Mean	BDL	0.790	3.130	25.199	0.690	8.875
	SD	BDL	0.090	0.295	1.360	0.085	0.120
	Max.	BDL	0.920	3.440	28.28	6.800	9.800
	Min.	BDL	0.640	2.600	23.84	0.560	7.920
FARM C	Mean	13.660	0.480	BDL	22.750	0.823	12.430
	SD	1.072	0.068	BDL	0.213	0.069	0.153
	Max.	15.680	0.600	BDL	26.440	0.960	12.720
	Min.	11.800	0.360	BDL	19.920	0.720	12.240
FARM D	Mean	13.640	0.510	BDL	20.850	0.880	11.315
	SD	0.043	0.063	BDL	0.363	0.037	0.753
	Max.	13.720	0.600	BDL	29.200	0.960	12.520
	Min.	13.520	0.400	BDL	18.400	0.840	9.960
CONTROL	Mean	0.386	0.006	0.213	6.805	0.058	0.970
	SD	0.219	0.002	0.005	0.988	0.018	0.200
	Max.	0.686	0.008	0.213	9.220	0.072	1.114
	Min.	0.124	0.004	0.200	6.220	0.041	0.579
Max. limit WHO/USEPA		**10**	**123**	**-**	**30**	**20**	**25**

SD-standard deviation, BDL-Below Detection Limit

The heavy metal Zn in the sediment from the fish farms was statistically significant at $p<0.05$. Post hoc analysis using the Tukey HSD revealed differences in the Zn concentrations between fish farms A and B ($p=0.019$). There were, however, no differences between fish farm A and C ($p=0.028$) and farm A and D ($p=0.004$). They were all different ($p=0.001$) from the control sites. The zinc (Zn) concentration varied between 0.006 mg/kg and 0.790 mg/kg in all sites considered for the study. The highest concentration of Zn was reported in fish farm B (0.790 ± 0.090 mg/kg), followed by fish farms D, A, C and the control in decreasing order. According to WHO and the USEPA, the maximum permissible amount for Zn in river sediments is 123 mg /kg, the average shale value (ASV) is 70 mg/kg. Values obtained for Zn were considered below the allowable limit set by USEPA, WHO and the average shale value.

The heavy metal manganese in the sediment showed a wide variation: 23.96 - 28.76 mg/kg (mean value 25.215 mg/kg), 23.24 - 28.28 mg/kg (mean value of 25.199 mg/kg), 16.92 – 26.44 mg/kg (mean value of 22.750 mg/kg), 18.40 - 29.20 mg/kg (mean value of 20.850 mg/kg), and 6.220 – 9.220 mg/kg (6.805 mg/kg) for fish farms A, B, C, D and control respectively. Fish farm A recorded the highest concentration of Mn, and the control recorded the least level. The mean levels of Mn in all the cage aquaculture sediments were higher than the controls. The concentrations of Mn in the present study were below the USEPA standard and the average shale value (ASV). Analysis of variance (ANOVA) revealed a significant difference in the Mn level in the sediment among the fish farms. Post Hoc analysis using the Tukey HSD revealed differences in manganese concentrations between the following fish farms: fish farms A and C and farms A and D. There was no difference between fish farms A and B.

There was a significant difference in the Cr level in the sediment among the fish farms ($p=0.002$) for Cr. However, a Post Hoc analysis using the Tukey HSD revealed differences in the Cr concentrations between farms A and B ($p=0.014$). There were no differences between Cr in fish farm A and farm C ($p=0.067$) and also fish farms A and D ($p>0.05$). The chromium (Cr) concentration varied between 0.970 mg/kg and 12.43 mg/kg in the study. In contrast, the most significant level of chromium (Cr) was reported in farm C (12.43 ± 0.153 mg/kg), followed by fish farm A, fish farm D, fish farm B and the control. The levels of Cr concentrations in the fish farms displayed in Table 4.8 were below the maximum permissible limit of 25 mg/kg set by ASV and USEPA. The observed levels for Cr from the sediment were also below the toxicity reference value (TRV) (26 mg/kg), as well as the world river system (WRS) value (87mg/kg) (Singh *et al.*, 2018).

4.3.7 Organochlorine and PCB compounds in the fish feed samples

In the case of the fish feed samples examined, ten organochlorine pesticides (δ-HCH, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDT, heptachlor, endrin, methoxychlor, *α*-endosulfan and *β*-endosulfan) were detected, and the OCPs concentrations ranged from 0.23 to 8.67 µg/kg as shown in Table 4.9. Nevertheless, endosulfans and DDT metabolites were the predominant OCPs detected in the fish feed

Table 4.9: OCPs and PCBs levels (µg/kg) in the fish feed samples

	FISH FARM A		**FISH FARM B**		**FISH FARM D**		
Pesti5ides	**Mean ±SD**	**Range**	**Mean ±SD**	**Range**	**Mean ±SD**	**Range**	**EU**
δ-HCH	0.38±0.16	0.25-0.56	NIL	NIL	7.87±2.55	5.10-10.11	10
o,p′-DDE	1.34±0.11	1.24-1.45	0.99±0.01	0.98-1.00	3.50±1.54	1.00-6.00	-
p,p′-DDE	1.77±0.50	1.20-2.14	2.57±1.24	1.32-3.80	3.11±2.68	1.21-5.00	-
o,p′-DDD	1.04±0.08	0.99-1.08	1.53±0.59	1.09-2.20	2.83±1.99	1.42-4.23	-
p,p′-DDT	NIL	NIL	2.25±0.89	1.56-3.25	NIL	NIL	-
ΣDDTs	**4.11±0.69**		**7.34±2.73**		**9.44±8.76**		**50**
Heptachlor	6.21±0.32	4.21-6.92	7.44±1.67	4.75-12.30	8.67±2.52	6.00-11.00	10
Endrin	NIL	NIL	0.59±0.26	0.32-0.84	NIL	NIL	10
Methoxychlor	NIL	NIL	NIL	NIL	2.56±2.12	1.32-5.00	-
α-endosulfan	2.21±0.79	1.42-3.00	4.02±1.67	2.84-5.20	2.05±0.93	1.14-3.00	5∗
β-endosulfan	1.58±0.74	1.00-2.41	0.23±0.08	0.16-0.32	1.05±0.32	0.82-1.27	5∗
Σendosulfan	**3.79±1.53**		**4.25±1.75**		**3.10±1.25**		**100**
∑OCPs	**14.49 ±2.70**		**19.62±6.37**		**31.64±17.2**		**-**
PCB 18	0.29±0.01	0.29-0.30	0.30±0.01	0.29-0.30	0.29±0.01	0.27-0.29	-
PCB 28	0.22±0.13	0.25-0.42	0.26±0.02	0.21-0.46	0.35±0.16	0.26-0.69	
PCB101	-	-	-	-	0.51±0.02	0.35-0.96	
PCB 180	0.50±0.09	0.39-0.63	0.30±0.05	0.26-0.36	0.37±0.06	0.33-0.44	-
ΣPCB	**1.01±0.23**		**0.86±0.08**		**1.52±0.25**		**200**

EU= European maximum limits of POPs in fish feed. Maule *et al.*, 2007; Amlund *et al.*, 2012, ∗values (Bataro *et al.*, 2011)

Moreover, the analysed feeds from different fish farms showed a total OCP load of 14.49± 2.70 µg/kg (ww) for fish farm A, 19.62 ± 6.37µg/kg (ww) for fish farm B and 31.64 ± 019.2µg/kg (ww) for fish farm D. Variations in the feed composition can be clarified by the higher OCP levels in feeds from farm D. Heptachlor, for instance, recorded the highest level of 8.67 µg/kg in farm D, whiles β-endosulfan recorded the least with 0.23 µg/kg in fish farm B. The DDT metabolites (*o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD and *p,p′*-DDT) were detected in all the fish feeds from the various farms except *p,p′*-DDT which was detected in only fish farm B and ranged 1.56 – 3.25 µg/kg.

The levels of δ-HCH, α-endosulfan Heptachlor, β-endosulfan endrin, ΣDDTs (*o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD and *p,p′*-DDT) and Σendosulfan (α-endosulfan and β-endosulfan) were all below the maximum limit of 10, 5,10, 5, 10, 50 and 100 µg/kg respectively in fish feed proposed by the EU (Amlund *et al.*, 2012; Bataro *et al.*, 2011).

PCB 18, PCB 28 and PCB 180 were the predominant congeners observed among the PCBs, accounting for 100% in the fish feed. PCB 101 was detected in only feeds from fish farm D, while PCB congeners 52, 138 and 153 were not detected in any of the samples analysed. PCB congener 101 recorded the highest concentration of 0.51±0.02 ng/g, observed in the fish feed from fish farm D, while PCB 28 recorded the least concentration of 0.22±0.13ng/g in the feed from fish farm A.

The total concentration of PCBs in the fish feed among the fish farms was in the order: 1.52±0.2513 ng/g (Fish farm D) > 1.01±0.2313 ng/g (Fish farm A) > 0.86±0.0813 ng/g (Fish farm B). The levels of the entire PCB congeners (ΣPCB) in the fish feed from the fish farms were below the maximum limit of 200 ng/g prescribed by Maule *et al.* (2007)

4.3.8 Heavy metals in fish feed

ANOVA analysis indicated no significant differences in the heavy metals among all the fish feed samples from all the sites (P > 0.05).

The highest concentration of Mn (11.8 mg/kg) was found in farm D feed. The lowest concentration of Mn (11.4mg/kg) was recorded in the feed of farm A. The concentrations of Mn in the feeds were 11.8 mg/kg, 11.5 mg/kg, and 11.4 mg/kg from fish farms D, B and A, respectively (see Fig. 4.1). The allowable limit of concentration of Mn in a fish feed ingredient is 7.7 mg/kg (Niemiec & Wisniowska-Kielian, 2015). Mn exceeded FAO level by 48 – 53% in all feeds from the farms

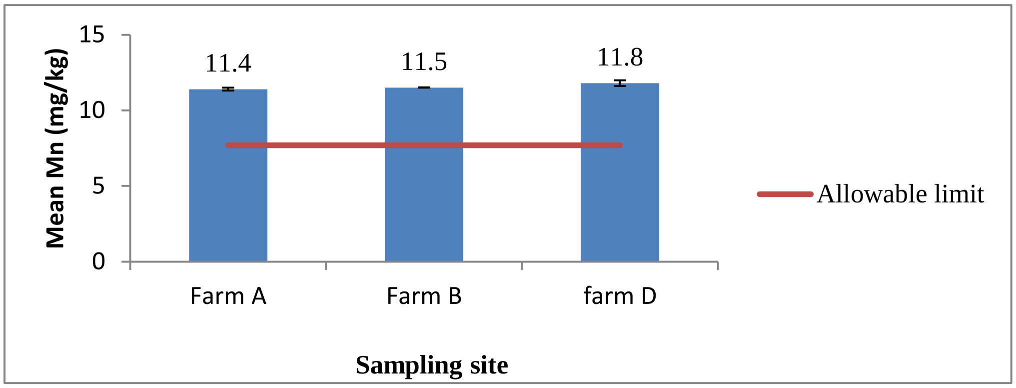


Figure 4.1: Mean Manganese of fish feed at sampling sites

In the fish farm, A feed, the lowest concentration (1.6 mg/kg) of Fe was found, and in fish farm D feed, the highest concentration (3.8 mg/kg) was found (as in Fig. 4.2). According to FAO/WHO, the permissible concentration of Fe in fish feed components is 100 mg/kg (Saha *et al.*, 2018). It was, therefore, deduced from this analysis that the Fe concentration was within the appropriate limit.

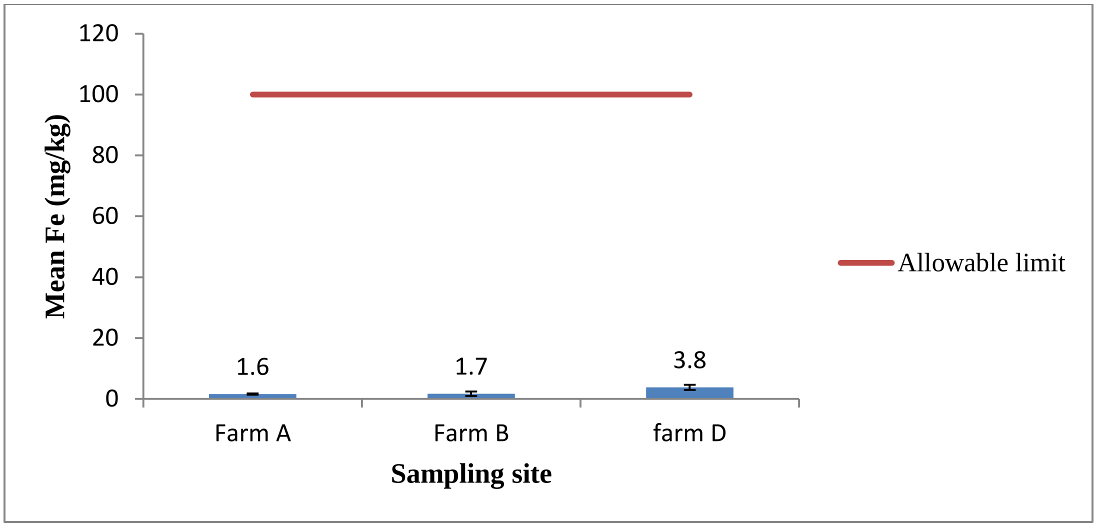


Figure 4.2: Mean Iron of fish feed at sampling sites

Nickel concentrations in fish farms A and B were 0.76 ± 0.13mg/kg and 0.12 ±0.006mg/kg. Nickel was not detected in fish farm D. The highest concentration of Ni was 0.76 mg/kg in fish farm A feed, and the lowest was observed in fish farm B feed (0.12mg/kg), as shown in Fig. 4.3. There are no maximum allowed concentrations of nickel in the current regulations for feed ingredients and compound feed. The limit for the allowed nickel content in fish feed adopted the European Commission standard value of 8.0mg/kg (EC, 2003; Saha *et al.*, 2018). Therefore, the recorded data for the concentration of Ni in the fish farms' feed materials were not appalling compared to acceptable nickel content for EC.

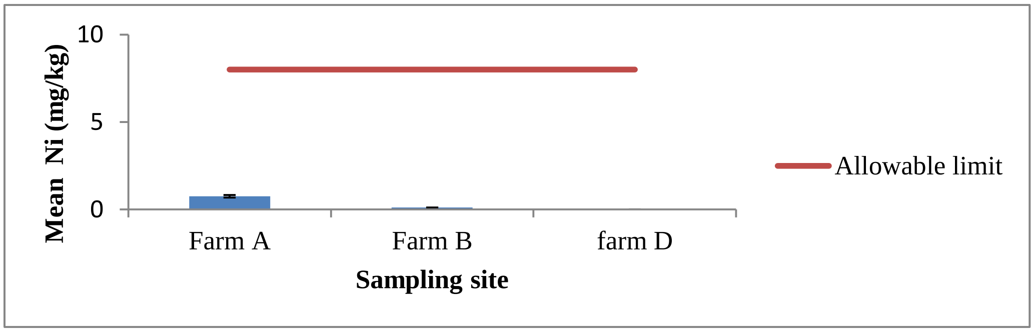


Figure 4.3: Mean Nickel of fish feed at sampling sites

Zinc concentration in fish feed was in a range of 0.10 to 0.480 mg/kg. The highest mean concentration of Zn (0.43 ± 0.09mg/kg) was found in fish farm B, while fish farm D had the lowest (0.10 ± 0.02mg/kg). Zn content in the tilapia feeds in all fish farms (Figure 4.4) were below the permissible limit (150 mg/kg) proposed by WHO and FAO (Saha *et al.*, 2018).

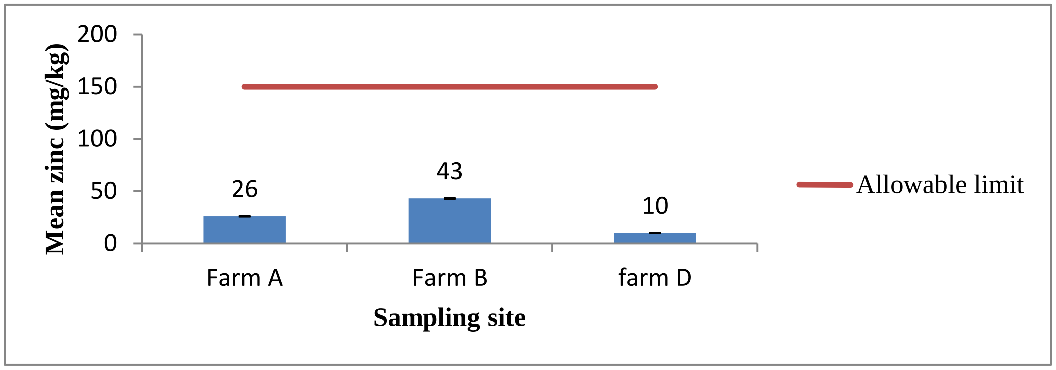


Figure 4.4: Mean Zinc of fish feed at sampling sites

In fish farm D, the concentration of Cr in fish feed was reported to vary from 0.40 to 0.48 mg/kg. Cr was not detected in fish farms A and B. The mean level of Cr from fish farm D feed was 0.44 ± 0.04mg/kg. Chromium concentration in all samples from fish farm D was below the EU (2011) standard limit of 1 mg/kg. The study results for Cr were not as alarming as detected in some of the feed samples.

4.3.9 OCP and PCB compounds in the fish samples

Tables 4.10 and 4.11 present the detected organochlorine pesticides and indicator PCBs in the tilapia from the Volta Basin. In all, ten organochlorine pesticides and six indicators of PCB congeners were detected in the fish.

The organochlorine pesticides, δ-HCH, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDT, heptachlor, endrin, methoxychlor, *α*-endosulfan and *β*-endosulfan were observed in all the fish samples. *p,p'*-DDT, *o,p'*-DDD, δ-HCH, and Heptachlor recorded the highest concentration in tilapia from farms A, B, D and controls, respectively. *δ*-HCH (6.109±4.530 µg/kg) recorded the highest level in fish from the farm. In contrast, p,p-DDE recorded the least of 0.455±0.276 µg/kg in fish from farm A. *δ*-HCH, p,p'-DDT, o,p'-DDD, and α-endosulfan were the predominant OCP compounds encountered. However, there was considerable variability among the farm samples. The levels of OCPs in the fish varied from <LOD to 3.42 µg/kg, <LOD to 6.00 µg/kg, and <LOD to 12.00 in fish farms A, B, D, and controls respectively. Although the levels of OCPs found in the fish samples were broadly comparable in the study areas, fish from farm D (Load =25.408) showed slightly higher concentrations than fish from farms A, B and the controls. Analysis of the fish samples showed the following order of concentrations: *p,p*-DDT> α-endosulfan > heptachlor > β-endosulfan> *o,p′*-DDE > *δ*-HCH > *p,p′*-DDE; *o,p′*-DDD > methoxychlor > α-endosulfan > endrin >*δ*-HCH > β-endosulfan> heptachlor > *o,p′*-DDE > *p,p*-DDT, *δ*-HCH> methoxychlor > endrin > heptachlor > *o,p′*-DDE> *p,p′*-DDE> α-endosulfan> *p,p*-DDT> β-endosulfan and heptachlor > α-endosulfan > *o,p′*-DDE >*δ*-HCH=methoxychlor > β-endosulfan in fish farms A, B, D and controls respectively. The levels of all the pesticides in the fish from the study were below the European Union (EU) default Maximum Residue Level (MRL) of 10 µg/kg (Koranteng, 2015). The trends of persistent organochlorine compounds distribution in the fish samples indicated higher organochlorine concentrations in fish than in the sediment and the water compartments.

The concentrations of indicator PCBs ranged from 0.296 ng/g to 0.494 ng/g wet weight, 0.054 ng/g to 1.807 ng/g wet weight and 0.801 ng/g to 8.524 ng/g, in fish farms A, B and D, respectively. The highest concentration was recorded in fish farm D for PCB 153 and the lowest in fish farm A for PCB 52. The predominant congeners were PCB 153 and PCB 180 in all the fish. The PCB loadings in the fish from the respective farms' A, B and D were 0.790 ± 0.1779 ng/g, 3.960 ± 1.0424 ng/g and 20.676 ± 7.0510 ng/g

Table 4.10: Concentrations (µg/kg) of pesticide residues in cage tilapia from fish farms

	FISH FARM A		**FISH FARM B**		**FISH FARM D**		**CONTROLS**	
Pesticides	**Mean ±SD**	**Range**	**Mean ±SD**	**Range**	**Mean ±SD**	**Range**	**Mean ±SD**	**Range**
δ-HCH	0.834 ± 0.444	<LOD - 1.40	2.078 ± 1.557	1.00 – 6.00	6.109 ± 4.530	0.42 – 12.00	0.546±0.093	ND– 0.64
***o,p′*-DDE**	1.393 ± 0.427	<LOD - 2.00	1.250 ± 0.500	<LOD – 2.00	2.828 ± 2.021	<LOD – 6.01	0.616±0.151	ND – 0.88
***p,p′*-DDE**	0.455 ± 0.276	0.26 – 0.65	<LOD	-	2.439 ± 0.338	<LOD – 9.00	0.532±0.074	ND – 0.62
***o,p′*-DDD**	<LOD	-	4.260 ± 0.994	3.22 – 4.36	< LOD	-	-	-
***p,p′*-DDT**	2.310 ± 0.438	2.00 – 2.62	1.22	ND – 1.22	1.500 ± 0.707	<LOD – 2.00	-	-
∑DDT	**4.158 ± 1.451**		**6.730±1.494**		**6.767 ± 5.066**		**1.148 ± 0.225**	
Heptachlor	2.126 ± 0.748	1.00 – 3.42	1.335 ± 0.670	<LOD – 2.34	2.890 ± 1.734	<LOD – 6.00	0.878±0.317	ND – 1.20
Endrin	ND	-	2.170 ± 0.240	<LOD – 2.34	3.080 ± 2.557	<LOD – 6.00	0.820±0.298	ND – 1.24
Methoxychlor	<LOD	-	3.171 ± 1.440	<LOD – 5.00	3.889 ± 3.343	<LOD – 10.25	0.546±0.093	ND – 0.64
***α*-endosulfan**	2.210 ± 0.790	<LOD– 3.00	2.305 ± 0.863	<LOD – 3.00	1.860 ± 1.316	<LOD –3.00	0.738±0.295	ND -1.12
***β*-endosulfan**	1.683 ± 0.639	1.00 – 2.41	1.340 ± 0.570	<LOD – 2.05	0.813 ± 0.506	<LOD – 1.20	0.520±0.111	ND – 0.62
∑endosulfan	**3.893 ± 1.429**		**3.645 ± 1.433**		**2.673 ± 1.822**		**1.258 ±0.406**	
	Load=11.011		**Load=19.129**		`		**Load=5.196**	

``

Table 4.11: Mean concentrations (ng/g) of indicator PCBs in tilapia from the cage fish farms

	FISH FARM A		**FISH FARM B**		**FISH FARM D**		**CONTROLS**	
PCBs	**Mean ±SD**	**Range**	**Mean ±SD**	**Range**	**Mean ±SD**	**Range**	**Mean ±SD**	**Range**
PCB 18	ND	-	0.300±0.0048	0.296-0.314	0.801±0.5640	0.296-2.574	0.163±0.013	ND – 0.172
PCB 28	ND	-	ND	-	0.360±0.1252	0.260-0.683	ND	-
PCB 52	ND	-	0.054±0.0105	0.042-0.061	2.564±1.2977	1.098-3.435	0.285±0.154	ND – 0.390
PCB 101	ND	-	ND	-	2.592±1.4961	1.160-4.345	ND	-
PCB 153	0.494±0.0021	0.296-0.305	1.807±0.5142	1.321-3.253	8.524±1.5960	6.393-10.657	ND	-
PCB 180	0.296±0.1758	0.288-0.931	1.799±0.5129	1.113-4.302	5.835±1.9760	4.112-8.035	0.297±0.001	ND – 0.398
ΣPCBs	**0.790±0.1779**		**3.960±1.0424**		**20.676±7.051**		**0.745±0.168**	

ND- Non detected

4.3.10 Heavy metals in cultured tilapia

The mean concentrations and standard deviations of heavy metals (Zn, Fe, Mn, Ni, Cr and As) in fish from fish farms (A, B, D and controls) are presented in Table 4.12. Arsenic was detected only in the control samples. Other heavy metals such as Cu, Cd, and Pb were below the fish samples' detection limit in the fish muscle. Heavy metals such as Zn, Fe, Mn, Ni and Cr recorded a 100% incidence in fish samples except for the Wild tilapia. Concentrations of the heavy metals at the different sampling points did not show a significant difference ($p < 0.05$).

The concentrations of the heavy metals ranged from 0.10 mg/kg to 50.11 mg/kg in the fish samples. Zn plays a crucial role in terms of the metabolic pathways of humans, and therefore its shortage may lead to loss of appetite, retarded growth, skin changes and dysfunction of the immune system (Ayanda *et al.*, 2019). The concentration of zinc ranged from 0.97 mg/kg to 2.13 mg/kg. Zn recorded mean concentrations of 2.07 ± 0.140 mg/kg, 2.13 ± 0.330 mg/kg, 1.82 ± 0.29 mg/kg and 0.97 ± 0.20 mg/kg in fish farms A, B, D and controls respectively. The obtained levels of Zn were lower than the benchmark values (30 mg/kg and 40 mg/kg) prescribed by FAO and WHO, respectively (Bawuro *et al.*, 2018). Concentrations of Zn metal in the investigated tilapia from fish farms were within the maximum permitted level for human ingestion recommended by England (i.e. 50 mg/kg) (Bawuro *et al.*, 2018).

Iron is necessary for many organisms, and its deficiency may cause anaemia in humans. US EPA recommends Rfd of 700 $\mu g kg^{-1}$ day^{-1} for Fe, and intake beyond this threshold will result in diseases such as Parkinson, Alzheimer and type-2 diabetes (Korkmaz *et al.*, 2019).

Table 4.12: Levels of heavy metals concentrations (mg/kg) in cage tilapia from fish farms

	FISH FARM A		FISH FARM B		FISH FARM D		CONTROLS	
Metals	**Mean±SD**	**Range**	**Mean±SD**	**Range**	**Mean±SD**	**Range**	**Mean±SD**	**Range**
Zn	2.07±0.140	1.80-2.28	2.13±0.33	1.92-2.80	1.82±0.29	1.80-2.28	0.97 ± 0.20	0.58-1.11
Fe	37.28 ±10.84	21.60-54.80	50.11±10.22	38.92-62.6	39.58±9.14	21.6-54.80	11.09± 2.03	8.21 – 14.21
Mn	3.41 ±2.03	1.64-8.80	1.76±0.69	1.04-3.08	2.46±0.60	1.64-8.80	0.77 ± 0.15	0.52 – 0.96
Ni	1.62±0.03	1.58-1.64	2.74±1.87	0.03-5.04	2.00±0.14	1.58-1.64	0.65 ± 0.11	0.52 – 0.81
Cr	0.31±0.07	0.20-4.00	–	–	0.33±0.07	0.20-0.40	0.10 ± 0.02	0.06 – 0.12
As	–	–	–	–	–	–	0.23 ± 0.07	0.15 – 0.32

This study observed that Fe in fish farms A, B, D and control were 37.28 mg/kg, 50.11 mg/kg, 39.58 mg/kg, and 11.09 mg/kg, respectively. The level of Fe was highest in farm B and lowest in the control samples. Fe concentrations in the fish from all the farms exceeded the international guidelines limit of WHO (2003), WPCL (2004) and USEPA (1986), except the control.

Mn is an integral element, and its deficiency contributes to severe skeletal and reproductive defects in mammals (Anim *et al.*, 2011). In the fish samples, manganese showed lower concentrations compared with Fe. The controls measured the lowest concentration at 0.77 ± 0.15 mg/kg, while the highest concentration was measured in the fish from farm A (3.41 ± 2.03 mg/kg). The average level of Mn in the biota exceeded the maximum allowable levels recommended by WHO, USEPA and WPCL for human consumption (Anim-Gyampo *et al.*, 2013), except for the wild tilapia.

Chromium is an essential trace metal, and its usable biological form plays a significant role in glucose metabolism (Anim *et al.*, 2011). In a related development, the highest Cr content (average value) in the edible part (fish flesh) of the studied tilapia was detected in fish farm D (0.33 ± 0.07 mg/kg), and the lowest recorded in farm A (0.31 ± 0.07 mg/kg). The levels of Cr from the two farms were higher than the guidelines value of 0.15 mg/kg set by FAO (Ahmed *et al.*, 2019). The maximum guideline, 12-13 mg/kg proposed by the USFDA (1993), was higher than the concentration of chromium measured in the tilapia from the studied farms.

Ni levels in the whole of the sampled *O. niloticus* as shown in the results ranging from 0.65 to 2.74 mg/kg of wet weight. All the tilapia fish sampled showed lower levels of Ni than the permissible levels (70-80 mg/kg) recommended by the USFDA (Anim *et al.*, 2011; USFDA 1993). The means (range) for Ni levels in the *O. niloticus* in the farms were: 1.62±0.03 (1.58-1.64 mg/kg), 2.74±1.87 (0.03-5.04 mg/kg), 2.00±0.14 (1.58-1.64 mg/kg) and 0.65±0.11 mg/kg for farms A, B, D and controls respectively

4.4 Discussion

4.4.1 Physico-chemical properties of water

The pH of the water for the study was slightly basic and was within the permissible limit of 6.5-8.5 for drinking, recreational purposes and aquatic ecosystems proposed by WHO (2004). The findings for the pH levels for the study were not different from Koffi *et al.* (2014) and Elegbede *et al.* (2015) in their study in Ivory Coast and Ghana, respectively. Although alkaline drinking water is considered safe, it may also result in some side effects. Firstly, it lowers the stomach's natural acidity, which functionally kills bacteria and expels undesirable pathogens from entering the bloodstream (WHO, 2010). Excess alkalinity of water may cause skin irritations and metabolic alkalosis. In the aquatic environment, water pH can alter the toxicity of heavy metals and other contaminants. At low pH (acidic medium), heavy metals become soluble and mobile and are most likely to be absorbed by aquatic organisms (Hadzi *et al.,* 2015). Human consumption of aquatic products and water at this acidic pH can cause health issues such as acidosis and damage to the digestive and lymphatic systems (Nkansah *et al.,* 2010).

The rise in water temperature accelerates chemical reactions, decreases gas solubility, amplifies taste and odour, and increases organisms' metabolic activity. This eventually decreases the amount of DO in the water. The temperature values reported in this work were lower than the limit set by the WHO in 2003 for portable drinking water and aquatic organisms.

Direct diffusion of oxygen from the wind and wave action, atmosphere, and photosynthesis are all methods for supplying DO to water. It is employed in aerobic degradation of organic waste, aquatic microorganism respiration, and mineral oxidation. Because many species in the water consume DO, it fluctuates frequently. The primary cause of oxygen depletion in water is excessive algae and phytoplankton growth driven by high levels of nitrogen and phosphorus. Fish farm D reported the lowest level of DO during the study. There have been high phytoplankton and aquatic weeds growth in the lower stream of the Volta Basin, where Fish Farm D is located. The photosynthetic activities and removal of the aquatic weeds by VRA resulted in the decomposition of the algae and weeds. This process requires a significant amount of dissolved oxygen. This phenomenon probably accounts for the lower DO level in fish farm D. The reported level of DO in farm D is similar to that of Barakat *et al.* (2016), who spatially recorded lower DO values downstream of Oum Er Rbia River in Morocco.

Similarly, the high BOD level in fish farm D may be due to the decomposition of the aquatic weeds and uneaten fish feed, which results in the uptake of oxygen in the oxidative breakdown of these wastes (Chatvijitkul, 2015). Introduction of oxygen-depleting organic wastes such as nutrients, sewage, changing water flow, and increasing water temperature are anthropogenic activities that decrease dissolved oxygen in watersheds. Excess dissolved organic material in the water column can cause eutrophic conditions.

The conductivity of a river is lowest the upstream and, as it flows along the course of the river, it leaches ions from the soils. Also, it picks up organic material from biota and its detritus (Karikari & Ansa-Asare, 2006). Koning & Roos (1999) reported that an unpolluted river body has an average conductivity value of about 350 µS/cm. Therefore, the finding from this study with regards to EC parameters gives no cause for concern. Therefore the water is suitable for direct domestic use. The reported values of the EC for this study are not different from those reported by Antwi & Ofori-Danson (1993) on the same Volta Lake at the Kpong stretch. The results, however, are different from the EC reported values in the Densu River by Karikari & Ansa-Asare, (2006). This probably implies a higher amount of the total dissolved solids, ions and other suspended matter in the Densu River compared to the Volta Basin.

4.4.2 Levels and distributions of OCPs, PCBs and HMs in water

Among the eighteen OCPs that were sought for in the study, eleven (11) of them (γ–HCH, delta-HCH, endrin, heptachlor, *p,p*′–DDT, *o,p*′– DDD, *p,p*′–DDE, *o,p*′–DDE, α–endosulfan, β–endosulfan as well as methoxychlor) were found in the water samples from the farms including the controls. This indicates the wide range of OCPs usage in the agricultural fields along the banks of the Volta Basin.

Among the isomers of HCH, δ- HCH was the only compound detected in all farms and the controls. In contrast, γ-HCH (lindane) was detected in only fish farm B. δ-HCH was predominant in fish farm A (0.799µg/l) and recorded the highest detection frequency among the farms as observed in Table 4.2. The δ-HCH levels reported at the four farms and the controls were far below WHO drinking acceptable water limits of 2.00 µg/l. However, the levels in the farms were higher than the Australian water guideline value of 0.05 µg/l (Kuranchie-Mensah *et al.,* 2012). Lindane enters into water directly from pesticides application for the control of mosquitoes and agriculture pests. The high concentrations of δ-HCH in farm A might be due to the ability of HCH isomers to break down quickly in water (Abagale *et al.,* 2014). Comparatively, the recorded concentration in cage aquaculture farm A was higher than the earlier investigation into OCP levels in water (0.669ug/l) from other parts of the Volta Lake by Gbeddy *et al.* (2015). Similarly, the concentration of δ-HCH in farm A is relatively higher than 0.07µg/l as observed by Darko *et al.* (2008) on Lake Bosomtwi, 0.095 – 0.140µg/l as reported by Kuranchie-Mensah *et al.* (2012) on Densu River and 0.008µg/l as detected by Fianko *et al.* (2011) on the Densu River.

At the international front, the average concentrations of δ- HCH in the present research were higher than the ones obtained by Guo *et al.* (2013) in the surface water of Meiling Bay of Lake Taihu in China but slightly lower than that of Baqar *et al.* (2018) in their post-monsoon results obtained in tributaries of River Ravi in Pakistan.

Yahaya *et al.* (2017) stated that "under anaerobic conditions, pesticides such as γ-HCH in active sewage sludge could be converted to alpha or δ-HCH in a certain proportion at a slow rate. Therefore, the high concentration of δ-HCH may be due to the unlawful discharge of waste from sludge, aerated treatment ponds, factories and households into areas closer to the cages compared to those at the international level".

Bempah *et al.* (2011) indicated that γ-HCH (lindane) is a reasonably stable compound, and it is only under alkaline conditions that it decomposes to yield trichlorobenzene. It is considered one of the less persistent organochlorine pesticides. For this study, γ-HCH was only detected in fish farm B with an average level of 0.031 ± 0.001µg/L. The higher concentration of δ-HCH than γ-HCH in fish farm B could be attributed to the natural conversion of γ-HCH (the active component) to other isomers due to past use. γ-HCH was not detected in the other studied farms; A, C, D and the controls. γ-HCH degrades rapidly in the environment (Shinggu *et al.*, 2015) due to past use and its natural conversion to other isomers. This probably explains why the non-detection of lindane in all the samples from fish farms A, C and D. Darko *et al.* (2008) reported a lindane level of 0.071 µg/l in the lake Bosomtwi and Kuranchie-Mensah *et al.*, (2012) 0.070 µg/l in Weija. These levels were slightly different from what was observed in fish farm B, with a concentration of 0.031 µg/l. Meanwhile, Ntow (2005) work on the same Volta Lake reported lindane levels of 0.008 µg/l, much lower than observed in fish farm B for the study. Although the lindane levels present in the water samples did not reach the WHO limit, it has been documented that exposure to significant quantities of lindane has adverse effects on the nervous system, with symptoms ranging from headaches and dizziness to cramps, less commonly, death.

Although DDT has been banned from agricultural use and restricted due to public health concerns under the Stockholm convention (Afful *et al.*, 2010; Agbeve *et al.*, 2014), it continues to be used. This is because of its low cost and non-availability of viable alternatives (Singh, 2001). For this study*, p,p'*-DDT were below the detection limit in fish farms B, C and D except in fish farm A and the controls where it was not detected at all. The observed trend could be attributed to the complete decomposition of DDT to its metabolites, DDE and DDD, by micro-organisms, heat and ultraviolet rays (Kafilzadeh, 2015). The higher levels of the metabolites than the parent DDT could also be due to its past use along the Basin or the residues brought by rivers through runoff and erosion. The finding agrees with other evaluations on the same Volta Lake by Fianko *et al.* (2011).

In this study, DDE (p*,p'*-DDE and *o,p*-DDE) was detected in fish farms B, C and D. The level of *p,p'*-DDE in fish farm B (0.041 µg/l) was similar to *p,p'*-DDE level reported by Amuzu (2012) in irrigation water in some farming communities in Accra. Observation from the study in farm B was not different from DDE levels reported by Teklit (2016) in water samples from Tekeze Dam, Tigray in Ethiopia. Also, in evaluating water in one of the study sites in Lake Naivasha in Kenya, Mutuku (2014) found similar *p,p´*-DDE levels as in the present study in fish farm B. On the other hand, levels of *p,p´*-DDE observed in this current study is higher than what was observed in the study by Gbeddy *et al.* (2015) and Kuranchie-Mensah *et al.* (2012) in the Volta Lake and station 2 of the Weija River, respectively. However, the amount of *p,p'*-DDEs in the current study were lower than that observed by Darko *et al*. (2008) and Abagale *et al.* (2014) in their studies on OCPs in Lake Bosomtwi and the irrigation water of the Golinga dam in Ghana, respectively. The *o,p'*-DDE concentration in fish fam B was slightly higher than that of Estii lagoon (0.0193 µg/l), Fosu lagoon (0.0361 µg/l), but lower than that of Korle lagoon (0.4844 µg/l) and Chemu lagoon (0.0718 µg/l) as observed by Essumang *et al.* (2009).

DDE is more stable than DDD, and hence its level is expected to be higher. However, in this study, the DDD (*p,p'*-DDD and *o,p*-DDD) concentrations in the experimental fish farms water were higher than their respective DDEs except in fish farm B. This observation could be due to the primary degradation of DDT to DDD by the reductive dechlorination process (Koranteng *et al.*, 2015). The finding of fish farm B follows that of Gbeddy *et al.* (2015) on *p,p'*-DDD on the same Volta Lake.

Generally, the presence of chlorinated cyclodiene pesticides (heptachlor, endrin, and the endosulfans) in the water ecosystem was partly due to their past use and continued atmospheric transport from remote regions. The high levels of the heptachlor in the water from the fish farms may be due to its presence in the commercial feeds from these farms (Amlund *et al.*, 2012).

Heptachlor recorded levels; 0.062 µg/l, 0.063 µg/l and 0.068 µg/l in fish farms A, B and D respectively. The levels were below the detection limit in fish farm C but were not even detected in the controls. The pesticide heptachlor was most encountered (50 %) in fish farm A, but predominant in farm D. The levels obtained in the three farms (i.e. A, B, and D) were above the WHO guideline limit of 0.03 µg/l for drinking water. Heptachlor does not dissolve easily in water as compared to its degraded product, heptachlor epoxide. This likely accounts for the high levels of water from the farms for this study. The findings were similar to the results obtained by Gbeddy *et al.* (2015) on the same Volta basin but slightly higher than findings of studies by Fosu-mensah *et al.* (2016) and Kuranchie-Mensah *et al.* (2012) in drinking water sources from the cocoa growing areas and Weija River respectively. The levels of heptachlor in water from the fish farms were similar to El Bouraie *et al.* (2011) in Egypt. Heptachlor affects human health during exposures, and it is known to cause Parkinson's disease, cancers, reproductive failures, congenital disabilities, immune system malfunction, and disrupts the endocrine properties (Okoya *et al.*, 2013).

The investigation results revealed that endrin concentrations in the fish farms ranged from ND (fish farm A) to 1.173 µg/l (fish farm C). Endrin was highly detected in 30 % of the water samples analysed with a mean value of 1.173 ±0.161 µg/L in farm C. The level of endrin recorded in farm C is about thirty, twenty-one and seventy times that of farms B, D and the controls, respectively. The higher level of endrin in farm C suggests that there was less photodecomposition or microbial degradation of endrin compound to other metabolites such as endrin ketone and endrin aldehyde (Agbeve *et al.*, 2014). The level of endrin in farm C was comparable with that reported for the water samples of 1.38 µg/l in the Manheam site of the Weija dam by Afful (2015). It was less than those in the flood regime of the Afram arm of the Volta Lake with an average concentration of 1.900 *µ*g/L as reported by Koranteng *et al.* (2016). At the international front, the average concentration of endrin in fish farm C agrees with Adeboyejo *et al.* (2011) study on lagoons in Nigeria, Ibigbami *et al.* (2015) in Ero River in Nigeria and Gakuba *et al.* (2018) in South Africa. The values of endrin recorded in fish farm B and D for the present study were also comparable with works done by Kurachie-Mensah *et al.* (2012) in the Densu River, Affum *et al.* (2018) in the Ankobra Basin of Ghana and Ezemonye *et al.* (2015) in Ogbesse River, Nigeria. The average concentrations observed for fish farms were below the WHO maximum limit of 0.60 µg/l for healthy drinking water, except for fish farm C. Meanwhile, irrespective of the pathway of human exposure to endrin, it will mainly affect the central nervous system, resulting in death by respiratory failure and convulsion (Syracuse Research Corporation, 2000).

The study revealed methoxychlor concentrations in the fish farms with their incidence of detection in the water as; 0.241 µg/l (90 %) in fish farm A, 0.040 µg/l (40 %) in fish farm B, 0.641 µg/l (30 %) in fish farm C and 0.238 µg/l (30 %) in fish farm D. Just like endrin, farm C recorded the highest average level of methoxychlor in the study. However, the frequency of the water samples detected for methoxychlor in farm C was smaller as compared to fish farms A and B. The high concentration of methoxychlor in fish farm C could be associated with its low conversion rate through photo-oxidation (Sailaukhanuly *et al.*, 2016; Yahaya *et al.*, 2017). The methoxychlor concentration recorded for fish farm B in this study was comparable to similar results documented in water samples from South Africa's Buffalo River (Yahaya *et al.*, 2017) and some lagoons in Nigeria (Adeyemi *et al.*, 2011)

Endosulfan is listed under restricted pesticides by the Stockholm Convention on Persistent Organic Pollutants (POPs) because of its ill effects on the environment. For this study, the average concentration of α-endosulfan residue in the farms was relatively less (0.034 – 0.184 µg/l) and so was of β-endosulfan (0.025 – 0.834 µg/l). A higher concentration of α-endosulfan residues was detected in farm C (0.184 µg/l). Similarly, a higher concentration of β-endosulfan residues was detected in fish farm C (0.834 µg/l). However, the levels of α-endosulfan and β-endosulfan were far below the MRL prescribed by WHO. The level of α-endosulfan in fish farm A revealed a similar trend observed by Kurachie-Mensah *et al.* (2012) in Weija, Fosu-Mensah *et al.* (2016) in water sources in Cocoa farms in Ghana, Fatoki & Awofolu (2004) in the Buffalo River in South Africa and Guo *et al. (*2013) in the Gonghu Bay of Lake Taihu in China. The average concentration of α-endosulfan in farm D was comparable with China's Xukou Bay of Lake Taihu. However, the concentration of α-endosulfan observed in fish farm C for the study was slightly lower than that of 0.22 µg/l reported by Ezemonye *et al.* (2015) in Ogbesse River in Nigeria. For the β-endosulfan, the reported concentration in fish farm C agrees with the findings of Ibigbami *et al.* (2015) in Ero River, Nigeria. Ezemonye *et al.* (2015) reported the level of β-endosulfan as 0.08 µg/l in Ogbesse River in Nigeria; their finding was in variance with the concentration reported for this study in fish farm B.

Despite the ban on PCB production, most PCB-containing equipment is still in operation. The chemical stability of PCBs has led to their use in hundreds of industrial and commercial applications, enabling them to persist to this day in the environment. With regards to the PCBs, two indicator congeners (CB-18, CB-180), three PCBs (CB-18, CB-52, CB-180), three congeners (CB-18, CB-101, CB-180), four indicator congeners of PCBs (CB-18, CB-52, CB-138, CB-180) and four indicator congeners (CB-18, CB-52, CB-138, CB-180) were detected in water from fish farms A, B, C, D and controls respectively. All the values of the individual PCB and total PCB congeners found in the water samples from all fish farms were lower than the standard approved freshwater contaminant level of 500µg/l suggested by USEPA (Bedi *et al.*, 2018). The PCB 180 and PCB 18 congeners were the most ubiquitous in the water samples from the study, with concentrations ranging from 0.296 – 0.471 ng/l and 0.391 – 0.508 ng/l, respectively. PCB 101 was predominant and recorded a concentration of 0.815 ng/l in fish farm C while PCB 138 was the least with a concentration of 0.070 ng/l in fish farm D. It has been shown that lighter PCBs (tri- and tetra- congeners) in fish farms B, C, D and controls contributed for most of the samples. Because of their high water solubility, the lighter PCBs tend to remain in the aqueous process (Eqani, 2012). Additionally, the lighter PCBs were more in the samples from these sites because it is most likely that anaerobic reductive dechlorination had occurred, thereby transforming more of the highly chlorinated congeners to the less chlorinated ones (Agbo & Abaye, 2016). Total PCB (ΣPCB_7) concentration (for all congeners) in water for the fish farms in decreasing order were; fish farm C (1.722 ng/l) > fish farm D (1.357 ng/l) > fish farm B (1.223 ng/l) > fish farm A (0.804 ng/l). The high total PCBs concentration measured in fish farm C could be due to certain industrial activities from which these hazard effluents are released. They include the Akosombo textiles, waste from nearby hotels, steelworks from the Volta River Authority and fertilizers from nearby farms. Nevertheless, it is a fact that

PCBs, just like all POPs may originate from long-range transport, especially effluents from boats and ferries from the upper course of the lake and its tributaries, are probably the source of the PCBs. The total PCB concentrations from this study were within other studies in China; Pearl River Estuary deep water column with the total concentration of PCBs (0.02–14.8 ng/l) and the USA; Houston Ship Channel and Delaware River, the PCBs level were 0.49–12.5 ng/l and 0.42–1.65 ng/l respectively by Dahshan *et al.*, (2016).

Six heavy metals (Pb, Zn, Fe, Mn, Ni and Cr) were detected in the water column of the aquaculture cages. Generally, the concentrations of the heavy metals in the water were relatively low except Pb and Mn.

The average lead (Pb) concentrations in the water samples from the fish farms A, B, C, D and controls were 0.542±0.019 mg/L, 0.373±0.063 mg/L, 0.263±0.060 mg/L, 0.172±0.097 mg/L and 0.047 ± 0.016 mg/L respectively. It is adduced that chronic adverse effects of Pb will probably occur from 0.5 mg/L to 1.0 mg/L. Chronic exposure to Pb has been linked to infant mortality and growth retardation with concentrations of Pb greater than 0.1 mg/L; this level is deleterious to foetuses and children (Darko *et al.*, 2015; Fianko *et al.*, 2007). Increased level of Pb has also been known to increase blood pressure, disrupts the smooth functioning of adults' reproductive and nervous systems as well as kidney damage (Edokpayi *et al.*, 2016). Abagale *et al.* (2013) reported that elevated levels of Pb in irrigation water might inhibit the growth of plant cells, thereby inhibiting photosynthetic activities.

The average concentrations of Pb in water samples from the farms were higher than the threshold values established by WHO and USEPA (0.015 mg/L) guidelines (Mohammadi *et al.*, 2019). However, the levels in the farms were lower than the aquatic life water permissible limits (CCME, 2007). The high levels suggest possible sources of Pb in the farms could be from domestic sewage and effluent discharge from rural and highway, seepage from waste disposal sites, and the geology of the catchment. The Pb level may also be due to atmospheric precipitation, plating processes, and gasoline containing lead leaks from fishery boats and various natural sources. Compared to other studies, Pb values obtained in farm A, C and D, respectively, were similar to those recorded in previous studies; Kacholi & Sahu (2018) recorded 0.46 - 0.55 mg/L from Temeke, Dar es Salaam, Xiao *et al.* (2019) reported 0.25 mg/L in Chinese river and well water, while Duncan *et al.* (2018) in the water sample from the Pra Basin in Ghana.

Zinc is a naturally abundant element in the environment and mostly a contaminant originating from agricultural, food, wastes, manufacturing of pesticides, and antifouling paints (Mortuza & Al-Misned, 2017). Zn is observed to be of biological significance to the physiological functions in most living organisms (Edokpayi *et al.*, 2016). Its deficiency or excessive amount may affect metabolic processes in humans (Edokpayi *et al.*, 2016). The zinc levels found in the studied farms complied with the WHO and AWPL recommended limits of 3mg/L and 30mg/L, respectively.

Fe is one of the fundamental components of the biological organism. It is a significant component of the haemoglobin and myoglobin, of proteins and different enzymes (Brody, 1998). It is usually more common in the freshwater system than other metals, owing to its high occurrence on earth. Fe deficiency can lead to anaemia and tiredness, usually in children of five, pregnant women and immunocompromised people, making them vulnerable to many infections (Edokpayi et al., 2016). Fe-rich water for domestic use, such as drinking and washing, is associated with an unpleasant metallic taste and clothing discolouration. It has been documented that haemochromatosis is the result of consuming large amounts of Fe. The USEPA argued that consuming water containing high Fe levels does not necessarily lead to adverse health effects because the intake of high Fe levels in humans is primarily due to the intake of food rich in Fe (Stone, 2003). Edokpayi *et al*. (2016) reported that Fe has both positive and negative effects on river ecosystems as it interferes with their natural metabolism, osmoregulation, and Fe affects lotic species. They also noted that many aquatic species, including fish, could be reduced by the combined effects of Fe emissions. For this study, the levels of Fe in the fish farms water were below the recommended limit for domestic water.

Manganese is one of the trace elements required by the body in a small amount to produce digestive enzymes, absorption of nutrients, wound healing, bone development and immune system defences (Jamshaid *et al.,* 2018). Deficiency of Mn leads to osteoporosis, muscle and joint pains and sexual dysfunction. Exposure to higher doses brings about a disorder in the nervous system, deficits in IQ, increased risk of attention deficit hyperactivity disorder (ADHD), and lower verbal function (Roels *et al.*, 2012). The levels of Mn in the water from the farms exceeded the WHO and EU standards for drinking water (WHO, 2011; Iyare, 2019). Mn level also exceeded the aquatic life permissible limits (CCME, 2007).

The order of Ni concentrations at all the sampled farms showed that levels detected at fish farm C (0.065 mg/L) > Fish farm B=fish farm D (0.041 mg/L) > fish farm A (0.016 mg/L) respectively. All the farms recorded comparatively lower Ni values than WHO, EPA and AWPL guidelines/standards. The most critical level of Ni was recorded at fish farm C when compared to other sites. The relatively lower Ni levels detected in the water may be due to the influence of domestic wastes, natural geological mineral rock and industrial wastes discharged into the water body. High exposure to nickel has been associated with various effects, including adverse gastrointestinal, neurological effects, fetus development, and respiratory cancer.

Therefore, if one drinks water from the sampled farms, he/she will not get any of the harmful effects mentioned above.

Cr concentrations in the sampling farms showed that levels detected at fish farm D (0.098 mg/L) > fish farm B (0.023 mg/L) > fish farm A (0.015 mg/L) > fish farm C (0.001mg/L). All the farms recorded comparatively lower Cr values than WHO, EPA and AWPL guidelines/standards except in fish farm D for safe drinking water. The high Cr level in fish farm D may be due to leaching from topsoil, rocks, and release from the Akosombo textile industry, located upward the fish farm where water samples were collected. Although some chromium types are non-toxic and may be needed for animals and humans in trace amounts, hexavalent chromium ($Cr^{6+)}$ is more water-soluble and highly toxic even at low concentrations. It is easily absorbed in the human body and can cause various toxic effects in cells, including irritation of the eyes, skin and mucous membranes (Tiimub *et al.*, 2015).

4.4.3 Levels of OCPs in sediment

Eleven organochlorine pesticides and 7 PCB residues were detected in sediment samples from the fish farms. The general concentration of OCPs in sediment ranged ND - 33.0 µg/kg. The highest concentration of OCP recorded in all the fish farms had a mean of 13.867 µg/kg (Endrin). The most frequently encountered OCPs in the farms were δ-HCH (100%) for fish farm A, *o,p'*-DDD (93 %) for fish farm D, α-endosulfan (68 %) for fish farm C, *o,p'*-DDD (45 %) for fish farm B and heptachlor (25 %) for the controls. All the eleven OCPs detected in the sediment were below the USEPA maximum residue levels.

The distribution of DDT and its metabolites (*o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDT) are shown in Table 4.4. Although DDT usage was banned in 1988, its detection, along with its metabolites (i.e., DDEs + DDDs) in the sediments, is expected because the reported environmental half-life of DDTs is estimated to be 10–

20 years (El Nemr *et al.* 2012). DDT metabolites were detected in all the farms and the controls sediment samples, but the contribution of individual metabolites showed differences. Among the metabolites, *o,p*- DDD in farm A recorded the highest mean value of 5.065 µg/kg followed by *p,p*-DDT of 5.000 µg/kg in farm D. However, the levels of the metabolite, DDD, were higher than the concentrations of DDEs in all the fish farms. DDD has been used as an insecticide and is usually applied to water in aquaculture farms to control weeds, algae, kill fish and invertebrates (Guo *et al.*, 2008). Therefore, increased levels of DDD in aquaculture sediments may be partially due to direct inputs from these activities. Additionally, in the present study, ∑DDT (equivalent sum of *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDT) in (µg/kg) in the fish farms were: 7.185 ± 4.455 µg/kg, 3.483 ± 1.849 µg/kg, 5.235±2.708 µg/kg, 12.263 ± 4.887 µg/kg and 0.163 ± 0.224 µg/kg for fish farms A, B, C, D and controls respectively. The concentration of total DDT reached a maximum value at fish farm D (12.263 µg/kg dry weight) followed by farm A (7.185 µg/kg dry weight) and farm C (5.938 µg/kg dry weight). The minimum value of total DDT was recorded in the controls (0.163 µg/g dry weight). The differences in the ∑DDTs in fish farms for the study is perhaps attributed to different sedimentation rates. The high-level ∑DDTs in farm D may be due to its high sedimentation rate compared to others. Also, a recent study has indicated that the run-off of antifouling paints during maintenance of fishing boat bodies was the predominant input source of DDT in aquaculture sediments collected in Hailing Bay of Guangdong Province, an important aquaculture zone in Southern China (Yu *et al.*, 2011a). The DDTs in different sediments from the culture farms in the present study could be due to the increasing use of DDT-containing antifouling paints from many fishing boats on Lake Volta. The high level of DDT in the sediments of Farm D is probably due to antifouling paints used by the majority of fishing boats in the area. The wide range of ∑DDTs (0.163 – 12.263 µg/kg) in the measured sediment was compared with studies within the global world. It was found to be in the range of measured sediment in water bodies from Nigeria (Williams,

2013), China (Sun *et al.*, 2010; Zhao *et al.*, 2010), Pakistan (Eqani, 2012) and Thailand (Sudaryanto *et al.*, 2011).

It was observed that the mean concentrations of DDE in the fish farms were more than their respective DDT concentrations. This finding is an indication that there was a degradation of DDT to DDE by microorganisms in the fish farms under heat, dry climatic conditions and ultraviolet rays (Kuranchie-Mensah *et al.*, 2012). This same phenomenon was similarly observed by Ntow (2005) and Darko *et al.* (2008) in Lake Volta and Lake Bosomtwi, respectively.

It is well established that DDT metabolites ratios act as useful indicators for understanding degradation processes, sources, and transportation of these compounds, and what is mainly taken as indicative of fresh/past DDT usage (Gomez *et al.*, 2011). Generally, a value of metabolite**:** parent compound greater than 1.0 indicates aged or historical pesticide use while a value less than 1.0 indicates new pesticide application (Koranteng, 2015). The pattern of DDT metabolites (*o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD) in all the sediment samples from fish farms A and B are that the metabolites accounted for 100 % of total DDTs, indicating the absence of DDT and total degradation of the parent compound. It can, therefore, be denoted that there has been no recent input of technical DDT to fish farms A and B. At fish farms C and D, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD and *p,p'*-DDT accounted for the total DDT concentrations. However, there was a dominance of DDDs concentration over DDEs concentrations in the surface sediments, which indicates reductive dechlorination of DDT to DDDs under anaerobic conditions (Gomez *et al.*, 2011) in fish farms C and D. Additionally, the ratios of *p,p'*-DDE*: p,p'*-DDT, *o,p'*-DDE*: p,p'*-DDT and *o,p'*-DDD*: p,p'*-DDT were all higher than 1.0 indicating no new inputs of DDT in fish farms C and D. Sources of DDT in the fish farms C and D may be attributed primarily to the influence of anthropogenic activities caused by inputs from agricultural and malaria campaigning activities as well as atmospheric deposition due to volatilization (Fosu-Mensah *et al.*, 2016; Gomez *et al.*, 2011).

In the manufacture of many insecticides and herbicides, methoxychlor is a highly significant ingredient. Initially, it was intended to substitute for DDT; however, its acute toxicity was prohibited. It is considered to be a carcinogen and a neurotoxin. (Bolor *et al.,* 2018). Elevated levels of methoxychlor detected in sediment samples taken from fish farm A indicate that this chemical's potential contribution may be from industrial effluents and urban waste discharged from various entry points into the water body. The high methoxychlor concentration in fish farm A may also be linked with its low photo-oxidation conversion (Sailaukhanuly *et al.,* 2016). The concentration of methoxychlor reported for the study in fish farm A agrees with that obtained by Musa *et al.* (2011) in their OCPs study in Yala/Nzoia River within the Lake Victoria Basin, Kenya.

Technically, HCHs has been used as a broad-spectrum pesticide for agricultural purpose. The HCHs generally contains 55–80% of α-HCH, 5–14% of β-HCH, 8–15% of γ-HCH and 2–16% of δ-HCH (El Nemr *et al.*, 2012). According to El Nemr *et al.* (2012), β-HCH, the most stable and relatively resistant to microbial degradation, has the lowest water solubility and vapour pressure. It is also worth noting that in the environment, α-HCH can be converted into β-HCH (Walker *et al.,* 1999). This phenomenon is reflected in the predominance of β-HCH in the fish farms as compared to δ-HCH. Meanwhile, 100 % of the sediment samples in farm A registered the presence of δ-HCH. Farm A also recorded the highest mean value for δ-HCH (8.154 µg/kg), this was found to be higher than the level of β-HCH (2.336 µg/kg) in the same farm. This, therefore, shows that there was one-time use of the technical HCH in the area. The reported levels of β-HCH in fish farms A, B and C and delta-HCH for fish farm A for this study were similar to an earlier investigation by Koranteng (2015). So also, are the reported levels of β-HCH and δ-HCH in fish farm D in agreement with

Gbeddy *et al.* (2015) on the same Volta Lake. The reported β-HCH levels for fish farm D in this study were similar to the 1.81 µg/kg and 1.54 µg/kg reported by Ezemonye et al. (2015), Kamel *et al.* (2015) in sediment from Ogbesser River in Nigeria and Manzala Lake in Egypt respectively. The reported β-HCH levels for fish farms A, B and C in this study were similar to the level reported by El Nemr *et al.* (2012) on the Egyptian Mediterranean coast.

Sum concentrations of HCHs (∑HCHs) (µg/kg) detected in sediment from the fish farms in the current study were: 10.490 ± 0.645 µg/kg, 2.862 ± 0.462 µg/kg, 4.155±1.144 µg/kg, 2.938 ± 0.469 µg/kg and 0.728 ± 0.419 µg/kg for fish farm A, B, C, D and controls respectively. The range of HCHs; 0.40 - 8.80 µg/kg, 0.42 – 3.20 µg/kg, 0.50 – 3.52 µg/kg, 0.76 – 2.42 µg/kg and 0.42 – 2.10 µg/kg in fish farms A, B, C, D and controls respectively, in the measured sediment were used to compare with studies within the global world. The range of ∑HCH was found to be in the range of measured sediment in waterbody from Thailand (Sudaryano *et al.*, 2011) and Pakistan (Baqar *et al.*, 2018). However, the range was lower than measured sediment in waterbody from China (Sun *et al.*, 2010; Zhao *et al.*, 2010).

The cyclodiene group of pesticides used to destroy termites and grasshoppers in the soil and combat rodents includes aldrin, dieldrin, and endrin. Due to their powerful insecticidal properties, these chemicals are commonly used for crop defence in cotton-growing areas, from where these harmful chemicals make their way to the aquatic environment. In this study, the average concentration of endrin for the four farms ranged from <LOD – 13.867 µg/kg. The range was within the measured sediment from Kala Shah in Pakistan (Syed & Malik, 2011). Endrin was predominant in fish farms D and C and accounted for 83 % and 33 % of the sediment samples, respectively. The average level of endrin in this study for fish farm D complied with the level found by Musa *et al.* (2011) in Yala/Nzoia River within the Lake Victoria Basin, Kenya. In the environment, endrin breaks down to endrin ketone and endrin

aldehyde through photodecomposition and microbial degradation (Bempah *et al.*, 2010). This probably accounted for its low levels in fish farms A and B. The low levels also suggest that the presence of this pesticide in the sediment as a result of old inputs.

For heptachlor, the concentration ranges from ND to 3.985 µg/kg, with the pesticides being predominant in fish farms A and accounted for about 57 % of the sediment sampled. This range was not different from others observed by Gbeddy *et al.* (2015) on the same Volta Basin and Malik *et al.* (2011) in River Chenab, Pakistan. The study's concentration recorded for fish farm D was 1.080 µg/kg, which agrees with Ezemonye et al. (2015) and Kamel et al. (2015) in sediment from sediment Ogbesser River in Nigeria and Manzala Lake in Egypt, respectively.

Concerning the endosulfans, α-endosulfan was higher than β-endosulfan in all the farms, although the water solubility of β-endosulfan was higher (Eqani, 2012). The reason for this phenomenon is that the technical mixture of endosulfan has higher rates of the α-endosulfan than its β-isomer. That β-endosulfan is converted to ∝-endosulfan in environmental matrices (Schmidt *et al.*, 2001). The study's range of ∝-endosulfan concentrations is 1.555 – 6.000 µg/kg, which was similar to the range; 0.01–14.21 µg/kg obtained by Kuranchie-Mensah *et al.* (2012) in the Nsawam stretch of the Densu River.

Sum concentrations of endosulfans (∑endosulfans) (µg/kg) detected in sediment from the fish farms in the current study were: 3.790 ± 1.963 µg/kg, 6.970 ± 1.909 µg/kg, 2.658 ±0.671 µg/kg, 2.718 ± 1.900 µg/kg and 0.503 ± 0.398 µg/kg for fish farm A, B, C, D and controls respectively. The broad sum of endosulfans in the measured sediment was 0.503 – 6.970 µg/kg.

4.4.4 Levels and distributions of PCBs in sediment

Six indicative PCB congeners (tri-18, 28, tetra-52, Penta-101, Hexa-153 and Hepta-180) were detected in the surface sediment from the fish farms, among which PCB-153 recorded the highest concentration of 3.328±1.700 ng/g in farm D. CB-18, and CB-180 tend to dominate the profiles in the sediment from all the farms. There were more congeners determined in the studied farm D as compared to the other farms. It was more likely that the PCBs were not originating from the uneaten fish feed in the bottom of the cages. According to Russell *et al.* (2011), if the input of PCBs into the sediment of fish farms was due to the input of fish feed and faeces, the profile will be expected to be dominated by more chlorinated PCBs, depending on the chemical composition of the fish feed. There was, however, a more significant proportion of tri-18 and hep-180 PCBs in the profile of all fish-farm sediments, probably suggesting mixed contributions from the atmosphere and particulate matter. The presence of some of the heavier chlorinated PCB (Penta-CB 101, Hexa-CB 153 and Hepta-CB or PCB 180) in some fish farms located near the hydro dam and urban areas, from where these contaminants are probably finding their way into the aquatic system via surface-runoff and direct disposal of wastewater from the Juapong textiles factory. In some farm sediments, these heavier chlorinated congeners may also be caused by their high affinity to adsorb particulate material, which eventually results in their sediment accumulation and deposition. Unlike lighter PCBs, they also have comparatively low mobility, which may be susceptible to microbial degradation and volatilization (Zhang *et al.*, 2003)

Tri-CBs (CB-18 and CB-28) are primarily used in electrical appliances and paint additives; thus, in some fish farms, the pollution of these congeners may be caused by the discharge of waste from the Akosombo power plants from the textile factory near the Volta Basin.

The Sum of the six PCBs concentrations (∑PCBs) (ng/g) detected in sediment from the fish farms ranged from 0.172 ng/g to 6.202 ng/g, where the sum of the PCBs in fish farm D was significantly higher than that of the other farms. Meanwhile, the range of ∑PCBs (0.172 – 6.202 ng/g) in the measured sediment compared with other studies globally was within the range of ∑PCBs in Hong Kong coast (0.1-461 ng/g), Fenhe Reservoir and Watershed in China (ND – 126.5 ng/g), and Haihe River in China (ND – 253 ng/g) obtained by Wong *et al.* (2000), Li *et al.* (2012) and Zhao *et al.* (2010a) respectively. The range of the ∑PCBs for the study was, however, lower than the measured sediment of ∑PCBs in Pearl River in China (19.8 – 111 ng/g), Canada Basin (24-600 ng/g), and Donggang River in Taiwan (25,5-63.5ng/g) established by Lai *et al.*, (2015), Wang *et al.* (2011), and Hsich *et al.* (2011) respectively.

4.4.5 Levels of Heavy metals in sediment from the cage aquaculture farms

The concentrations of six heavy metals (Pb, Zn, Fe, Mn, Ni, Cr) in the surface sediments of the fish farms are summarized in Table 4.9. Heavy metal concentrations in sediment were much higher than those in the surface water. In general, the levels of heavy metals in sediment from the fish farms were examined in the order: Mn > Cr > Fe > Ni > Zn >Pb, Mn > Cr > Fe > Zn > Ni >Pb, Pb > Cr > Mn > Ni > Zn > Fe, Pb > Mn > Cr > Ni > Zn > Fe and Mn > Cr>Pb>Fe>Ni>Zn for fish farms A, B, C, D and controls respectively. The data indicated that the average value of Mn (25.215mg/kg) in farm A recorded the highest concentration, followed by Pb (13.660mg/kg) in fish farm C for the study.

Except for Pb in fish farms C and D, all heavy metal concentrations in the sediment samples were lower than the maximum limits set by WHO/USEPA. It was worth noting from the observation that the high level of Pb in the sediment in farms C and D could be due to the effect from the point and non-point sources; such as leaded gasoline, petroleum, municipal runoffs, atmospheric deposition, and steelworks nearby the farms (Ali *et al.*, 2016). Other sources of Pb in the farms could also be from industrial effluents, antifouling paints by shipping activities, and possible leaked old lead pipes from the Kpong waterworks.

Comparisons of heavy metal concentrations with the other observed values by different authors in Ghana and around the world showed that heavy metal concentrations in the sediment of the present study were found to be lower in all investigated metals by Ansah *et al. (*2018), Darko *et al.* (2017), Duncan *et al.* (2018), and Duodu *et al. (*2011) except the levels of Pb, Mn and Cr in the Densu River obtained by Ansah *et al. (*2018). Compared with other international studies, the lowest averaged Pb, Mn, and Cr concentrations were 10.36 mg/kg, 23.69 mg/kg and 1.12 mg/kg, respectively, in the Nile River and Ohii Miri River Nigeria. The levels of all other heavy metals for the study were lower than the compared international levels.

Table 4.13: Mean metal levels in sediments from local and international studies compared to the present study

River, Country	**Heavy metal concentration (mg/kg)**						**References**
	Pb	**Zn**	**Fe**	**Mn**	**Ni**	**Cr**	
Volta Basin, Ghana	*BLD*	*0.495*	*2.771*	*25.215*	*0.920*	*11.565*	*This study (A)*
Volta Basin, Ghana	*BLD*	*0.790*	*3.130*	*25.199*	*0.690*	*8.875*	*This study (B)*
Volta Basin, Ghana	*13.660*	*0.480*	*BLD*	*12.170*	*0.823*	*12.430*	*This study (C)*
Volta Basin, Ghana	*13.640*	*0.510*	*BLD*	*12.895*	*0.880*	*11.315*	*This study (D)*
Volta Basin, Ghana	*0.386*	*0.006*	*0.213*	*6.805*	*0.058*	*0.970*	*Control*
Weija dam, Ghana	20.03	19.07	14124	433.61	58.65	87.62	Duodu *et al.(*2011)
L. Bosomtwi, Ghana	628	129	32	122	48	-	Darko *et al.* (2015)
Densu R., Ghana	1.86	15.9	22.56	22.93	13.24	6.03	Ansah *et al.* (2018)
River Pra, Ghana	335.38	118.32	1354.5	234.74	79.92	218.73	Duncan *et al.* (2018)
Ohii Miri R., Nigeria	43.40	44.08	26.55	23. 69	9. 65	1. 12	Jonah *et al.* (2014)
Nile River, Egypt	10.36	61.70	-	774.63	48.88	72.68	Rifaat (2005)
Zijiang River, China	35.68	141.90	-	1322.89	34.66	67.51	Zhang *et al.* (2018)
Jinjiang R., China	23.81	104	-	787	24.47	58.66	Liu *et al.* (2018)
Xiangjiang R, China	214.91	443.32	-	1805.17	57.14	120.44	Chai *et al.*(2017)
Polluted river, Brazil	36.27	63.27	3002	1482	3.01	9.10	Silva *et al.* (2019)
Mekong R., Vietnam	25.05	31.93	-		26.81	10.47	Strady *et al.* (2017)

L- Lake, R-River

4.4.6 Levels of OCPs PCBs and HMs in fish feeds from fish farms

It is commonly accepted that the direct absorption of compounds found in the water and fish diet can be traced to toxic substances in fish and that these contaminants can bioaccumulate (Botaro *et al.*, 2011). The study revealed the presence of 10 OCPs (δ-HCH, o,p'-DDE, p,p-DDE, o,p-DDD, p,p-DDT, endrin, heptachlor, methoxychlor, α-endosulfan, and β-endosulfan) and 4PCBs congeners (CB-18, CB-28, CB-101 and CB-180) in the fish feed. For this study, the OCPs and PCBs present in fish feeds sampled from three fish farms are presented in Table 4.14.

The OCPs had an average range of 0.22 – 8.67 µg/kg. The highest concentration was measured for heptachlor (8.67 ±2.52 µg/kg) followed by δ-HCH (7.87 ±2.55 µg/kg) in fish farm D. In contrast, the lowest (0.23±0.08 µg/kg) was recorded for *β*-endosulfan in fish farm B.

In the organochlorine pesticides, the predominant contaminants were endosulfans and DDT, their derivatives DDE and DDD. The predominant form of DDT in the fish feed was the metabolite *o,p'*-DDE, *p,p'*-DDE, followed by *o,p*-DDD and the parent compound *p,p'*-DDT. This study detected p,p'-DDT in fish farm D with a 1.56µg/kg level. This was following the findings of Easton *et al.* (2002) for Taplow feed (TA-fd3) produced in Canada for Salmon. The ∑DDT (4.11µg/kg, 7.34 µg/kg and 9.44 µg/kg) and ∑Endosulfan (3.79 µg/kg, 4.25 µg/kg and 3.10 µg/kg) in fish farms A, B and D respectively. Fish farm D feeds exhibited a higher composition of DDTs compared to farms A and B feeds. The feed samples contained lower concentrations of total DDTs (range: 4.11– 9.44 µg/kg wet weight) than were reported by Mac *et al.* (1979) for several lots from one commercial feed manufacturer (80– 340 µg/kg wet weight), but samples contained about the same concentration of DDT as another feed manufacturer examined (3.3 – 31.0 µg/kg wet weight) by Maule *et al.* (2007). Feeds manufactured in Scotland reportedly had levels of total DDT (range: 34–52 ng/g lipid adjusted) (Jacobs *et al.*, 2002) higher than those obtained for this study.

α, β-endosulfans were among the most prevalent contaminants in the fish feeds samples, where its concentration was almost on an average the same as those observed in the fish muscle tissues. These pollutants for this study may be linked to the ingredients used in manufacturing the feeds, such as grains and soybeans oil (Botaro *et al.*, 2011). A study in Brazil conducted by Correa *et al*. (2005) has reported high levels of endosulfans in Soybeans oil used to prepare commercial feeds for fish. The analysis of the feeds used on the different fish farms showed a total OCP load of 8.28 µg/kg (ww) for fish farm A, 12.18 µg/kg (ww) for fish farm B and 31.64 µg/kg (ww) for fish farm D (Table 4.12). The highest OCP load in feeds from farm D may be explained due to the variations in the composition of the feed. The feed was probably formulated with higher animal protein and fat levels in fish farm D, especially fishmeal and fish oil. Such ingredients are the source of several commercial feeds used in aquaculture and maybe the significant contamination of OCP residues (Botaro *et al.*, 2011). Alternative ingredients such as vegetable food, synthetic amino acids and vegetable oils can avoid this source of contamination without compromising the growth of fish (Botaro *et al.*, 2011). In a related study by Serrano *et al.* (2008), fish feed supplied to farmed fish presented a total load of organochlorine analysed of 12 µg/kg in the Spanish Mediterranean Coast. Their findings are in variance with the total loading in fish farm B (12.18µg/kg) for this study.

In all, the levels of the ten pesticides detected (δ-HCH, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p'*-DDT, *α*-endosulfan, *β*-endosulfan, endrin, heptachlor, and methoxychlor), ΣDDTs as well as ∑endosulfan were all below the European union maximum residue level (EU MRL) for fish feed

With the PCBs, the congener (CB-18, CB-28, CB-101 and CB-180) profile patterns observed in the aquafeeds were slightly different among the three farms. Easton *et al.* (2002) reported the levels of CB-18 and CB-28 in Moore-Clark (0.26ng/g) and Taplow (0.21ng/g) fish feeds, respectively. Their finding was not different from the same congeners obtained in the feeds for the studied farms. The levels of PCB congeners CB-28 and CB-180 for the study in fish farms D and A, respectively, were similar to the one reported by Carubelli *et al.* (2007).

The analysis of the feeds used on the different fish farms showed a total PCB load of 1.01 ng/g (ww) for fish farm A, 0.86 ng/g (ww) for fish farm B and 1.52 ng/g (ww) for fish farm D. ΣPCBs loading in farms A and B, showed lower levels than farm D, and this could be partly linked to the higher lipid content of the fish meal and oil used for the manufacturing of fish feed in farm D. The feed samples contained lower concentrations of total PCBs (range: 0.86 – 1.52 ng/g wet weight) than were reported by Johnson *et al.* (2010) for the feed from Washougal Hatchery and Little White Salmon Hatchery (5.3– 25 ng/g wet weight), but samples contained about the same concentration of ∑PCBs as in feed manufactured in the US for fish and Wildlife hatcheries (<1 – 11 ng/g wet weight) by Maule *et al.* (2007). The levels of the PCB congeners reported for this study were also relatively lower than the PCB concentrations in the salmon feed from Scotland reported by Jacobs *et al.* (2002).

The fish culture was entirely dependent on the application of fish feed in the present study area. It is adduced that fish feed ingredients from marine sources contain high concentrations of heavy metals and that the presence of these metals presents health risks to culture fish and the ultimate consumers. The presence of Pb, Mn, Fe, Zn, Ni, Cr, Cd, and As in fish feed used on aquaculture farms was investigated in the current study.

Manganese (Mn) is an essential micronutrient in animals as well as in plants. Its deficiency results in severe reproductive abnormalities and skeletal consequences in the animal. It is not naturally occurring as metal but is linked often to iron deposits. In the aquatic environment, it has been attributed to ferromanganese minerals, clay minerals and so on (Laar *et al.*, 2011). However, the levels of Mn in the fish feed samples from the farms significantly exceeded the permissible limit of 7.7 mg/kg (Niemiec & Wisniowska-Kielian, 2015). The high content of Mn in the feed may increase its content in the water, which eventually results in ionic exchange, particularly sodium, causing malfunctioning of the gills of cage fish (Niemiec & Wisniowska-Kielian, 2015). Therefore, heavy metal Mn is concerned in the present study.

For humans, the primary source of nickel (Ni) is food uptake natural and food-processing sources (Mannan *et al.*, 2018). High intake of Ni can cause cancer of the lung and nasal cavity. Ololade (2010) reported nickel toxicity includes skin rash (nickel dermatitis), nausea, dizziness, diarrhoea, headache, vomiting, chest pain, weakness and coughing. Contact with nickel vapour can lead to swelling of the brain and liver, degeneration of the liver, irritation to the eyes, throat and nose and various types of cancer. For this study, the levels of Ni obtained in fish farms A and B were 0.76 mg/kg and0.12 mg/kg, respectively. The results in fish farm A agree with those obtained in Multi and top fish feed in Nigeria by Salawu *et al.* (2016). The observed levels were below the maximum level proposed by the European Commission (8.0 mg/kg) (EC, 2003; Saha *et al.*, 2016).

Zinc (Zn) is an essential human health trace element required for normal metabolic functions and growth. When its concentration exceeds the physiological requirements, it becomes a toxicant, resulting in reduced fertility (Abdel-Warith *et al.*, 2011;

Mannan *et al.,* 2018). Zn toxicity results in general enfeeblement, retardation of growth and may bring about metabolic and pathological changes in various organs in fish. Zinc concentration in the fish feed ranged 0.10 - 0.480 mg/kg. This concentration range was lower than 1.21 – 3.52 mg/kg and 8.224 – 12.661 mg/kg obtained by Salawu *et al.* (2016) and Anhwange *et al.* (2012), respectively, in the fish feed from Nigeria. The estimated levels of Zn metal in the present study were lower than the limits permitted by the Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO) and European Community Regulation (EU) guidelines (Saha *et al.*, 2018). Since Zn is an essential element required for biological functions, especially enzymes and growth functions, the lower content in the feed may necessitate supplementation of this element for a more productive and efficient aquaculture fishery on the Volta Basin.

Chromium is an essential mineral. It stimulates the action of insulin and improves carbohydrate, fat, protein metabolism, and storage. However, excessive chromium levels in fish feed damage the kidney, liver and blood cells due to oxidation reactions in the fish's body. The results obtained from the study were not alarming. The average chromium content was found in the study was 0.44 mg/kg in fish farm D only. The content of Cr in fish farm D might be due to poultry and tannery wastes in the fish feed where K2Cr2O7 plays a crucial role in cleaning (Das *et al.*, 2017). The high Cr level in the feed from farm D could also result from formulating it with some food additives and colours of high chromium content. The assessment showed that the chromium level in the fish feed was lower than the maximum chromium level (8 mg/kg) proposed by the European Commission (EC, 2003; Saha *et al.*, 2018).

4.4.7 Levels of OCPs and PCB residues in fish samples from the fish farms

Ten organochlorine pesticides-OCPs (δ-HCH, heptachlor, α-endosulfan, β-endosulfan, p,p'-DDT, p,p'-DDE, *o,p′*-DDE, *o,p′*-DDD, endrin and methoxychlor) were quantified in the muscle tissues of the cage tilapia (*Oreochromis niloticus*) species from three fish farms (A, B, D as well as the controls). In general terms, the concentrations of OCPs detected showed slightly higher levels in the fish compartment in most cases compared to those in the sediment compartment but significantly higher than the concentrations in the water compartment. This trend of the result was not surprising as organochlorines are hydrophobic. Therefore, they are prone to concentrate in fatty tissues of living organisms such as fishes and other related aquatic organisms in the aquatic environment.

The concentrations of organochlorine pesticides varied from ND to 2.310 µg/kg, <LOD to 4.260 µg/kg, <LOD to 6.109 µg/kg and ND to 0.878 µg/kg in fish samples from farm A, B, D and controls respectively. The mean concentration range recorded in the tissues of the fishes was ND – 6.109 µg/kg. The highest concentration of 6.109 µg/kg was recorded for δ-HCH in the muscle tissue of tilapia in fish farm D, while *p,p′*-DDE recorded the lowest concentration in the muscle tissue of tilapia in fish farm A. The European Union (EU) default Maximum Residue Level (MRL) of any pesticide in fish tissue is 10 µg/kg (Koranteng, 2015). In line with this, all the OCPs residues in the muscle tissues of the cage tilapia from the fish farms were below the MRL.

Regarding the DDT metabolites, DDE (total *p,p*-DDE and *o,p*-DDE) in all the farms except farm A was the predominant isomer. This phenomenon was not surprising because its incorporation into the muscle tissue usually involves altering some form of the residual metabolite and is due to the lesser half-life of *p,p*-DDT (8 months) as compared to DDE (7years) in the fish (Yahia & Elsharkawy, 2014). Also, the uptake of DDE from the environment, rather than DDT in farms B, D and controls, indicates that no substantial fresh input of DDT has occurred in those sites. Bioconcentration depends on the food chain transfer and the feeding habit of the individual fish. Therefore, it can be established that the higher levels of the DDE in farms B, D and the controls are due to the differences in their bioconcentrations. For fish farm A, the calculated ratio of *p,p'*-DDT/total-DDE in tilapia yielded 1.25. This indicates that in recent years, in tandem with the primary source of technical DDT (probably due to past use in agriculture and public health), a new contaminated source of technical DDT has been introduced in farm A. It has been reported that almost 1 tonne of technical DDT and HCB was imported into Ghana recently, and this might be in line with the observed levels of DDT in farm A (Adu-Kumi *et al.*, 2010).

The ∑DDTs concentrations measured in the fish muscle samples from Lake Taabo (109.35 µg/kg) (Roche *et al.*, 2007), River Densu (16.82 µg/kg) (Afful *et al.,* 2010) and Lake Bosomtwi (8.88 µg/kg) (Darko *et al.,* 2008) were higher than the reported values from farm A, B, and D. Fish samples collected from Lake Manzala in Egypt (1.89 µg/kg) (Kamel *et al.,* 2015) and Lake Ziway in Ethiopia (4.15 µg/kg) (Yohannes *et al.*, 2014) were lower in ∑DDTs level as compared to those in farm A, B and D for the study. In a laboratory study, Jarvinen and Ankley (1999) observed adverse impacts in freshwater fish exposed to ∑DDT at concentrations of up to 0.500 µg/kg ww. Based on this data, the ∑DDT concentrations obtained in adult fish muscle from farm A (4.158 µg/kg), farm B (6.730 µg/kg), farm D (6.767µg/kg) and controls (1.148 µg/kg) could damage the fish, impair their normal physiological functions and/or reduce their growth ratio. However, these concentrations do not pose a risk to human consumption of fish since ∑DDT levels in muscle were well below the EU limits.

Low concentrations of endosulfan were observed in all samples, and the endosulfan- α / β isomer ratio ranged between 1.30 and 2.29, as also reported by Botaro *et al.* (2011) for tilapia. Higher concentrations of α-endosulfan instead of-β are anticipated, given the higher concentration (70 per cent) of the endosulfan isomer relative to the β-isomer in technical endosulfan mixtures. Further, the level of β-isomer in fish could be even lower due to its higher rate of metabolism in fish compared to α-isomer. The ∑endosulfan concentrations measured in the fish muscle samples from Lake Taabo in Cote d'Ivoire (0.39 µg/kg) (Roche *et al.*, 2007), Ogbesse River in Nigeria (0.39 µg/kg) (Ezemonye *et al.*, 2015) and Lake Geriyo in Nigeria (171.10 µg/kg) (Shinggu *et al.*, 2015) were higher than those obtained for this study.

Other pesticides detected in the fish included methoxychlor, δ-HCH, heptachlor, and endrin in the farms' fish samples. However, their levels were very low in the samples indicating past use.

The pesticide loads (sum of all detected pesticides) in the tilapia from the farms were; 11.011 µg/kg, 19.129 µg/kg, 25.408 µg/kg and 5.196 µg/kg in fish farms A, B, D and controls respectively. The highest pesticide load of 25.408 µg/kg was obtained from fish farm D. This could be due to the age and large sizes of tilapia fish used for the laboratory analyses from fish farm D; hence their high lipid content makes them susceptible to bioaccumulation of more organochlorine residue.

The current research findings are compared in Table 5.2 with those from other regions of the world and some from local studies in Ghana. Comparison of the mean OCP residue ranges in muscle tissues from the present study with results from other local studies shows that values from this study were lower. Whereas the highest local OCP concentration range in the muscle of fish (0.78 – 94.00 µg/kg) was quoted by Koranteng (2015) for fish species from the Afram arm of Volta Lake study was ND –

6.109 µg/kg. However, comparing the results to the ranges by some works from other world regions, the concentration range for this study was lower. For instance, as shown in Table 5.2, Abbassy (2018) reported a mean concentration range less than the limit of detection – 6.71µg/kg for fish species from Rosetta Nile branch estuary in Egypt; Deribe *et al.* (2011) also recorded a range of 1.86 – 6.90 µg/kg for species from Lake Koka in Ethiopia; Eqani *et al.*, (2013) reported a mean concentration range 0.75 - 20 µg/kg for River Chenab in Pakistan while Polder *et al.*, (2014) obtained a mean concentration range <LOD – 273 µg/kg for OCPs in muscle tissues of *Oreochromis niloticus* from Lake Victoria, Lake Tanganyika, Lake Nyasa and Lake Babati in Tanzania. Cage aquaculture tilapia from the Ghanaian aquatic ecosystems can, therefore, generally be considered relatively less contaminated.

Ghana has never manufactured PCBs, but imported products containing PCBs such as Transformers, capacitors, paint lubricants, glue and carbonless paper have been used. While PCB levels were considerably lower, they were detected in fish from all the farms studied. The highest mean concentration of PCB 153 (8.524±1.5960 ng/g) was found in farm D followed by PCB 180 (5.835±1.9760 ng/g) in farm D. The

Table 4.14: Mean concentrations of OCPs residues in fish muscles from local and international studies compared to the present study

Reference	No. of OCPs	Range (µg/kg)	Location
Studies from Ghana			
Afful *et al.* (2010)	14 OCPs	0.3 – 71.30	Densu basin
Adu-Kumi *et al.* (2010)	17 OCPs	ND –290.00	Weija, Bosomtwi and Volta
Fianko *et al.* (2011)	15 OCPs	0.51 – 7.99	Densu River basin
Gbeddy *et al.* (2012)	15 OCPs	0.10 – 17.35	Kpando (Volta Lake)
Koranteng (2015)	3 OCPs	0.78 – 94.00	Afram Lake arm of Volta
Present study			
Fish farm A	*9 OCPs*	*ND - 2.310*	*Volta Basin*
Fish farm B	*10 OCPs*	*<LOD - 4.260*	*Volta Basin*
Fish farm D	*10 OCPs*	*<LOD - 6.109*	*Volta Basin*
Studies from other regions			
Abbassy (2018)	7 OCPs	<LOD - 6.71	Rosetta Nile branch estuary
Deribe *et al.* (2011)	8 OCPs	1.86 – 6.90	Lake Koka
Eqani *et al.* (2013)	11OCPs	0.75 – 20	River Chenab
Norli *et al.* (2011)	11 OCPs	1.36 – 329	Superior Lake
Polder *et al.* (2014)	10 OCPs	<LOD – 273	Lake Victoria, L. Tanganyika, L. Nyasa and L. Babati

ND-Non detected, <LOD-Below detection limit

dominance of PCB-153 and PCB-180 samples in the farms, except the controls, was similar to the dominance of PCB-153 to PCB-138 and PCB-180 reported in other studies (Asante *et al.,* 2013; Mwakalapa *et al.*, 2018; Polder *et al.,* 2016), and this is related to high persistence of PCB-153 to other PCB congeners. These congener profiles of PCBs (PCB-153 and PCB-180) for study farms were similar to the profile of the technical PCB mixture (Aroclor 1260), which suggests that it has been used in Ghana. In general, PCB 153 is one of the main contributors to the total PCB content in freshwater fish species worldwide due to its long half-life (Kampire *et al.*, 2015).

Moreover, the bioaccumulation of PCBs in tissues is related to their log octanol-water partition coefficient (log Kow). Lipophilicity and log k_{ow} increase with increasing chlorine content, which reduces the biodegradability of PCB compounds (Kampire *et al.*, 2015). The higher chlorinated congeners are less soluble in water. Therefore, they are observed at higher concentrations in aquatic organisms as observed in PCBs (Hexa-CB and Hepta-CB) for this study. The bioaccumulation of PCBs in aquatic organisms is directly related to their chlorination level and lipophilicity. The level of PCB-153 in fish from farm D was similar to the one obtained by Kampire *et al.* (2015) (8.57 ng/g) in South Africa.

Generally, the low concentration of the lower chlorinated congeners in the fish samples could be attributed to the less chlorinated PCBs having a lower log Kow than the more chlorinated PCB congeners. They, therefore, have a lower tendency to leave the aqueous medium for organic compartments and thus, when present in organisms, they are usually more rapidly metabolized than the higher chlorinated congeners because of the presence of more unsubstituted ring positions on their biphenyl rings (Kuranchie-Mensah *et al.*, 2011).

The ∑PCBs concentrations were measured in the fish muscle samples from Brenya lagoon in Ghana (150 ng/g) (Asante *et al.,* 2013) and Jakarta Bay in Indonesia (400 ng/g) (Sudaryanto *et al.*, 2007) were higher than the reported values for the studies. However, total PCB reported for the Indian Ocean in Tanzania (0.2 ng/g and 0.6 ng/g) (Mwakalapa *et al.*, 2018) and Napoleon Gulf in Uganda (0.073 ng/g) (Ssebugere *et al.*, 2014) were lower than those reported for the study. The total concentration of PCBs in the cage *Oreochromis niloticus* for the study was significantly higher than the one obtained by Kuranchie-Mensah *et al.* (2011) on the same Volta Basin except in fish farm A and the controls where the levels were low.

4.4.8 Distribution of heavy metals residues in cage tilapia from fish farms

Heavy metal pollution has been reported to inevitably end up in the aquatic environment (Ayanda *et al.*, 2019). For evaluating heavy metal emissions in the aquatic ecosystem, fish are considered very useful biomonitors (Authman *et al.*, 2015). Heavy metal's redox potential can trigger oxidative stress in fish that eventually affects the quality of their flesh (Authman *et al.*, 2015). The long-term health implications of this on the population relying on the water resources cannot be overemphasized.

The concentration of the detected metals (Zn, Fe, Mn, Ni, and Cr) in the tilapia fish are presented in Table 4.17. The mean concentration range recorded in the tissues of all the fishes was 0.31 mg/kg – 50.11 mg/kg. The highest of 50 mg/kg was recorded for Fe in the muscle tissues of tilapia in fish farm B. In contrast, Cr recorded the lowest concentration in the muscle tissue of tilapia in fish farm A. Five heavy metals (Cr, Mn, Fe, Zn and Ni) were detected in the muscle of the fishes from the farms except for Cr that was not detected in fish farm B. The order of heavy metals concentrations in the tilapia muscle from the fish farms were: Fe > Mn > Zn > Ni > Cr (for fish farm A), Fe > Zn > Ni > Mn (for fish farm B), and Fe > Mn > Zn > Ni > Cr (for fish farm D). The concentration values of metals in muscles of *O. niloticus* in the farms were below the USEPA/WHO MRL except for Mn and Fe that exceeded the permissive levels and the maximum allowable concentrations of metals in fish organs for human consumption, suggesting that fishes from the fish farm could cause serious Fe and Mn related problems to human health over time.

A low amount of Mn intake is needed for growth and healthy development in humans. The US EPA has set Rfd for Mn to be 140 µgkg^{-1}day$^{-1,}$ which will ultimately become harmful if one consumes above this value (US EPA, 2018). Mean Mn levels measured in the muscles tissues of the tilapia was between 0.77 – 3.41 mg/kg dry weight. The Highest Mn level was measured in muscle tissues of tilapia caught in farm A. The high values of Mn observed in the fish may be due to the bioaccumulation phenomenon. Elevated concentrations of heavy metals in aquatic organisms' tissues indicate accumulative exposure to water and/or food (Ezemonye *et al.,* 2019). Aquatic organisms absorb pollutants from water and store them in their tissues to far higher levels than their surrounding ecosystems.

Similarly, El-Moselhy *et al.* (2014) reported a high level of Mn in the gills of pelagic fish in the Red Sea of Egypt. The higher levels in fish compared with water for this study were also attributed to biological accumulation. Mn levels in the muscles of fish reported for the study were in agreement with levels reported in fish from the Mediterranean Sea (0.05 – 4.64 mg/kg) (Turkmen *et al.,* 2005) and (0.07 - 3.62 mg/kg) (Ates *et al.*, 2016).

Fe is an essential element present in organisms for cellular functions. Intake of iron above 700 µgkg^{-1}day^{-1} in food may result in diseases such as Alzheimer and type-2 diabetes (Korkmaz *et al.*, 2019). Present results revealed that the mean Fe levels varied between 11.09 – 50.11 mg/kg dry weight. These elevated levels may be due to the uptake of fish feed formulated with Fe. Fe levels were within 5.15 -135.00 mg/kg (Ates *et al.*, 2015) but were above 0.21 – 3.59 mg/kg (Ersoy and Çelik, 2010) in fishes from the Mediterranean Sea.

Table 5.3 compares the current study's findings with some from other regions of the world and those from some local studies. Comparison of the mean heavy metals residue in the muscle tissues from the present study with results from other local studies shows that values from this study were higher than those obtained in the muscle tissues of fish by Anim-Gyampo *et al.* (2013) and Anim *et al.* (2011) from the Tono River and Densu River respectively, except Zn in fishes from River Densu that was about fourteen (14) times higher than those from the study (Table 5.3). The levels of the heavy metals in the Weija reservoir obtained by Ansah *et al.* (2018) were significantly higher than those obtained from cage tilapia from the Volta Basin

When compared with other studies (Table 5.3), the metal concentrations were comparable with those from Egypt (El-Batrawy *et al.*, 2018); China (Liang et al., 1999; Leung *et al.*, 2014); Malaysia (Taweel *et al.*, 2011; Baharom & Ishak, 2015); Taiwan (Ju *et al.*, 2017) and Palestine (Elnabris *et al.*, 2013).

The level of Cr in this investigation is similar to Rajeshkumar & Li (2018) and that of Shrivastava *et al.* (2003) in China and India, respectively. The level of Ni for the study also agrees with that of Ju *et al.* (2017) in Taiwan.

Table 4.15: Concentration of heavy metals (mg/kg) in cage tilapia compared to the levels of heavy metals in fish from other studied areas

Location	Cr	Mn	Fe	Zn	Ni	Reference
Volta Basin, Ghana	*0.31*	*3.41*	*37.28*	*2.07*	*1.62*	*This study (A)*
Volta Basin, Ghana	-	*1.76*	*50.11*	*2.13*	*2.74*	*This study (B)*
Volta Basin, Ghana	*0.33*	*2.46*	*39.58*	*1.82*	*2.00*	*This study (D)*
Weija, Ghana	4.3	8.20	6.53	4.30	4.30	Ansah *et al.*, 2018
Tono, Ghana	-	0.693	3.610	0.004	-	Anim-Gyampo *et al.*, 2013
Densu River, Ghana	BLD	1.60	5.96	28.24	0.24	Anim *et al.*, 2011
Burullus Lake, Egypt	-	1.34	11.85	4.46	0.52	El-Batrawy *et al.*, 2018
Taiwan	1.85	-	-	20.00	2.28	Ju *et al.*, 2017
Galas River, Malaysia	-	ND	-	0.434	-	Baharom & Ishak, 2015
Selangor, Malaysia	5.70	-	-	45.00	3.00	Taweel *et al.*, 2011
Gaza Strip, Palestine	-	0.386	-	7.522	0.892	Elnabris *et al.*, 2013
China	0.31	-	-	31.7	0.276	Liang *et al.*, 1999
Pearl River, China	0.51	6.91	-	29.5	3.50	Leung *et al.*, 2014

4.5 Conclusion

The entire PCB, OCPs, and heavy metal profiles in surface sediment, water, fish feed, and highly consumed tilapia from cage aquaculture farms in Ghana were evaluated first in this study. Although their use is currently prohibited, the findings of this study revealed that PCB and OCP contamination is pervasive in the aquaculture environment, owing to ongoing and/or historical use. The OCPs, PCBs and heavy metals concentrations in the water, sediments, fish feed and tilapia in the present study range among the allowable values, except heptachlor in water from farms A, B, and D and endrin in farm C, Pb and Mn level for drinking water in all the farms, Pb in sediment from farm A, Mn in the fish feed from all farms, as well as Mn and Fe in the fish exceeded the MRL recommended by WHO, USEPA, FAO and EU. The pollutants contents in biological matrices were comparable to or less than some other values found in the literature, including those documented in China, Egypt, Malaysia, Pakistan, and Taiwan. To minimize the effects of OCPs, heavy metals, PCBs, and other toxins on human health and the environment, continuous monitoring of these toxicants is required.

CHAPTER FIVE

SOURCES AND ECOLOGICAL RISK OF PESTICIDES AND HEAVY METALS IN SURFACE SEDIMENTS

5.1 Background

The Volta Basin, where this research was carried out, is an extension of the Volta River, which takes its source from the Burkina Faso, Côte d'Ivoire, and Togo. Lake Volta boasts the world's largest surface area (8729 km^2) and a 4800-kilometre shoreline (Kuranchie-Mensah *et al.*, 2011). It contributes the most to Ghana's domestic fisheries, contributing to over 80% of total capture (Directorate of Fisheries, 2007). Agricultural and industrial activities in the basin's watershed have made it eutrothrophic. Within the catchment of the basin is a public factory, such as the Akosombo textile factory and a hydroelectricity plant, which release waste into the aquatic environment, the same space within which aquaculture is practised. Contamination has surged significantly as a result of these operations, as well as population growth over the years. The concentrations of contaminants, particularly pesticides and heavy metals, entering the water and its biota have been intensively researched by Ntow (2005), Gbeddy *et al*. (2012), Gbeddy *et al.* (2015), and Koranteng (2015). These pollutants have always been a matter of concern. It is critical to keep track of their pollution sources and assess their potential toxicity to benthic species in the sediment. Therefore, the findings of this study may help formulate policies on sustainable cage aquaculture development and products safe for consumption

5.2 Materials and method

This chapter uses the measurable quantities (data) of chapter 4, established through laboratory analyses as well as various pollution indices and models to assess ecological risks and sources of contaminants.

5.2.1 Data analyses

Detailed levels of the OCPs, PCBs and heavy metals in sediment are given in Chapter four. The Pearson correlation coefficients and the principal component analysis (PCA) were used to assess the sources of the contaminants in the sediment. The measurable quantities (i.e. the levels of the OC pesticides and the heavy metals in the sediment) were run in the PCA to obtain the sources of the OCPs and heavy metals in the sediment.

5.2.1.1 Ecotoxicological Risk Assessment of the Pesticides in Sediment to Aquatic Species

Sediment quality values that provide a benchmark for evaluating the adverse effects in the aquatic ecosystem were used to calculate the sediment toxicity. Hong Kong Interim Sediment Quality Value (HK-ISQV), Canadian Sediment Quality Guidelines (CSQG), USEPA and some published sediment quality guidelines (Eqani, 2012) including, threshold effect concentrations (TECs) for freshwater, probable effect concentrations (PECs), and Interim Sediment Quality Guidelines (ISQG). The Canadian Sediment Quality Guidelines (CSQG) uses the Threshold Effect Level (TEL) and Probable Effect Level (PEL); USEPA (1997) uses Effect Range Low (ERL) and Effect Range Median (ERM) whiles the Hong Kong Interim Sediment Quality Value (HK-ISQV) uses Lowest Effect Level (LEL) and the Severe Effect Level (SEL).

These benchmarks have been used as EPA Ghana does not have its benchmarks. TEC (TEL, LEL, ERL and CB-TEC) indicates concentrations at which pollution will start to be detected in sensitive aquatic life or concentrations at which adverse effects will not occur, while PECs (PEL, SEL, ERM and CB-PEC) indicate concentrations above which adverse effects will occur in aquatic species. The range of sediment sample OCPs and PCBs observed in all four fish farms were compared with the sediment quality criteria for assessing the overall quality of sediments and the potential risk to aquatic life in the Volta Basin.

5.2.1.2 Potential ecological risk of heavy metals in sediments

The impact of anthropogenic activities and the ecological risk of heavy metals to aquatic organisms in the sediment was evaluated using pollution indices such as I_{geo}, EF, PLI and RI.

5.2.1.2.1 Geo-accumulation Index (I_{geo})

The determination of the geochemical accumulation index (Igeo), as proposed by Müller in 1979, is a well-established technique for evaluating the accumulation of metal concentrations beyond the background or baseline concentration. Sediment Igeo is the numerical indicator of concentrations of heavy metals in aquatic sediments. This index is essentially a unit-metal value approach to estimate the metal load in sediments when the level of toxic heavy metals is 1.5 times or higher than their latent background levels. This method identifies the extent of contamination or accumulation of metals in sediments by comparing their current concentrations with their pre-industrial levels. The formula is expressed mathematically as equation 5.1:

$$I_{geo} = log_2 \frac{[Cn]}{1.5Bn} \quad \text{……………………………………………… (Equation 5.1)}$$

Where Bn is the background chemical concentration of the metal(n) in the global average shale, Cn is the measured concentration of metal n in the sediment (Gonzalez-Macias *et al.*, 2006; Yu *et al.* 2011; Karbassi *et al.*, 2008) and 1.5 is the correction factor of the background matrix due to lithogenic influence. The world average shale values of the heavy metals used are: Zn = 95, Cu = 45, Pb = 20, Cd = 0.3, Ni = 68, Mn = 850, Fe = 47600, As = 13 and Cr = 90 (Jonathan *et al.*, 2016; Hassaan *et al.*, 2016). The seven classes of Igeo of the element in the sediment is shown in Table 5.1

5.2.1.2.2 Enrichment factor (EF)

Various approaches have been presented for assessing the rate of heavy metal accumulation in the sediment. Various authors have recommended pollution scales that turn the results into broad, detailed pollution categories varying from low to higher intensities.

In the present analysis, the enrichment factor is used to determine the extent of contamination of each heavy metal and the potential anthropogenic effects in sediments from the fish farms. The EF calculation evaluates the degree of an anthropogenic effect on element load in the sediments and distinguishes between elements derived from natural or anthropogenic action. This possible contamination index is determined by normalizing one heavy metal content in the surface sediment compared to the reference element concentration. There is no consensus as to the most suitable constituent of the sediment to be used for normalization. The selected variable should also be associated (relative to grain size) with finer particles, and its level should not be altered anthropogenically (Barbeiri, 2016). The EF process normalises the recorded heavy metal content for reference metal samples such as Fe, Al, Mn, and Co (Stewart, 1989; Ravichandran *et al.*, 1995; Akoto *et al.*, 2017). The use of cobalt (Co) as a normalizing element to distinguish anthropogenic sources of pollution in marine deposits was developed by Matthai and Birch (2001). Fe was suggested by Deely and Fergusson (1994) as a practical normalizing element to decide the enrichment factor since they assumed that Fe's abundant distribution is not linked to other heavy metals. Fe also usually has a relatively high environmental abundance, so the anthropogenic sediment source is not required to be substantially enriched (Elias *et al.*, 2014). However, iron (Fe) has not been used as a reference element for this research because iron is not a matrix element and its geochemistry are similar to that of many trace elements in the oxic and anoxic environment (Barbieri *et al.*, 2014; Barbieri, 2016)

According to Loska et al. (2003), the reference element has low occurrence variability and is present in trace amounts in the environment. They further claimed that it is possible to apply to the examined element of geochemical nature whose significant quantities exist in the environment but have no characteristic effects, i.e. synergism or antagonism. Manganese (Mn) recorded the highest level in sediment from the study locations and has a slight variability in terms of the levels from the farms. For this reason, Mn was used as the indexed metal for the EF calculations. The EF, as formulated by Zoller (1974), is as follows:

$$\mathrm{EF} = \frac{\left[{}^{C_x}/_{Mn}\right]\boldsymbol{Sediment}}{\left[{}^{C_x}/_{Mn}\right]\boldsymbol{Shale}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Equation 5.2)}$$

Where C_x is the mean concentration of the element of interest and Mn is the mean concentration of reference element for normalization in sediment, the concentration of the reference element is used for normalization in the Shale. The highest recorded Mn value of 25.215 mg/kg in the sediment and its average shale value of 850 mg/kg was used for the EF computation. Otherworld average shale values of heavy metals used were: Zn = 95, Cu = 45, Pb = 20, Cd = 0.3, Ni = 68, Fe = 47600, As = 13 and Cr = 90 (Jonathan *et al.,* 2016; Hassaan *et al.,* 2016).

Table 5.1: Pollution Grades of Geo-accumulation and Enrichment factor Index of Metals

Class	I_{geo} Class	I_{geo} Sediment Quality	EF Class	EF Sediment Quality
0	$I_{geo} \leq 0$	Uncontaminated	EF < 1	No enrichment
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated	EF < 3	Minor enrichment
2	$1 < I_{geo} < 2$	Moderately contaminated	EF = 3-5	Moderate enrichment
3	$2 < I_{geo} < 3$	Moderately to heavily contaminated	EF =5-10	Moderately severe enrichment
4	$3 < I_{geo} < 4$	Heavily contaminated	EF = 10 – 25	Severe enrichment
5	$4 < Ig_{eo} < 5$	Heavily to extremely contaminated	EF = 25 – 50	Very severe enrichment
6	$I_{geo} \geq 5$	Extremely contaminated	EF > 50	Extremely severe enrichment

I_{geo} –Geoaccumulation index, EF-Enrichment factor

The values calculated for EF from the equation represented the contamination status of the sediment and are defined as follows:

Values of $0.5 \leq EF \leq 1.5$ indicate that the levels of heavy metals are due to normal weathering (Duncan *et al.*, 2018). A value greater than 1.5 indicates the effect of anthropogenic operation (Taylor *et al.*, 2010). The classes of enrichment factors are shown in Table 5.1

5.2.1.2.3 Pollution load index (PLI)

The PLI gives a straightforward, comparative method of evaluating sediment conditions. PLI also provides some understanding about the quality of wildlife in a habitat and information to the decision-makers on the pollution of a region (Kouchesfehani & Aziz, 2019). The PLI was therefore computed to know the pollution status of the cage aquaculture farms. The PLI of 0 indicates excellence, according to Tomilson (1980); the value of 1 indicates the baseline value of the elements concerned, while the values above 1 are deterioration indicators. Although the EF offers the possible impact of metals at a specific location, the PLI appears to provide the total influence of all metals examined at the site.

The PLI, as defined by Duncan *et al.* (2018), is the nth root of the EF products of the metals concerned. It is mathematically denoted by the equation:

$PLI = (EF_1 \text{ x } EF_2 \text{ x } EF_3 \text{ x } EF_4 \text{ x } EF_n)^{1/n}$ ………………………………..(Equation 5.3)

5.2.1.2.4 Potential ecological risk index (RI)

The Hakanson index is a diagnostic tool used to evaluate the possible ecological risk for water pollution management. It helps to decide which bodies of water and substances need to be given special attention. However, as the sediment shows the level of chemical contamination in water, the index is now applied to monitoring sediment contamination. This approach not only measured the extent of pollution in sediments but also combined ecological and environmental effects with toxicology to better evaluate the possible risks of contamination of heavy metals at the index level. RI is calculated using the following formula in equation 5.4:

$\mathrm{RI} = \sum_{i=1}^{n} E_i$ .... (Equation 5.4)

Where E_i is the possible environmental risk factor for each of the pollutants examined. The formula of E_i for the single heavy metal pollution is deduced as follows

$E_i = T_i \times \left(\frac{C_i}{C_o}\right)$ .... (Equation 5.5)

Where C_i *is* the value of the concentration of heavy metal and C_o is the background value. The ratio of C_i to C_o is called the contamination factor (CF). T_i is the toxic factor of the heavy metal, the values for Zn, Cu, Pb, Cd, Ni, Mn, Fe, As and Cr were 1, 5, 5, 30, 5, 1, 1, 10 and 2, respectively (Hakanson, 1980; Soliman *et al.*, 2015; Zhu *et al.*, 2013; Elmorsi *et al.*, 2019). RI is categorized into four classes (Hakanson, 1980; Zhu *et al.*, 2013).

The ecological risk (E_i) factors adopted from Elias *et al.* (2014) was used to describe the potential ecological risk factor as shown in Table 3.3. The classes, as shown in Table 5.2 was used to describe the ecological risk index (RI) as classified by Hakanson (1980)

Table 5.2: Potential ecological risk index (RI) categories

Risk class	Risk Indication	Ecological risk factors	Risk indication
RI < 150	Low ecological risk	Ei < 40	Low potential risk
150 ≤ RI < 300	Moderate ecological risk	$40 \leq Ei < 80$	Moderate potential risk
300 ≤ RI < 600	Considerable ecological risk	$80 \leq Ei < 160$	Considerable risk
RI ≥ 600	Very high ecological risk	$160 \leq Ei < 320$	High potential risk
		Ei≥ 320	Very high risk

5.3 Results

5.3.1 Sources of the OCPs in the sediment

The average concentrations of OCPs in the sediments data from the fish farms were used in a Pearson correlation analysis and PCA. The Pearson correlation coefficients and the results of the PCA for the investigated OCPs were generally consistent with each other. Specifically, the sources of the measured OCPs using the PCA extraction technique with eigenvalues greater than one (1) are presented in Table 5.3. The Kaiser-Meyer-Olkin (KMO) measurement was 0.738, which was higher than 0.5, and PCA results passed the Barlett sphericity test (P< 0.001), which indicates that PCA was appropriate for assessing the OCPs in the sediments of aquaculture farms. Ten principal components (PCs) were extracted, but only three had eigen values > 1. The first three accounted for 84.0% of the total variance.

Table 5.3: Rotated component matrix of organochlorine pesticides in sediment

	Component		
OCPs	**PC_1**	**PC_2**	**PC_3**
β- HCH	0.243	**0.945**	-0.220
δ-HCH	**0.967**	-0.105	0.230
o,p-DDE	**0.977**	0.101	0.186
p,p'-DDE	-0.344	0.685	-0.643
o,p'- DDD	**0.716**	-0.698	0.012
Heptachlor	**-0.861**	-0.101	-0.499
Endrin	0.698	-0.500	0.514
Methoxychlor	**-0.955**	0.020	0.296
α-endosulfan	**-0.861**	0.464	-0.208
β-endosulfan	0.052	-0.228	**0.972**
Eigenevalues	*5.47*	*2.40*	*2.14*
% of variance	*44.65*	*23.97*	*15.38*
% of cumulative	*44.65*	*68.62*	*84.00*

The first principal component (PC_1) had 44.65 % of the overall variance and a significant positive loading (> 0.70) for δ-HCH (0.967), *o,p*-DDE (0.977), *o,p*-DDD (0.716) and a strong negative loading for methoxychlor (-0.955), heptachlor (-0.861) and α-endosulfan

(-0.861). Those OCPs in PC1 exhibited unexpectedly higher concentrations in some of the farms. The Pearson correlation analysis coefficients showed that there were significant positive correlations ($P < 0.01$) between δ-HCH and other OCPs, including *o,p*-DDE ($r = 0.73$, $p < 0.01$), and *o,p*-DDD ($r = 0.88$, $p < 0.01$), suggesting that δ-HCH and these OCPs may have the same source. In addition, there were significantly negative correlations ($P < 0.01$) between methoxychlor and other OCPs, including heptachlor ($r = 0.83$, $p < 0.01$), and α-endosulfan ($r = 0.78$, $p < 0.01$), suggesting that methoxychlor and these OCPs may have the same source. The second principal component (PC_2) had 23.97 % of the total variance and a strong positive loading (> 0.70) for β- HCH (0.945). The third principal component (PC_3) had 15.38 % of the total variance and a strong positive loading (> 0.70) for β-endosulfan (0.972).

5.3.2 Sources of Heavy Metals in sediment

The Kolmogorov-Smirnov (K-S) standard test was used to investigate the probability distributions of heavy metal concentrations in the samples. The results showed that the contents of Mn, Pb, Zn, Fe, Ni, and Cr were normally distributed in the sediment ($P < 0.05$). To analyse the potential sources of the heavy metals, Pearson’s correlation analyses (see Table 5.4) and the principal component analyses (see Table 5.5) were performed. A significant ($p<0.01$) high-positive correlation between metals was recorded in the analysis (Fe vs. Mn, $r = 0.958$) and a high negative correlation (Pb vs. Mn, $r = -0.986$; Zn vs. Cr, $r = -0.852$; and Pb vs. Fe, $r = -0.974$). There was also significant correlation between metals (Fe vs. Cr, $r = -0.612$; Pb vs. Cr, $r = 0.576$; Zn vs. Fe, $r = 0.526$; Ni vs. Cr, $r = 0.519$ Pb vs. Zn, $r = -0.514$; Zn vs. Ni, $r = -0.572$; and Mn vs. Cr, $r= -0.558$). Though the significant correlations between the heavy metals do not always mean they originate from a common source, some insights on the origins and routes of heavy metals may still be provided by the inter-element correlation (Zhang *et al.*, 2018).

Table 5.4: Pearson's correlation matrix for heavy metal concentrations in sediment

	Pb	**Zn**	**Fe**	**Mn**	**Ni**	**Cr**
Pb	1					
Zn	−0.514**	1				
Fe	−0.974**	0.526**	1			
Mn	−0.986**	0.517**	0.958**	1		
Ni	0.219	−0.572**	-0.309	-0.222	1	
Cr	0.576**	−0.852**	−0.612**	−0.558**	0.519**	1

**Correlation is significant at P < 0.01 level (two-tailed)

Therefore, further identification of the sources of measured heavy metals was achieved by employing the PCA approach.

Table 5.5: Rotated component matrix of heavy metals

Heavy Metals	**PC$_1$**	**PC$_2$**
Pb	**-0.973**	0.206
Zn	0.364	**-0.843**
Fe	**0.941**	-0.276
Mn	**0.967**	-0.204
Ni	-0.010	**0.858**
Cr	-0.450	**0.788**
Eigenvalues	*4.062*	*1.267*
% of variance	*51.679*	*37.134*
% of cumulative	*51.679*	*88.812*

PCA loadings > 0.70 are shown in bold.

The Kaiser-Meyer-Olkin (KMO) measurement was 0.738, which was higher than 0.5, and PCA results passed the Berlet sphericity test (P< 0.001), which indicates that PCA was appropriate for assessing heavy metals in the aquaculture farms' sediments. Six principal components (PCs) were revealed, but only two had eigenvalues > 1. These two PCs explained 88.81% of the total variance in the heavy metals' dataset. 51.679% of the overall variance and a strong positive load (> 0.70) for Fe (0.941), Mn (0.967) and a strong negative load for Pb (-0.973) is accounted for by PC1. For Fe, Mn and Pb, the PC1 was consistent with Pearson's correlation coefficient analysis. The second component (PC2) contributed about 37.134 % of the overall variance and was correlated (loading > 0.70) with Ni (0.858) and Cr (0.788) and negative loading for Zn (-0.843). It was also consistent with the result of Pearson's correlation coefficient analysis.

5.3.3 Ecotoxicological concern for OCPs and PCBs in the sediment of fish farms

Using the freshwater sediment quality guidelines (SQG) published by Canada, USEPA and some of Eqani (2012), the possible risk of OCPs and PCBs pollutants in the sediments of the fish farms in the Volta Basin was assessed. These benchmarks were used since EPA Ghana does not have its benchmarks. TEC (TEL, LEL, ERL and CB-TEC) describes concentrations at which toxicity will begin to be detected in susceptible aquatic organisms or concentrations at which adverse effects may not occur whereas, PECs (PEL, SEL, ERM and CB-PEC) indicate concentrations above which adverse effects will occur in aquatic species.

The levels of OCPs and PCBs in confirmed sediment samples in all four fish farms (A, B, C, D and controls) were cross-checked against the sediment content guidelines (Table 5.6) to establish the overall sediment quality and potential risk to aquatic life in the Volta Basin aquaculture facilities. Among the pesticides, *p,p'*-DDE mean concentrations in the detected samples were ranged 1.113-1.510 µg/kg in all the four farms, but fish farms B and D exceeded TEL (threshold effect level). None of the values of the *p,p'*-DDE in the sediment from all the farms showed high values than the lowest effect level (LEL), effect range low (ERL) as well as the consensus-based threshold effect concentration (CB-TEC; below which adverse effects are not expected to occur). *p,p'*-DDE levels in all the farms were lower than the probable effect concentrations (PECs). *p,p'*-DDT concentrations in sediments from fish farms C and D were higher than the effect range low (ERL). Only *p,p'*-DDT in the sediment from farm D was slightly higher than the consensus-based threshold effect concentration (CB-TEC). However, the farms' *p,p'-DDT* findings were below the probable effect concentrations (PECs). The study revealed that the ∑DDT (sum of *o,p'*-DDE, *p,p*-DDE, *o,p'*-DDD and *p,p'*-DDT) in the farms' sediment was higher than all TECs except that of farm B, whose ∑DDT was slightly lower than TEL. The ∑DDT was lower than all the PECs. On the other hand, ∑HCH in all four farms exceeded the threshold effect level (TEL) and the probable effect levels (PEL). However, the ∑HCH in the control experiment also exceeded the TEL but was lower than the probable effect levels (PEL).

Table 5.6: Risk assessment of OCPs and PCBs detected in sediment samples using sediment quality guidelines

	TECs				**PECs**				**Pesticides concentration in sediment**				
Pesticides	**TEL**	**LEL**	**ERL**	**CB-TE**	**PEL**	**SEL**	**ERM**	**CB-PEC**	**FF_A**	**FF_B**	**FF_C**	**FF_D**	**CC**
***p,p′*-DDE**	1.42	5	2.2	6.75	6.75	190	27	31.3	-	1.48	1.113	1.510	-
***p,p′*-DDT**	-	-	1	4.16	-	710	7	62.9	-	-	1.803	5.000	-
∑DDT	3.89	7	1.58	5.28	51.7	120	46.1	572	7.185	3.483	5.938	12.263	0.163
∑HCH	0.32	-	-	-	0.99	-	-	-	10.490	2.862	4.155	2.938	0.728
∑PCBs	34.1	-	22.7	-	277	-	180	-	0.788	1.618	1.271	6.202	0.172

FF_A = Fish farm A, FF_B = Fish farm B, FF_C = Fish farm C, FF_D= Fish farm D and CC= Controls

For this research, concentrations of ∑PCBs in sediments from all the farms and the controls were lower than those of TEL, ERL, PEL and ERM values.

5.3.4 Potential ecological risk of heavy metals pollution

PLI, Igeo and EF were introduced to accurately and comprehensively evaluate the sediment's pollution status. In this study, the average Shale values of the heavy metals were chosen as background references for the assessment. Table 5.7 summarizes the estimated values of the pollution load index (PLI) of metals in sediments. The PLI values ranged from 0.230 to 1.315. The highest PLI value was observed in fish farm D and the least in the control samples. The PLI order according to the fish farms in the study area includes, Fish farm D (1.315) > Fish farm C (1.291) > Control (0.404) > Fish farm A (0.234) > Fish farm B (0.230).

Heavy metals assessment requires a broad knowledge of pre-industrial metal concentration to represent the reference against which measured values can be compared (Abrahim & Parker, 2002). Therefore, to better understand sediment quality from the aquaculture facilities in the Lake Volta, the enrichment factor (EF), which differentiates between human-generated and naturally existing heavy metal sources, was used. The results are presented in Table 5.7.

Table 5.7: Geo accumulation index, PLI & enrichment factor for metals in sediment samples

	FISH FARM A		**FISH FARM B**		**FISH FARM C**		**FISH FARM D**		**CONTROL**	
Metal	**EF**	**I_{geo}**	**EF**	**I_{geo}**	**EF**	**I_{geo}**	**EF**	**I_{geo}**	**EF**	**I_{geo}**
Pb	–	–	–	–	23.023	-1.135	22.990	-1.137	0.653	-6.282
Zn	0.176	-8.170	0.281	-7.495	0.170	-8.214	0.181	-8.126	0.010	-14.537
Fe	0.002	-14.654	0.002	-14.477	–	–	–	–	0.360	-21.679
Mn	1.000	-5.660	1.000	-5.661	0.483	-6.710	0.511	-6.628	1.00	-7.551
Ni	0.456	-6.793	0.342	-7.208	0.408	-6.953	0.436	-6.857	0.098	-10.780
Cr	4.332	-3.545	3.324	-3.927	4.656	-3.441	4.238	-3.577	1.641	-7.122
PLI	**0.234**		**0.230**		**1.291**		**1.315**		**0.404**	

PLI – Pollution Load Index, EF – Enrichment factor, Igeo – Geo-accumulation index

The measured EF values of the metals from the fish farms revealed that Zn, Fe, Ni and Mn were less than two, except Cr and Pb, which have EF >2. Fe and Zn recorded the least values of EF in the study area. The EF values calculated using Mn as a normalizer are: Cr (moderate enrichment) > Mn (minor enrichment) > Ni (no enrichment) > Zn (no enrichment) > Fe (no enrichment) for fish farms A and B. Similarly, EF values of heavy metals for farm C and D are: Pb (very severe enrichment) > Cr (moderate-severe enrichment) > Mn (minor enrichment) > Ni (no enrichment) > Zn (no enrichment). This implies that the order of EF of heavy metals in farms A and B is the same likewise farms C and D. There was no heavy metals enrichment at the control sites.

The values of the studied heavy metals' geo-accumulation index (Igeo) are presented in Table 5.7. Based on the seven classifications proposed by Muller (1979), the negative Igeo values found in the table are the results of relatively low levels of contamination for all the metals in the sediment from the farms.

The assessment suggested by the Swedish scholar Hakanson as a diagnostic method for monitoring water pollution was used to determine the possible potential ecological risk factor (E_i) and the potential ecological risk index (RI), as summarized in Table 5.8.

Table 5.8: Potential Ecological Risk Assessment of heavy metals in the sediment

	FISH FARM A		**FISH FARM B**		**FISH FARM C**		**FISH FARM D**		**CONTROL**	
Metal	**CF**	**E_i**	**CF**	**E_i**	**CF**	**E_i**	**CF**	**E_i**	**CF**	**E_i**
Pb	BDL	BDL	BDL	BDL	6.83E-01	3.415	6.82E-01	3.410	1.93E-02	0.097
Zn	5.20E-03	0.005	8.32E-03	0.008	5.05E-03	0.005	5.37E-03	0.005	6.32E-05	6.32E-05
Fe	5.82E-05	5.82E-05	6.58E-05	6.6E-5	BDL	–	BDL	–	4.48E-06	4.48E-06
Mn	2.96E-02	0.030	2.96E-02	0.030	1.43E-02	0.014	1.52E-02	0.015	8.00E-03	0.008
Ni	1.36E-02	0.068	1.01E-02	0.051	1.21E-02	0.061	1.29E-02	0.065	8.53E-04	0.001
Cr	1.29E-01	0.257	9.86E-02	0.197	1.38E-01	0.276	1.26E-01	0.251	1.08E-02	0.022
RI		**0.360**		**0.286**		**3.771**		**3.746**		**0.128**

CF-Contamination factor, Ei – Ecological risk, RI-Risk Index

The order of potential ecological risk coefficient (Ei) of heavy metals in sediments each of fish farms A and B were Cr > Ni> Mn> Zn> Fe. The order for farms C and D were Pb>Cr>Ni>Mn>Zn. The order for the control was: Pb>Cr>Mn>Ni>Zn>Fe. As stated by Elias *et al.* (2014), all the possible ecological risk coefficients (Ei) of heavy metals were less than forty (Ei<40). Following the IR values classified by Hakanson (1980), the overall risk indices for all the fish farms, including the controls, were less than 150, (i.e. RI < 150. The order of RI of the heavy metals in sediments from the fish farms was: Fish farm C (RI=3.771) > Fish farm D (RI=3.747) > Fish farm A (RI=0.360) > Fish farm B (RI= 0.286)>control (RI =0.128).

5.4 Discussion

5.4.1 Sources and ecotoxicological concerns of OCPs and PCBs in sediment

The data variance (84%) was explained by three (3) eigen vector-principal components. The first component (PC_1) was highly correlated with *o,p*'-DDE (0.977), α-HCH (0.967), *o,p'*-DDD (0.716), endrin (0.698), methoxychlor (-0.955), α-endosulfan (-0.861) and heptachlor (-0.861). These OCPs are used as pesticides, fungicides and herbicides in agriculture and control vector-borne diseases such as malaria. It is also worth noting that a large volume of these pesticides applied on land reaches the Basin through atmospheric transport (GESAMP, 1989) and from the fish feed. In Ghana, for instance, these pesticides are clandestinely used under unknown trade names. Therefore, the phenomenon in component one might be caused by the long-term use of these pesticides in agricultural fields, atmospheric transport, and fish feed.

The second component (PC_2) and third component (PC_3) are positively loaded on β-endosulfan (0.972), β-HCH (0.945) and *p,p'*-DDE (0.685). In this study, the Juapong textile factory and major cities such as Akosombo and Kpong are close to some fish farms, suggesting that their effluents during runoff could result in heavier farm pollution. As revealed in the present study, the chemicals in the second and third components could be related to sewage discharge and some localized anthropogenic inputs from variable sources.

The potential risk of organochlorine and PCB compounds in sediments from fish farms in the Volta Basin was assessed based on the sediment quality guidelines (SQG) developed for freshwater. Sum concentrations of ∑DDTs ranged from 0.163-12.263 µg/kg during the period of observations. Sum concentrations of DDT (∑DDTs) in fish farms A, C and D exceeded the threshold effect concentrations (TECs) and the consensus-based threshold effect concentration (CB-TEC) except ∑DDT concentration in fish farm B and the controls that were less than TEL. None of the sediment samples exceeded consensus-based probable effect concentrations (CB-PECs) of 572 µg/kg for ∑DDTs from all four areas. In all sediment samples, the values p, p'-DDE surpassed the threshold effect level (TEL) for fish farms B and D, while p,p'-DDT surpassed the low effect range (ERL) for fish farms C and D in all sediment samples. However, in sediment samples from fish farm D, *p,p'*-DDT concentrations (µg/kg) surpassed the Census Based Threshold Effect Concentrations (CB-TECs) for this metabolite but were below the PECs. This comparison of the levels of DDTs with the appropriate sediment criteria for evaluating the contamination of DDTs and their metabolites shows that adverse biological effects are not likely to occur in the studied areas examined. Indoor residual spraying has been used in many parts of Ghana, especially in areas vulnerable to malaria epidemics. This situation naturally presents DDT and its metabolites in the aquatic environment, though it is no longer used in agricultural settings. Therefore, routine measures should be put in place to minimize the pollution of fish farms with DDT.

In the case of ΣHCH, all the mean concentrations of the sediment samples from the farms and the controls showed higher values than the threshold effect level (TEL) and the probable effect concentration (PEL), except the controls that recorded mean value less than the PEL. It can therefore be seen that the comparison of ∑HCHs with the quality guidance available shows that the risk from HCHs is very high, except for HCHs from the controls. The levels of HCHs should therefore be regularly monitored and primary sources established and abated.

Eqani (2012) proposed the effect range low value (ERL) of 22.7 µg/kg (dry weight) at which PCBs can cause toxic effects on aquatic organisms. The effect range median value

(ERM) of 180 µg/kg (dry weight) shows a high possibility of PCBs posing toxic effects on aquatic organisms. According to the Canadian Sediment Quality Guidelines (CSQGs), a probable effect level (PEL) of 277 µg/kg (dry weight) can cause toxic effects on aquatic life frequently. In contrast, at a concentration of threshold effect level (TEL) of 34.1 µg/kg (dry weight), the effects are negligible (CCME, 1999). Therefore, in this study, ∑PCB concentrations in sediments were lower than TEL, ERL, PEL, and ERM values. So ∑PCBs concentration will not probably pose a threat to the aquatic ecosystem.

5.4.2 Pollution, potential ecological risk assessment, and Sources of HMs in sediment

Measured PLI, Igeo and EF levels of metals in the environment are presented in Table 5.7. The controls, EF values for Fe, Zn, Ni, and Pb, were within $0.5 \leq$ EF ≤ 1.5. This shows that the measured metal concentrations metals in the controls sediment for the areas under review may be due to the natural weathering of rocks. In contrast, Pb and Cr were due to anthropogenic activities, and their EF values were greater than 1.5 (EF > 1.5). The enrichment factors of the farms were in order: Cr > Ni > Zn > Fe (fish farms A and B), Pb > Cr > Ni > Zn (fish farms C and D) and Cr > Pb > Fe > Ni >Zn (for controls). All the fish farms sediment showed no enrichment for Zn, Fe and Ni, minor enrichment for Mn, moderate enrichment for Cr and very severe enrichment for Pb in fish farms C and D.

The PLI varies from 0.230 to 1.315 for the fish farms. Fish farms A, B, and controls had PLI values within the PLI < 1 category range. This indicates that the quantity of these heavy metals found in the sediment was minimal. Therefore, the sediments at farms A, B and controls were considered to be excellent for pollution. However, a comprehensive analysis of other contaminants should be carried out. The PLI values were higher than one (PLI >1). This implies that sampled sediment from fish farms C and D showed a sign of progressive deterioration concerning the heavy metals.

Muller (1979) proposed that the geo-accumulation index scale consists of seven grades (0–6), defining pollution levels from unpolluted to highly polluted. The computed Igeo indexes for the six (Pb, Zn, Cr, Mn, Fe and Ni) heavy metals obtained in sediment from the fish farms during the study are presented in Table 5.8. It can be deduced from the analyses that none of the cage fish farms as well as the controls showed signs of sediment contamination (Igeo < 0) for Pb, Zn, Cr, Mn, Fe and Ni.

Hakanson defined a method for calculating the possible ecological risk index for control of aquatic pollution to establish the water bodies and substances that should be given special attention. As a diagnostic method for water pollution control purposes, assessing the potential ecological risk of heavy metal contamination was suggested due to the rising content of heavy metals in sediments and their eventual release into the water, which could threaten ecological health. The order of potential ecological risk coefficient (Ei) of heavy metals in sediments for each of fish farms A and B is Cr > Ni> Mn> Zn> Fe, and that of farms C and D is: Pb>Cr>Ni>Mn>Zn. All the potential ecological risk coefficients (Ei) of heavy metals were less than forty (Ei<40). This indicates that the heavy metals posed little potential ecological risks in sediment from all the fish farms in the Volta Basin. Following the potential ecological risk index (RI) classified by Hakanson (1980), the overall risk indices for all the fish farms were less than 150, i.e. RI < 150. These indicate low ecological risk in the fish farms during the period of observation. The order of potential ecological risk of the heavy metals in sediments from the fish farms is: Fish farm C (RI=3.771) > Fish farm D (RI=3.747) > Fish farm A (RI=0.360) > Fish farm B (RI= 0.286).

High correlations between the different heavy metal pairs in sediments suggest that these metals have the same spatial distribution or may represent similar levels of contamination and/or release from the same risk of pollution (Yi *et al.*, 2011). PCA has been used to assist in the characterization of the contamination from lithogenic and/or anthropogenic sources by heavy metals (Yohannes, 2014). The results of PCA for heavy metal are listed in Table 5.5. Six principal components (PCs) were revealed, but only two had eigenvalues > 1; these PCs explained that 88.81% of the total variance in the heavy metals' dataset. The initial component matrix showed that Fe, Mn and Pb were highly correlated. The Fe and Mn phenomenon in the first component might be caused by two possible reasons. Firstly, considering that Fe and Mn are conservative elements present in the natural sources, it could be concluded that Mn and Fe are from lithogenic sources. It has been established that in the aquatic environment, Mn is associated with Iron deposits to form ferromanganese minerals, particularly in clay minerals (Laar *et al.*, 2011). Secondly, fish feeds are fortified with trace elements, including Fe and Mn, for proper physiological functioning of the body organs of fish (Mannan *et al.,* 2018). Their source in the first component of the PCA may also be attributed to the fish feed. Lead is used in car batteries, and antifoulants paint for aquaculture structures, pesticides and herbicides (Dinku, 2015). It is most likely that the metal Pb was sourced from the farmlands during runoff and the aquaculture activities, such as antifoulant paints.

Levels of Zn in the current study in the PC_2 could be related to unconsumed fish feeds and antifouling paints suggested in a similar study by Aslam *et al.* (2020) and Lagerstrom e*t al.* (2016). High Cr concentrations were found in all the farms' sediments. Its primary sources are industrial wastewater, primarily from domestic wastewater, as well as industrial leather and dye wastewater (Algul & Beyhan, 2020). For this study, the primary source of Cr pollution is the industrial wastewater probably originating from the Akosombo textile factory, reaching the Basin via runoff. The spread of Ni from the farms could also be attributed to lithogenic sources and anthropogenic sources such as vehicular emissions, household, industrial and municipal waste, fossil fuel burning, fertilisers from farms, and organic manure (Rathor *et al.,* 2014).

5.5 Conclusion

Heavy metals, OCPs, and PCBs in cage aquaculture farm sediment were investigated for potential ecological threat and source identification. Diagnostic ratios and statistical methods of the OCPs proposed industrial, agricultural activities, and municipal waste discharge into the Basin as significant sources. The accumulation of the heavy metals in the sediments also showed lithogenic and anthropogenic activities as the primary sources. Low ecological risk of the heavy metals was observed in the fish farms sediment at the study time. Toxicity risk assessment of surface sediment of the farms identified ΣHCHs as the only contaminant whose concentration level in the sediment poses a health risk to benthic organisms. Because these pollutants' harmful effects may have a detrimental effect on the ecosystem, some corrective actions or remedial efforts should be implemented to avoid their contamination.

CHAPTER SIX

HEALTH RISKS ASSOCIATED WITH THE DIETARY INTAKE OF CULTURED-TILAPIA (*Oreochromis niloticus*) FOR OCPS, PCBS AND HEAVY METALS POLLUTION

6.1 Background

Fish, in general, have the propensity to bioconcentrate chemicals from aqueous environments, making them an excellent bioindicator of pesticide contamination levels in aquatic systems. Fish is a significant source of animal protein in Ghana due to its accessibility and cost. However, according to Adu-Kumi *et al.* (2010) and Koranteng (2015), fish in Ghana are not always devoid of detectable contaminants especially, pesticides.

However, the simple data on the contaminants (OCPs, PCBs and heavy metals) content of the fish samples obtained from the analysis is insufficient to describe the entire risk that fish consumption may cause by the general populace. Health risk assessment is necessary to estimate the likelihood and the severity of an adverse occurrence resulting from a hazard over a given time. Many studies on exposure of pesticides to humans suggest health implications. Exposure to these contaminants may lead to associated problems such as endocrine disruption, congenital disabilities, reproductive failures, carcinogenicity, immune system dysfunctions and many more. The health risk is a function of hazard and exposure. As a result, this chapter examined the potential health risk caused to humans by eating caged fish.

The adverse health effects on humans during exposure to contaminants in fish were assessed using the analysis model of the USEPA (Kamunda *et al.,* 2018).

6.2 Materials and method

This chapter, just like chapter 5, uses generated data in chapter 4 and employs various appropriate risk assessment models to investigate the health risk associated with dietary intake of cultured tilapia.

6.2.1 Data analyses

The measurable levels of the OCPs, PCBs and heavy metals in Tables 4.10, 4.11 and 4.12, respectively, were put into equations 6.1, 6.2, 6.3 and 6.4 for the estimation of the health risk indices

6.2.2 Risk Assessment

It is assumed that the per capita consumption of cage culture tilapia at the national level will be different from that of the local level where the study was conducted, so also is the associated health risk. Therefore, two health risk assessments were estimated—one for the national and the other for the Patrons of tilapia from the local restaurants

6.2.2.1 Exposure Assessment

The concentrations of the pollutants in the studied fish were used in this study for the estimated daily intake (EDI) (mg/kg/day) using the models proposed by USEPA (2012) via ingestion of fish. The approximate exposures were calculated separately for children and adults using the equation 6.1

$$\text{EDI} = \frac{(Food\ chemical\ concentration, C\ \ (mg/kg)\ x\ Food\ consumption,\ \ IR\ (kg/day))}{(BW\ (kg))} \text{……(Eqn. 6.1)}$$

Where BW is body weight (15 kg for children and 70 kg for adults), C is the concentration of the examined contaminants (OCPs, PCBs and heavy metals) in the fish, and IR is the per capita consumption of tilapia. The per capita consumption of fish (IR) in Ghana, as reported by Akuffo & Quagrainie (2019), is 26 kg/head/year, which is equivalent to 0.071 kg/person/day. Thus, the Estimated Daily Intakes (EDIs) for the pollutants were compared with the Reference Dose values (Rfds). The pollutant will present a relatively high risk if EDI >Rfd.

6.2.2.2 Non-carcinogenic effects of contaminants in fish

The hazard quotient (HQ) is a commonly used method for characterising risk. It is the ratio of the predicted exposure to the chemical above the level at which no detrimental effects are expected. The hazard quotient is mathematically expressed as in equation 6.2.

HQ $= Estimated\ Daily\ Intake\ (EDI) /\ Reference\ Dose (Rfd)$ ……(Equation 6.2)

Hazard quotients were also calculated individually for children (0-12 years) and adults (>12 years). Hazard quotient (HQ) > 1 indicates a non-carcinogenic effect on health, while HQ ≤ 1 shows no harmful influence.

The oral Rfd of the heavy metals were:(As = 3 x 10^{-4} mg kg^{-1} day^{-1}, Cu = 4.0 x 10^{-2} mg kg^{-1} day^{-1}, Zn = 3.0 x 10^{-1} mg kg^{-1} day^{-1}, Fe = 3.6 x 10^{-1} mg kg^{-1} day^{-1} , Ni = 2.0 10^{-1} mg kg^{-1} day^{-1}, Pb = 3.5 x 10^{-5} mg kg^{-1} day^{-1}, Cd = 1.0 x 10^{-3} mg kg^{-1} day^{-1}, Cr = 3.0 x 10^{-3} mg kg^{-1} day^{-1} and Mn = 1.4 x 10^{-2} mg kg^{-1} day^{-1} (Darko *et al.*, 2015; Gbogbo *et al.*, 2018; Magna *et al.*, 2018). The oral reference dose (Rfd) (µg/kg/day) of the pesticides were: (delta-HCH =0.3; *o,p'*-DDE = 0.5; *p,p'*-DDE = 0.5; *o,p'*-DDD = 0.5; *p,p'*-DDT = 0.5; Heptachlor = 0.5; Endrin = 0.3; Methoxychlor = 5.0; PCB = 0.02; α-endosulfan = 0.05 (Afful, 2015; Raslan *et al.*, 2018; Omar & Mahmoud, 2017). The oral reference dose values for the individual indicator PCB congeners were not available in literature. The detected PCBs were therefore summed up and the general Rfd value for ∑PCB, i.e. 0.02µg/kg/day (Omar & Mahmoud, 2017) used for the risk calculations.

Additionally, the cumulative toxicity risk of pollutants, particularly heavy metals, may also present an adverse health effect to consumers. The Hazard Index (HI), which measures the sum of the hazard quotients of all metals in fish from each farm, was therefore obtained to measure the non-carcinogenic threats to humans (Gyimah *et al.*, 2018):

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{HQ}_i \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(Equation 6.3)}$$

where HQi represents the hazard quotient for the ith metal. Hazard Index (HI) > 1 indicates a non-carcinogenic effect on health, while HI ≤ 1 shows no harmful effect. The cumulative (additive) effects of the pesticides have not been established; therefore, hazard indices of the pesticides were not estimated

6.2.2.3 Carcinogenic Risk Assessment

Individuals may be exposed to cancer through the consumption of fish contaminated with a carcinogen. To examine this, a carcinogenic risk evaluation, which predicts the likelihood of a person developing cancer over a lifespan, resulting from exposure to possible carcinogens (Gyimah *et al.,* 2018), was estimated. The main assessment parameter, the cancer slope factor (CSF), was obtained from the EPA carcinogen risk assessment. The CSF represents the probable upper-bound estimate of the likelihood that a person will develop cancer if exposed to a chemical (cancer-causing agent) for a lifetime of 70 years. Therefore, the target risk of cancer was estimated using the following equation 6.4

$\mathrm{TCR} = \mathrm{EDI} \times \mathrm{CSF}$ ………………………………………………………………… (Equation 6.4)

Where CSF is the cancer slope factor of the individual pollutant, EDI is the estimated daily intake and TCR is the target cancer risk. The CSF for carcinogens; δ-HCH = 1.80 mg/kg/day, *p,p'*-DDE = 0.34 mg/kg/day, *p,p'*-DDT = 0.34 mg/kg/day, heptachlor = 4.5 mg/kg/day, endrin = 17.00 mg/kg/day, and PCBs = 2.00 mg/kg/day were obtained from US EPA (2014), Raslan *et al.* (2018) and Omar & Mahmoud (2017).

For the heavy metals, only Ni, Cd, Pb, Cr and As were carcinogenic. Therefore, their CSF values used for the carcinogenic estimation were as follows, Ni = 0.91 mg/kg/day, Cd= 0.38 mg/kg/day, Pb= 0.0085 mg/kg/day, Cr = 0.5 mg/kg/day and As = 1.5 mg/kg/day (Onyedikachi *et al.*, 2018; Zeng *et al.*, 2015)

6.2.2.4 A Survey conducted to ascertain the Health Risk of Patrons of tilapia from the local restaurant

The per capita consumption (IR) of caged tilapia by the Patrons of tilapia from the local restaurants was estimated using a questionnaire. Five restaurants that purchased the caged tilapia from the farms were used for the study. Survey questionnaires were used to solicit information from 445 randomly selected participants who eat fish from the five restaurants in the communities. The questionnaire solicited basic information such as the sex, age, and education level of the participants. In the case of fish, respondents indicated the amount and frequency of consumption in a day, week and month. To determine the quantity, they were given samples of already weighed fish and asked to indicate how much was consumed at a time. The indicated quantities were immediately recorded. Additional information on the bodyweight of the adults (>12years) and children (≤12 years) respondents were documented on the questionnaire. The average per capita consumption was obtained from the questionnaire analysis. Health consequences of the OCPs, PCBs and heavy metals were established using equations 6.1, 6.2, 6.3 and 6.4.

6.3 Results

6.3.1 Risk Assessment

6.3.1.1 Exposures, non-carcinogenic and carcinogenic risk assessment of pesticides

Table 6.1 presents the estimated daily intake (EDI) of the pesticides; δ-HCH, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDT, heptachlor, endrin, methoxychlor, *α*-endosulfan, *β*-endosulfan and PCBs in young children and grown-ups through the consumption of tilapia from the Volta Basin. The EDI values for the national range from 8.91E-04 to 9.79E-02. PCBs in fish from farm D recorded higher values (9.79E-02 µg/kg/day and 2.10 µg/kg/day) for children and adults than the Rfd. All other EDI values for the age categories were considerably below the reference doses (Rfd). Similarly, the hazard quotients (HQs) of the pesticides are shown in Table 6.2. The HQs levels range 9.24E-04 to 4.00E-02 (fish farm A), 7.03E-03 to 9.35E-01 (fish farm B), 7.88E-04 to 4.90 (fish farm D), and 5.16E-04 to 1.77E-01 (control). For children and adults, the hazard indices calculated for these dietary exposure scenarios for PCBs were greater than 1 for the tilapia samples in fish farm D. All other HQ levels of pesticides in fish ingested by both adults and children from the farms were below one. However, children were relatively at higher non-carcinogenic risk in all instances via consuming pesticides-contaminated tilapia than the adult.

Table 6.1: Estimated Daily Intake (µg/kg/day) of pesticides in cage fish

		FISH FARM A		FISH FARM B		FISH FARM D		CONTROL	
Pesticides	Rfd	Children	Adult	Children	Adult	Children	Adult	Children	Adult
δ-HCH	0.30	3.95E-03	8.46E-04	9.84E-03	2.11E-03	2.89E-02	6.20E-03	2.54E-03	5.54E-04
***o,p′*-DDE**	0.50	6.59E-03	1.41E-03	5.92E-03	1.27E-03	1.34E-02	2.87E-03	2.92E-03	6.25E-04
***p,p′*-DDE**	0.50	2.15E-03	4.62E-04	NIL	NIL	1.15E-02	2.47E-03	2.52E-03	5.40E-04
***o,p′*-DDD**	0.50	NIL	NIL	2.01E-02	4.32E-03	NIL	NIL	NIL	NIL
***p,p′*-DDT**	0.50	1.09E-02	2.34E-03	5.77E-03	1.24E-03	7.10E-03	1.52E-03	NIL	NIL
Heptachlor	0.50	1.01E-02	2.16E-03	6.32E-03	1.37E-03	1.37E-02	2.93E-03	4.16E-03	8.91E-04
Endrin	0.30	NIL	NIL	1.03E-02	2.20E-03	1.46E-02	3.12E-03	3.88E-03	8.32E-04
Methoxychlor	5.00	NIL	NIL	1.50E-02	3.22E-03	1.84E-02	3.94E-03	2.58E-03	5.54E-04
***α*-endosulfan**	0.05	1.05E-02	2.24E-03	1.09E-02	2.34E-03	8.80E-03	1.89E-03	3.49E-03	7.49E-04
***β*-endosulfan**	NIL	7.96E-03	1.71E-03	6.34E-03	1.36E-03	3.85E-03	8.25E-04	2.46E-03	5.27E-04
∑PCB	0.02	3.94E-03	8.01E-04	1.87E-02	4.02E-03	9.79E-02	2.10E-02	3.53E-03	7.56E-04

RfD= Reference dose (µg/kg/day)

Table 6.2: Hazard Quotient of pesticides through consumption of cage tilapia for Non-carcinogenic

	FISH FARM A		**FISH FARM B**		**FISH FARM D**		**CONTROL**	
Pesticides	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**
δ-HCH	1.32E-02	2.82E-03	3.28E-02	7.03E-03	9.63E-02	2.07E-02	8.47E-03	1.85E-03
***o,p′*-DDE**	1.32E-02	2.82E-03	1.18E-02	2.54E-03	2.68E-02	5.74E-03	5.84E-03	1.25E-03
***p,p′*-DDE**	4.30E-03	9.24E-04	NIL	NIL	2.30E-02	4.94E-03	5.04E-03	1.08E-03
***o,p′*-DDD**	NIL	NIL	4.02E-02	8.64E-03	NIL	NIL	NIL	NIL
***p,p′*-DDT**	2.18E-02	4.68E-03	1.15E-02	2.48E-03	1.42E-02	3.04E-03	NIL	NIL
Heptachlor	2.02E-02	4.32E-03	1.26E-02	2.74E-03	2.74E-02	5.86E-03	8.32E-03	1.78E-03
Endrin	NIL	NIL	3.43E-02	7.33E-03	4.86E-02	1.04E-02	1.29E-02	2.77E-03
Methoxychlor	NIL	NIL	3.00E-03	6.44E-04	3.64E-03	7.88E-04	5.16E-04	1.11E-04
***α*-endosulfan**	2.10E-01	4.48E-02	2.18E-01	4.68E-02	1.76E-01	3.78E-02	6.98E-02	1.50E-02
***β*-endosulfan**	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
PCB	1.97E-01	4.00E-02	9.35E-01	2.01E-01	4.90	1.05	1.77E-01	3.78E-02

Table 6.3: Cancer Risk Estimations of pesticides in cage fish for Children and Adults from the Volta Basin

		FISH FARM A		**FISH FARM B**		**FISH FARM D**		**CONTROL**	
Pesticides	**CSF(µg/kg/day)**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**
δ-HCH	1.80E-03	7.11E-06	1.52E-06	1.77E-05	3.80E-06	5.20E-05	1.12E-05	4.57E-06	9.97E-06
***p,p′*-DDE**	3.40E-04	7.31E-07	1.57E-07	NIL	NIL	3.91E-06	8.40E-07	8.57E-07	1.84E-07
***p,p′*-DDT**	3.40E-04	3.71E-06	7.96E-07	1.96E-06	4.22E-06	2.41E-06	5.17E-07	NIL	NIL
Heptachlor	4.50E-03	4.55E-05	9.72E-06	2.84E-05	6.17E-06	6.17E-05	1.32E-05	1.87E-05	4.01E-06
Endrin	1.70E-02	NIL	NIL	1.75E-04	3.74E-05	2.48E-04	5.30E-05	6.60E-05	1.41E-05
PCB	2.00E-03	7.88E-06	1.60E-06	3.74E-05	8.04E-05	1.96E-05	4.20E-05	7.06E-06	1.51E-05

CSF=Cancer slope factor

The carcinogenic risk was also calculated using the respective cancer slope factor (CSF) of the individual pesticide in Table 6.3. The requirements on cancer risk developed by USEPA ranged from 1.0 x 10^{-6} to 1.0 x10^{-4} (USEPA, 2012). They were higher TCR values for endrin in processed tilapia in farm B (1.75E-04) and farm D (2.48E-04) for children than the required USEPA cancer risk guidelines. Accordingly, the studies also showed the estimated cancer risks for other pesticides (δ-HCH, *p,p'*-DDE, heptachlor, and *p,p'*-DDDT) from the ingestion of tilapia from the Volta Basin were within the USEPA guidelines.

6.3.1.2 Exposures, non-carcinogenic and carcinogenic risk assessment of heavy metals

The estimated daily intake (EDI) of heavy metals through the consumption of cage tilapia (*Oreochromis niloticus*) from fish farms on Volta Lake is given in Table 6.4. The calculated EDIs of Zn, Fe, Mn, Ni and Cr were below the limits for the reference dose of 0.3, 0.36, 0.014, 0.2 and 0.003 mg/kg, respectively (Darko *et al.*, 2015; Gbogbo *et al.*, 2018; Magna *et al.*, 2018). For HQ, the appropriate threshold limit is 1, proposed by USEPA (2012). For this study, except HQ value of As for children in the wild tilapia, all other HQ values for the heavy metals for the different age categories were distinctly lower than the hazard unit limit, as shown in Table 6.5.

The addictive effects (HI) of the heavy metals in fish from all the farms as well as the wild (control) for children surpassed the suggested unit limit. The HI of the heavy metals in fish for children were in order: Control (4.22)>fish farm A (2.16) > fish farm D (1.94) > fish farm B (1.35)

Table 6.4: **EDI (mg/kg/day) of heavy metals in tilapia for Children and Adults**

		FISH FARM A		FISH FARM B		FISH FARM D		CONTROL	
Metal	**Rfd**	**Child**	**Adult**	**Child**	**Adult**	**Child**	**Adult**	**Child**	**Adult**
Zn	3.00E-01	9.79E-03	2.09E-03	1.00E-02	2.16E-03	8.61E-03	1.85E-03	4.59E-03	9.84E-04
Fe	3.60E-01	1.76E-01	3.78E-02	2.37E-01	5.08E-02	1.87E-01	4.01E-02	5.25E-02	1.12E-02
Mn	1.40E-02	1.61E-02	3.46E-03	8.33E-03	1.79E-03	1.16E-02	2.50E-03	3.64E-03	7.81E-04
Ni	2.00E-01	7.67E-03	1.64E-03	1.30E-02	2.78E-03	9.47E-03	2.03E-03	3.08E-03	6.59E-04
Cr	3.00E-03	1.47E-03	3.14E-04	–	–	1.56E-03	3.35E-04	4.73E-04	1.01E-04
As	3.00E-04	–	–	–	–	–	–	1.09E-03	2.33E-04

Table 6.5: **Non-carcinogenic HQ of HM in cage tilapia for Children and Adults**

	FISH FARM A		FISH FARM B		FISH FARM D		CONTROL	
Metal	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**
Zn	3.26E-02	6.97E-03	3.33E-02	7.20E-03	2.86E-02	6.17E-03	1.53E-02	3.28E-03
Fe	4.48E-01	1.05E-01	6.58E-01	1.41E-01	5.19E-01	1.11E-01	1.45E-01	3.11E-02
Mn	1.15	2.47E-01	5.95E-01	1.28E-01	8.29E-01	1.79E-01	2.60E-01	5.58E-02
Ni	3.84E-02	8.20E-03	6.50E-02	1.39E-02	4.74E-02	1.02E-02	1.54E-02	3.30E-03
Cr	4.90E-01	1.05E-01	-	-	5.20E-01	1.11E-01	1.58E-01	3.37E-02
As	-	-	-	-	-	-	3.63	7.77E-01
HI	**2.16**	**0.47**	**1.35**	**0.29**	**1.94**	**0.42**	**4.22**	**0.90**

Table 6.6: Cancer Risk Estimations of Heavy Metals in cage tilapia for Children and Adults

		FISH FARM A		FISH FARM B		FISH FARM D		CONTROL	
Metal	**CSF**	**Child**	**Adult**	**Child**	**Adult**	**Child**	**Adult**	**Child**	**Adult**
Cr	0.50	7.35E-04	1.57E-04	–	–	7.80E-4	1.68E-04	2.37E-04	5.05E-05
Ni	0.91	6.98E-03	1.49E-03	1.18E-02	2.53E-03	8.62E-03	1.85E-03	2.80E-03	5.99E-04
As	1.50	–	–	–	–	–	–	1.64E-03	3.50E-04

6.3.1.3 Target carcinogenic risk estimation of heavy metals

For the target carcinogenic risk assessment, the cancer risk of Cr was in the range 2.37E-04 to 7.80E-04 for children and 5.05E-05 to 1.68E-04 for adults, whiles Ni ranged 2.80E-03 to 1.18E-02 for children and 5.99E-04 to 2.53E-02 for adults. Also, the results in Table 6.6 showed that As ranged from 1.64E-03 to 3.50E-04 for both children and adults. It is important to note that the estimated range of carcinogens was above the cancer risk provisions set by USEPA, except for the wild fish polluted with Cr for the adults. However, the results also specified that children were more susceptible to carcinogenic risk due to Cr, As and Ni exposure in cage tilapia consumption than adults.

6.3.1.4 Consumption trends of tilapia and the Health Risk Assessment of Patrons of tilapia from the local restaurants

A total of 442 participants responded to the survey, representing a response rate of 99.3%. Non-participation was due to refusal to grant interviews (0.7%). The interview schedule shows that the majority of the people (56%) patronising tilapia from the restaurants were in the age group 13-45 years, 25% in the age group 46-75 years, while 19% in the group ≤12 years. The frequency of consumption showed that women (51.23%) patronize more tilapia fish than men (48.77%).

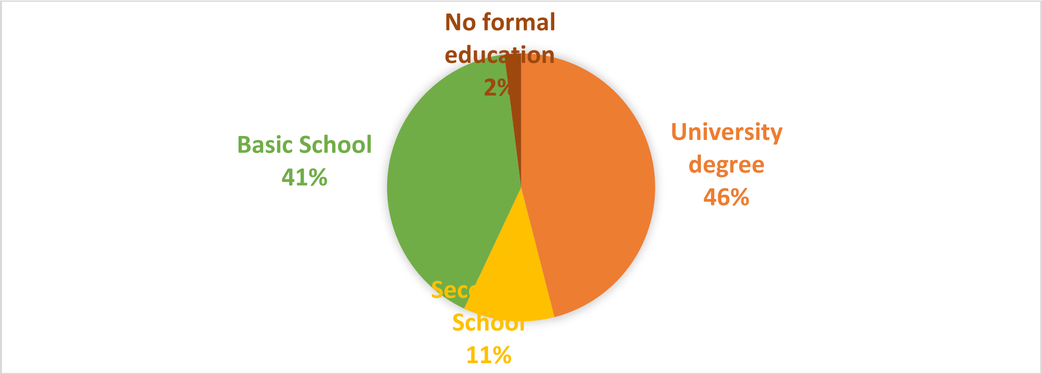


Figure 6.1: Educational level of tilapia consumers among Local folks

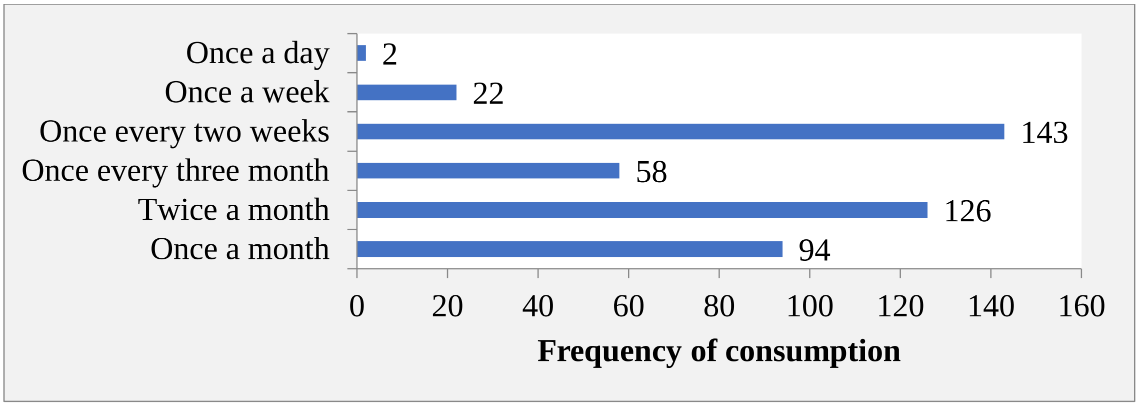


Figure 6.2: Frequency of tilapia consumption by the Patrons of tilapia from the local restaurants

From figure 6.1, forty-six percent of the survey participants had university degrees, 41 % had completed Basic schools, and 2 % had no formal education. In terms of the frequency of consumption of the fish, 143 participants agreed that they consume tilapia once every two weeks, 126 claims twice a month, twenty-two (22) consumed once a week, whiles two participants eat the fish once every day. From the study, tilapia consumers consume an average of 18.6g per meal, and the average daily per capita consumption was 27.4 gd^{-1}. The average body weight of adult consumers (> 12 years) was 68.13 kg, while that of children was 28.50kg.

From the results in appendix V, EDIs of the OCPS and PCBs through the intake of the tilapia for children and adults, were all less than the Rfd values, except ∑PCBs in fish from farm D for children that recorded a higher value of 3.78 µg/kg/day than the Rfd. EDIs for heavy metals in fish from the farms were similarly below the reference doses except in the wild tilapia for the age category. Additionally, the non-cancer hazard quotients of PCBs and As in the fish farm D and the wild tilapia, respectively, for children were higher than the unit value. The hazard index of the metals also obtains a greater value of 1.63 in the controls samples.

For the cancer risk, the results showed that the estimated cancer risk for the pesticides were within limits proposed by USEPA. Along the same line, the cancer risk for Ni and As for both children and adults were higher than 1 x 10^{-4}. The results also showed that the estimated cancer risks for consuming Cr for tilapia from farms (A and D) for children were higher than the required cancer limit (10^{-6} to 10^{-4}).

6.4 Discussion

6.4.1 OCPs and PCBs health risk estimates

The estimated daily intake (EDI) of the pesticides; δ-HCH, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDT, heptachlor, endrin, methoxychlor, *α*-endosulfan, *β*-endosulfan and PCB in children and adults through the intake of the cage tilapia from aquaculture farms on the Volta Basin. The EDIs of the pesticides were substantially lower than the USEPA prescribed reference dose (Rfd) values except for consumption of fish from farm D polluted with PCBs. The implication is that the consumed tilapia from farm D may pose health risks to children and adults regarding PCBs pollution. Examination of Table 6.2 shows that only fish from farm D contain pesticides with hazard quotients indicating health risk association. PCBs had significant non-carcinogenic hazard indices in fish. The index of PCBs indicates potential for non-carcinogenic systemic toxicity in both adults and children. However, this observation was contrary to Afful (2015) for PCBs intake in *Tilapia zilli, Nile tilapia and Tilapia galilaea* from the Lake Weija and Bosomtwi.

Exposure to δ-HCH, PCBs, heptachlor, *p,p*-DDE, and *p,p*-DDT due to consuming caged tilapia in cage farms had no carcinogenic effect because their HQs values were below the significance level. However, carcinogenic HQs for children exposed to endrin contamination due to eating *Oreochromis niloticus* from farms B and D have HQs greater than 1. The toxicological consequence is that more than one in a million affected people is at risk of carcinogenic effects in consuming endrin polluted fish from farms B and D.

6.4.2 HMs carcinogenic and non-carcinogenic risk assessment

Table 6.4 shows the mean daily intake of Cr, Mn, Zn, Ni, and Fe in both children and grown-ups through the consumption of tilapia fish from the various cage aquaculture systems in the Volta Basin. The EDIs of heavy metals in *O. niloticus* from all the fish farms, including the Wild, were remarkably lower than the Rfds established by USEPA

(2012). The estimates for HQ of metals for children and adults based on fish consumption are given in Table 6.5. None of the estimated HQs for Cr, Ni, Zn and Fe in fish from the farms was greater than 1, indicating that no adverse non-carcinogenic health effect is likely to occur for consumption of tilapia contaminated with Cr, Ni, Zn and Fe for children and adult. However, the estimated HQs for Mn and As in the fish from farm A and the wild reported values higher than one. This implies that a potential non-carcinogenic health effect is likely to occur for consumption of tilapia from farm A and the wild tilapia children. This phenomenon was not surprising since the concentrations of Mn found in the muscle tissue of the *O. niloticus* studied exceeded the WHO/USEPA guideline. Mn is a necessary component of human health, and its deficiency leads to skeletal and reproductive problems. However, too much Mn can cause psychological and neurological problems (Ahmed *et al.*, 2016). The cumulative impacts of all metals under consideration for children were higher than the acceptable limit of 1 for hazard indices (HIs) in all the farms' tilapia. However, the HI may overestimate the risk of noncancer health consequences. This is because the toxicological effects of several substances, typically via separate exposure paths, may not be cumulative (Ahmed *et al.*, 2016). Furthermore, due to the competitive absorption of metal ions in target organs of concern, the effect of one metal is thought to be reliant on the action of others.

The cancer risk regulation established by USEPA ranged from 1.0×10^{-6} to 1.0×10^{-4} (USEPA, 2012). The target cancer risk ranged from 5.05E-05 to 1.18E-02, as shown in Table 6.6. The study results showed that the accumulation of Cr, As, and Ni in all fish suggest significant cancer risk through consumption of these fish from cage aquaculture facilities and the wild for the different age category, except the consumption of Cr-contaminated wild tilapia for the adult.

6.4.3 OCPs, PCBs and heavy metals health risk estimates from the survey

The majority of the respondents (56%) who patronized tilapia from the restaurants were within the age group 13-45 years. The analysis revealed that females patronized the tilapia more than males and that many respondents had university degrees. This is so because the graduates understand the nutritional value of tilapia in terms of animal protein supplements. One hundred and forty-three (143) of the respondents claim they consume tilapia once every two weeks, and 126 claimed they consume the fish twice every month.

In this study, consumers of tilapia consume an average of 18.6g per meal, and 143 consumers claim they consume this tilapia once every two weeks and 126 twice a month. Only two consumers claim they eat tilapia once a day. The mean per capita consumption was recorded as 27.4gd$^{-1,}$ whiles the average body weights of adults and children's consumers were recorded as 68.13kg and 28.50kg, respectively.

Examination of analysed data presented in Appendices V-VII reveals that the EDIs of the pesticides were lower than their reference doses. The hazard quotients and the target cancer risks for the pesticides were within the required guidelines. The pesticides, therefore, posed no potential health hazard to human health, particularly to the different age categories within the local folks.

Evaluation of analysed heavy metals data presented in appendix reveals that As levels in various wild tilapia present non-carcinogenic health hazards to children. The HIs for the metals in each case were below one (1), except As in the wild fish that presented HI more significant than 1. The TCR were also within the USEPA guideline. So, no health risk could directly be associated with the consumption of the caged and wild tilapia by the local folks, except wild fish contaminated with As consumed by children. It should, however, be borne in mind that, although the HQs and HIs of the contaminants were below one, there was no zero-risk attached because contaminants were present in fish muscle samples.

6.5 Conclusion

Estimation of health risks associated with pesticides and heavy metals in the fishes indicate that PCBs (in children and adults) and As (in children only) have the potential for non-carcinogenic health risk to the populace. Similarly, estimation of health risks associated with consuming fish from farms B and D contaminated with endrin for children only, and Cr, Ni, and As for both ages could pose a cancer risk to consumers at the national level. No other health risk was associated with the dietary intake of the tilapia concerning the pollutants detected; however, regular monitoring is required to safeguard consumers

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusion

This study investigated the ecological and human health implications of contaminants (Organochlorine pesticides, polychlorinated biphenyls, and heavy metals) linked with cage aquaculture in the Volta Basin of Ghana. The study's general objective was to investigate the presence of POPs and heavy metals residues in the Nile tilapia (Oreochromis niloticus) cultured on the Volta Basin and its potential toxicological risk on humans consumers.

The following conclusions can be drawn from the results of the study:

Eleven (11) OCPs were detected in the water column from the four cage aquaculture farms. Methoxychlor, *o,p'*-DDD, α-endosulfan, methoxychlor and δ-HCH were the predominant pollutants in the studied fish farms A, B, C, D and controls, respectively. The concentrations of nine OCPs from the water samples were below the maximum residue levels except for heptachlor in fish farms A, B, D, and endrin in fish farm C, whose level exceeded WHO MRL for safe drinking water. Further analysis revealed the presence of two indicator PCBs (CB-18 and CB-180), three indicator PCBs (CB-18, CB-52 and CB-180), three indicator PCBs (CB-18, CB-101 and CB-180), four indicator PCBs (CB-18, CB-52, CB-138, and CB-180) and four indicators (CB-18, CB-52, CB-138, and CB-180) in fish farms A, B, C, D and controls respectively. PCB congener CB-101 recorded the highest level of 6.815ng/L in fish farm C. The analyses of the PCB loading of all congeners in the water compartments for each farm revealed the concentration; fish farm C (1.722±0.5252 ng/l) > fish farm D (1.357±0.2588 ng/l) > fish farm B (1.223±0.4186 ng/l) >

fish farm A (0.804±0.1772 ng/l) > control (0.566±0.027 ng/L). The levels of the congeners in the water were below the MRL proposed by WHO/USEPA for safe drinking water. Cr, Pb, Mn, Zn, Fe, and Ni were detected in the water samples for the heavy metals. Apart from Pb and Mn that exceeded the threshold values WHO/USEPA for safe drinking water in the farms except for the controls, all other obtained heavy metals levels were below the MRL. The levels of the metals were below the aquatic life water permissible limit (AWPL) except Mn in the farms, which was above AWPL. Therefore, the water in the cage farms was safe for aquatic life regarding heavy metals pollution.

Generally, eleven (11) OCPs were detected in the sediment, and the level ranged <LOD – 33.0µg/kg. δ-HCH (8.154±0.414 µg/kg), α-endosulfan (6.000±1.414 µg/kg), *o,p'*-DDD (2.010±1.406 µg/kg), endrin (13.867± 8.716 µg/kg) and α-endosulfan (0.503 ± 0.398 µg/kg) recorded the highest average levels in fish farms A, B, C, D and controls respectively. The OCPs; δ-HCH (7.72-8.80 µg/kg), *o,p'*-DDD (0.52-2.12 µg/kg), *α*-endosulfan (<LOD-2.00 µg/kg), *o,p'*-DDD (1.00-28.00 µg/kg) and heptachlor (0.24 – 0.46 µg/kg)were predominant with the frequency of detection 100 %, 45 %, 68 %, 92 % and 25 % in fish farms A, B, C, D and controls respectively. Seven biological PCB indicators were detected in sediment from the farms, and their concentration ranged from 0.042 – 5.320 µg/kg dry weight. CB-18 and CB-180 were the predominant congeners in the entire sediment observed from the farms accounting for a detection frequency of 100 % each. Other OCPs, *p,p'*-DDE, *p,p'*-DDT, ∑DDT, and ∑PCBs, were also a potential threat to the aquatic ecosystem. However, further study is needed to establish their status. Analysis of nine heavy metals revealed the presence of Pb, Zn, Fe, Mn, Cr, and Ni residue in the

sediment samples. Except for Lead (Pb) in fish farms C and D, higher than the proposed WHO/USEPA limit in the sediment, all other metals were remarkably low.

Analysis of fish feed from three fish farms (A, B and D) for OCPs, PCBs and heavy metals residue revealed ten organochlorine pesticides; δ-HCH, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDT, heptachlor, endrin, methoxychlor, *α*-endosulfan and *β*-endosulfan, four PCBs; CB-18, CB-28, CB-101 and CB-180, and five heavy metals; Mn, Ni, Fe, Zn and Cr in the fish fed. Endosulfans and DDT metabolites were the predominant OCPs detected in the fish feed. PCB 18, PCB 28 and PCB 180 were the predominant congeners observed among the PCBs, accounting for 100 % of the fish feed from all the farms. The levels of the detected pesticides and PCBs residues were below the European Union (EU) Maximum Residue Limit (MRL) for fish feed. Among the heavy metals detected in the fish feed, only Mn in the fish feed samples from the various farms significantly exceeded the permissible limit of 7.7 mg/kg. Therefore, it means that the fish feed contamination in terms of OCPs, PCBs, and heavy metals pollution was safe and could be used in the aquaculture industry during the study period.

The concentrations of organochlorine pesticides varied across all the farms: A (ND to 2.310 µg/kg), B (<LOD to 4.260 µg/kg), D (<LOD to 6.109 µg/kg) and controls (ND to 0.878 µg/kg) in fish samples. Comparison of the mean OCP residue ranges in the muscle tissues from the present study with results from other local and international studies shows that this study's levels were lower. The highest mean level of *p,p′*-DDT (2.310 ± 0.438 µg/kg), *o,p′*-DDD (4.260 ±0.994 µg/kg), δ-HCH (6.109 ±4.530 µg/kg) and heptachlor (0.878±0.317µg/kg) were recorded in fish farms A, B, D and controls respectively. Six PCBs congeners; CB-18, CB-28, CB-52, CB-101, CB-153 and CB-180 were detected in the cage tilapia. The concentrations of indicator congeners ranged from 0.288 µg/kg to

0.931 µg/kg dry weight, 0.042 µg/kg to 1.321 µg/kg dry weight, 0.260 µg/kg to 10.657 µg/kg and ND to 0.298 µg/kg, in fish farms A, B, D and controls respectively. The OCPs and PCBs levels in the cage tilapia from the fish farms were below the MRL proposed by the EU.

The studied heavy metal concentrations (Cr, Mn, Fe, Zn, and Ni) differed among the cage tilapia from the studied locations. The farm B contained the highest loadings of the heavy metals compared to fish farms A and D. Fortunately, and this study revealed that the heavy metals concentrations in all the analysed fish from the various sites were generally low and safe for consumption except Mn and Fe, which exceeded the guidelines limit of WHO, WPCL, and USEPA.

The study revealed that the OCPs were from anthropogenic sources such as agricultural activities, industrial and municipal waste. Evaluating the ecotoxicological risk of the OCPs and PCBs in the surface sediment using the SQGs, it was evident that ∑HCH in the sediment from all the farms except the controls pose a health risk to the benthic organisms. Therefore, a comprehensive remedial intervention is required to arrest the situation. The heavy metals originated from both anthropogenic and lithogenic sources. The overall potential risk indices (RI) for the studied metals in sediments were less than 150 ($RI < 150$). These indicate low ecological risk in the fish farms during the period of observation.

Consumption of fish from farms B and D contaminated with endrin for children only and other heavy metals (Cr, Ni, and As) for both ages could pose a cancer risk to consumers at the national level. No other health risk was associated with the dietary intake of the tilapia concerning the pollutants detected; however, regular monitoring is required to safeguard consumers

7.2 Recommendations

The study was conducted in the Volta Basin cage aquaculture farms and the levels and sources of the organochlorine pesticides, PCBs and heavy metals residues established in the water, sediment, fish feed, and the caged tilapia. Therefore, the following recommendations are proffered from the key findings of the study:

1. Ghana Standard Authority, Food and Drug Authority, Environmental Protection Agency and other institutions must collaborate to randomly and periodically monitor and assess the sources, distributional trend and ecotoxicological effects of POPs in samples (Tilapia, fish feed, water and sediment) from the fish farms for the sustainability of the aquaculture industry
2. MoFAD should periodically organize refresher training on aquaculture products safety for fish farmers
3. Local and national environmental agencies should enforce strict policies regarding the use of banned chemicals in both agricultural and the industrial sector
4. Government and private developers along the Volta Basin should establish waste treatment plants to treat industrial and municipal waste effectively.
5. Further Laboratory-based research should be conducted on other contaminants and a detailed potential health risk assessment estimated for national guidelines
6. Systematic awareness campaigns for the safe use of pesticides through social and electronic media should be promoted, as most pollutants come mainly from anthropogenic sources. The government and other agencies should educate farmers on appropriate agricultural pesticide practices.

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APPENDICES

APPENDIX I: Descriptives statistics of organochlorine pesticides levels in sediment from cage Aquaculture farms

						95% Confidence Interval for Mean			
		N	Mean	Std. Deviation	Std. Error	Lower Bound	Upper Bound	Minimum	Maximum
Beta HCH	Farm A	5	2.3360	1.37566	.61521	.6279	4.0441	.40	3.52
	Farm B	2	2.1550	1.47785	1.04500	-11.1230	15.4330	1.11	3.20
	Farm C	3	2.3600	1.61929	.93490	-1.6625	6.3825	.51	3.52
	FArm D	3	1.6133	.82882	.47852	-.4456	3.6722	.76	2.42
	control	0	.	.	.	.	.	.	.
	Total	13	2.1469	1.20903	.33533	1.4163	2.8775	.40	3.52
Delta HCH	Farm A	7	8.1536	.41390	.15644	7.7708	8.5364	7.72	8.80
	Farm B	2	.7100	.41012	.29000	-2.9748	4.3948	.42	1.00
	Farm C	3	1.7933	1.05306	.60798	-.8226	4.4093	1.06	3.00
	FArm D	2	1.3250	.14849	.10500	-.0092	2.6592	1.22	1.43
	control	0	.	.	.	.	.	.	.
	Total	14	4.7518	3.58261	.95749	2.6832	6.8203	.42	8.80
0,P-DDE	Farm A	2	2.1200	2.65872	1.88000	-21.7677	26.0077	.24	4.00
	Farm B	2	.7100	.41012	.29000	-2.9748	4.3948	.42	1.00
	Farm C	6	1.0117	.12465	.05089	.8809	1.1425	.84	1.23
	FArm D	3	1.1633	.14224	.08212	.8100	1.5167	1.00	1.26
	control	1	.0000	.	.	.	.	.00	.00
	Total	14	1.0871	.92015	.24592	.5559	1.6184	.00	4.00

P,P-DDE	Farm A	0	.	.	.	.	.	.	.
	Farm B	2	1.7900	.50912	.36000	-2.7842	6.3642	1.43	2.15
	Farm C	4	.8350	.57928	.28964	-.0868	1.7568	.00	1.34
	FArm D	8	1.3188	2.02019	.71424	-.3702	3.0077	.00	6.00
	control	1	.0000	.	.	.	.	.00	.00
	Total	15	1.1647	1.52590	.39399	.3197	2.0097	.00	6.00
O,P, DDD	Farm A	4	5.0650	1.79560	.89780	2.2078	7.9222	2.82	7.21
	Farm B	2	1.9700	.21213	.15000	.0641	3.8759	1.82	2.12
	Farm C	5	2.0100	1.40552	.62857	.2648	3.7552	1.00	4.00
	FArm D	11	6.2264	7.92969	2.39089	.8991	11.5536	1.00	28.00
	control	1	.0000	.	.	.	.	.00	.00
	Total	23	4.4670	5.81732	1.21300	1.9514	6.9826	.00	28.00
P,P, DDT	Farm A	0	.	.	.	.	.	.	.
	Farm B	0	.	.	.	.	.	.	.
	Farm C	4	1.8025	.98117	.49058	.2412	3.3638	1.00	3.00
	FArm D	1	5.0000	.	.	.	.	5.00	5.00
	control	1	.0000	.	.	.	.	.00	.00
	Total	6	2.0350	1.79091	.73113	.1556	3.9144	.00	5.00
HEPT	Farm A	4	3.9850	1.47983	.73992	1.6303	6.3397	1.85	5.21
	Farm B	2	1.1700	.24042	.17000	-.9901	3.3301	1.00	1.34
	Farm C	0	.	.	.	.	.	.	.
	FArm D	3	1.0800	.50478	.29143	-.1739	2.3339	.62	1.62
	control	0	.	.	.	.	.	.	.
	Total	9	2.3911	1.78320	.59440	1.0204	3.7618	.62	5.21

ENDRIN	Farm A	0	.	.	.	.	.	.	.
	Farm B	2	.2750	.09192	.06500	-.5509	1.1009	.21	.34
	Farm C	3	5.0000	3.60555	2.08167	-3.9567	13.9567	1.00	8.00
	FArm D	10	13.8670	8.71630	2.75634	7.6317	20.1023	5.23	33.00
	control	1	.0210	.	.	.	.	.02	.02
	Total	16	9.6401	9.02208	2.25552	4.8325	14.4476	.02	33.00
METH	Farm A	4	8.2525	5.25195	2.62598	-.1045	16.6095	2.25	13.00
	Farm B	2	1.8600	1.61220	1.14000	-12.6251	16.3451	.72	3.00
	Farm C	0	.	.	.	.	.	.	.
	FArm D	5	.9080	.27142	.12138	.5710	1.2450	.43	1.11
	control	1	.0000	.	.	.	.	.00	.00
	Total	12	3.4392	4.54438	1.31185	.5518	6.3265	.00	13.00
Alpha Endo	Farm A	3	2.7533	1.26176	.72848	-.3810	5.8877	2.00	4.21
	Farm B	2	6.0000	1.41421	1.00000	-6.7062	18.7062	5.00	7.00
	Farm C	6	1.5550	.49201	.20086	1.0387	2.0713	1.00	2.00
	FArm D	4	1.1025	.71369	.35685	-.0331	2.2381	.26	2.00
	control	0	.	.	.	.	.	.	.
	Total	15	2.2667	1.79222	.46275	1.2742	3.2592	.26	7.00
Beta Endo	Farm A	3	1.0367	.70059	.40449	-.7037	2.7770	.47	1.82
	Farm B	2	.9700	.49497	.35000	-3.4772	5.4172	.62	1.32
	Farm C	3	1.1033	.17898	.10333	.6587	1.5479	1.00	1.31
	FArm D	11	1.6145	1.18633	.35769	.8176	2.4115	1.00	5.00
	Control	0	.	.	.	.	.	.	.
	Total	19	1.3747	.96863	.22222	.9079	1.8416	.47	5.00

APPENDIX II :Descriptives statistics of PCBs levels in Water

						95% Confidence Interval for Mean			
		N	Mean	Std. Deviation	Std. Error	Lower Bound	Upper Bound	Minimum	Maximum
PCB 18	Farm A	11	.29620	.000838	.000253	.29564	.29676	.296	.299
	Farm B	10	.30415	.079972	.025289	.41783	.53225	.373	.645
	Farm C	10	.471370	.050528	.015978	.35755	.42984	.323	.488
	Farm D	12	.29691	.000168	.000048	.29580	.29601	.296	.296
	Control	10	.16300	.084260	.026645	.00472	.12528	.000	.172
	Total	53	.30465	.144787	.019888	.26474	.34456	.000	.645
PCB 52	Farm A	0	.	.	.	.	.	.	.
	Farm B	6	.59425	.042132	.014321	.32633	.46281	.173	.847
	Farm C	0	.	.	.	.	.	.	.
	Farm D	5	.52800	1.700859	.760647	1.21611	5.43989	.420	.920
	Control	7	.17264	.186965	.070666	-.01027	.33556	.000	.512
	Total	18	1.48154	1.930730	.557354	.25481	2.70827	.000	5.320
PCB 101	Farm A	0	.	.	.	.	.	.	.
	Farm B		.	.	.	.	.	.	.
	Farm C	5	.81537	.228481	.102180	.05472	.51267	.194	1.477
	Farm D	0	.	.	.	.	.	.	.
	Control	0	.	.	.	.	.	.	.
	Total	5	.26003	.301261	.086967	.06862	.45145	.000	.999
PCB 138	Farm A	0	.	.	.	.	.	.	.
	Farm B	4	.24810	.100563	.050281	.08808	.40812	.129	.375
	Farm C	4	.14095	.051622	.025811	.05881	.22309	.101	.216
	Farm D	0	.	.	.	.	.	.	.
	Control	0	.	.	.	.	.	.	.
	Total	8	.19453	.093576	.033084	.11629	.27276	.101	.375

PCB 180	Farm A	11	.50819	.168160	.050702	.37822	.60416	.297	.793
	Farm B	10	.39120	.099979	.031616	.32968	.47272	.311	.647
	Farm C	10	.43640	.075422	.023851	.30044	.40835	.269	.458
	Farm D	12	.39638	.075766	.021872	.35224	.44852	.277	.493
	Control	10	.15963	.000609	.000193	.29619	.29707	.296	.298
	Total	53	.39113	.116194	.015961	.35910	.42316	.242	.793

APPENDIX III: One-way ANOVA to compare PCBs concentrations in Water

		Sum of Squares	df	Mean Square	F	Sig.
PCB 18	Between Groups	1.033	4	.258	85.330	.000
	Within Groups	.148	49	.003		
	Total	1.181	53			
PCB 52	Between Groups	36.919	1	36.919	41.476	.000
	Within Groups	11.572	13	.890		
	Total	48.490	14			
PCB 101	Between Groups	.008	1	.008	.084	.778
	Within Groups	.990	10	.099		
	Total	.998	11			
PCB 138	Between Groups	.018	1	.018	136.748	.000
	Within Groups	.002	15	.000		
	Total	.020	16			
PCB 180	Between Groups	.837	4	.209	17.105	.000
	Within Groups	.587	48	.012		
	Total	1.424	52			

APPENDIX IV: Multiple Comparisons of PCB's in water

Tukey HSD

Dependent Variable	(I) Sampling site	(J) Sampling site	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
PCB 18	Farm A	Farm B	-.178842*	.024036	.000	-.24691	-.11077
		Farm C	-.097495*	.024036	.002	-.16556	-.02943
		Farm D	.000292	.022963	1.000	-.06474	.06532
		Control	.237109*	.023457	.000	.17068	.30354
	Farm B	Farm A	.178842*	.024036	.000	.11077	.24691
		Farm C	.081347*	.024602	.015	.01168	.15102
		Farm D	.179134*	.023554	.000	.11243	.24584
		control	.415951*	.024036	.000	.34788	.48402
	Farm C	Farm A	.097495*	.024036	.002	.02943	.16556
		Farm B	-.081347*	.024602	.015	-.15102	-.01168
		Farm D	.097787*	.023554	.001	.03108	.16449
		control	.334604*	.024036	.000	.26654	.40267
	Farm D	Farm A	-.000292	.022963	1.000	-.06532	.06474
		Farm B	-.179134*	.023554	.000	-.24584	-.11243
		Farm C	-.097787*	.023554	.001	-.16449	-.03108
		control	.236817*	.022963	.000	.17179	.30185
	Control	Farm A	-.237109*	.023457	.000	-.30354	-.17068
		Farm B	-.415951*	.024036	.000	-.48402	-.34788
		Farm C	-.334604*	.024036	.000	-.40267	-.26654
		Farm D	-.236817*	.022963	.000	-.30185	-.17179

PCB 180	Farm A	Farm B	.089989	.048329	.351	-.04698	.22696
		Farm C	.136792	.048329	.050	-.00018	.27377
		Farm D	.090808	.046171	.298	-.04005	.22166
		control	.378491*	.048329	.000	.24152	.51546
	Farm B	Farm A	-.089989	.048329	.351	-.22696	.04698
		Farm C	.046803	.049466	.877	-.09339	.18700
		Farm D	.000818	.047361	1.000	-.13341	.13505
		control	.288501*	.049466	.000	.14831	.42870
	Farm C	Farm A	-.136792	.048329	.050	-.27377	.00018
		Farm B	-.046803	.049466	.877	-.18700	.09339
		Farm D	-.045985	.047361	.867	-.18021	.08824
		control	.241699*	.049466	.000	.10150	.38189
	Farm D	Farm A	-.090808	.046171	.298	-.22166	.04005
		Farm B	-.000818	.047361	1.000	-.13505	.13341
		Farm C	.045985	.047361	.867	-.08824	.18021
		control	.287683*	.047361	.000	.15346	.42191
	Control	Farm A	-.378491*	.048329	.000	-.51546	-.24152
		Farm B	-.288501*	.049466	.000	-.42870	-.14831
		Farm C	-.241699*	.049466	.000	-.38189	-.10150
		Farm D	-.287683*	.047361	.000	-.42191	-.15346

*. The mean difference is significant at the 0.05 level.

APPENDIX V: Estimated Daily Intake (µg/kg/day) of pesticides in cage fish for Non-carcinogenic risk assessment by Patrons from the local restaurants

		FISH FARM A		**FISH FARM B**		**FISH FARM D**		**CONTROLS**	
Pesticides	Rfd	Children	Adult	Children	Adult	Children	Adult	Children	Adult
***δ*-HCH**	0.30	1.54E-03	3.26E-04	3.80E-03	8.13E-04	1.12E-02	2.39E-03	9.97E-04	2.14E-04
o,p'-DDE	0.50	2.54E-03	5.45E-04	2.28E-03	4.89E-04	5.17E-03	1.11E-03	1.13E-03	2.41E-04
p,p'-DDE	0.50	8.31E-04	1.78E-04	NIL	NIL	4.46E-03	9.55E-04	9.72E-04	2.08E-04
o,p'-DDD	0.50	NIL	NIL	7.78E-03	1.67E-03	NIL	NIL	NIL	NIL
p,p'-DDT	0.50	4.22E-03	9.04E-04	2.23E-03	4.78E-04	2.74E-03	5.87E-04	NIL	NIL
Heptachlor	0.50	3.88E-03	8.32E-04	2.44E-03	5.23E-04	5.28E-03	1.13E-03	1.60E-03	3.44E-04
Endrin	0.30	NIL	NIL	3.96E-03	8.49E-04	5.63E-03	1.21E-03	1.50E-03	3.21E-04
Methoxychlor	5.00	NIL	NIL	5.79E-03	1.24E-03	7.10E-03	1.52E-03	9.97E-04	2.14E-04
α-endosulfan	0.05	4.04E-03	8.65E-04	4.21E-03	9.02E-04	3.40E-03	7.28E-04	1.35E-03	2.89E-04
β-endosulfan	-	3.07E-03	6.59E-04	2.45E-03	5.25E-04	1.49E-03	3.18E-04	9.50E-04	2.04E-04
PCBs	0.02	1.44E-03	3.09E-04	7.23E-03	1.55E-03	3.78E-03	8.09E-03	1.36E-03	2.92E-04

APPENDIX VI: Hazard Quotient of pesticides through the consumption of tilapia by Patrons from the local restaurants for Non-carcinogenic

	FISH FARM A		**FISH FARM B**		**FISH FARM D**		**CONTROL**	
Pesticides	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**
δ-HCH	5.13E-03	1.09E-03	1.27E-02	2.71E-03	3.73E-02	7.97E-03	3.32E-03	2.14E-04
o,p'-DDE	5.08E-03	1.09E-03	4.56E-03	9.78E-04	1.03E-02	2.22E-03	2.26E-03	2.41E-04
p,p'-DDE	1.66E-03	3.56E-04	NIL	NIL	8.92E-03	1.91E-03	1.94E-03	2.08E-04
o,p'-DDD	NIL	NIL	1.56E-02	3.34E-03	NIL	NIL	NIL	NIL
p,p'-DDT	8.44E-03	1.81E-03	4.46E-03	9.56E-04	5.48E-03	1.17E-03	NIL	NIL
Heptachlor	7.76E-03	1.66E-03	4.88E-03	1.05E-03	1.06E-02	2.26E-03	3.20E-03	3.44E-04
Endrin	NIL	NIL	1.32E-02	2.83E-03	1.88E-02	4.03E-03	5.00E-03	3.21E-04
Methoxychlor	NIL	NIL	1.16E-03	2.48E-04	1.42E-03	3.04E-04	1.99E-04	2.14E-04
α-endosulfan	8.08E-02	1.73E-02	8.42E-02	1.80E-02	6.80E-02	1.46E-02	2.70E-02	2.89E-04
PCBs	7.20E-02	1.55E-02	3.62E-01	7.75E-02	1.89E-01	4.05E-01	6.80E-02	2.04E-04

Rfd = Reference dose (µg/kg/day)

APPENDIX VII: Cancer Risk Estimation of pesticides in cage tilapia by the Patrons of tilapia from the local restaurants

		FISH FARM A		FISH FARM B		FISH FARM D		CONTROL	
Pesticides	**CSF(µg/kg/day)**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**
δ-HCH	0.0018	2.77E-06	5.87E-07	6.84E-06	1.46E-06	2.02E-05	4.30E-06	1.79E-06	3.85E-07
p,p'-DDE	0.00034	2.83E-07	6.05E-08	NIL	NIL	1.52E-06	3.25E-07	3.30E-07	7.07E-08
p,p'-DDT	0.00034	1.43E-06	3.07E-07	7.58E-07	1.63E-07	9.32E-07	2.00E-07	NIL	NIL
Heptachlor	0.0045	1.75E-05	3.74E-06	1.10E-05	2.35E-06	2.38E-05	5.09E-06	7.20E-06	1.55E-06
Endrin	0.0170	NIL	NIL	6.73E-05	1.44E-05	9.57E-05	2.06E-05	2.55E-05	5.46E-06
PCBs	0.002	2.88E-06	6.18E-07	1.45E-05	3.10E-06	7.56E-05	1.62E-05	2.72E-06	5.84E-07

CSF = Cancer Slope Factor

APPENDIX VIII: EDI (mg/kg/day) of Heavy Metals in cage fish for Non-carcinogenic risk assessment for the Patrons of tilapia from the local restaurants

	FISH FARM A		**FISH FARM B**		**FISH FARM D**		**CONTROL**	
Metal	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**
Zn	3.79E-03	8.09E-04	3.90E-03	8.33E-04	3.33E-03	7.12E-04	1.78E-03	3.79E-04
Fe	6.81E-02	1.46E-02	9.16E-02	1.96E-02	7.22E-02	1.54E-02	2.03E-02	4.34E-03
Mn	6.23E-03	1.33E-03	3.22E-03	6.88E-04	4.38E-03	9.38E-04	1.41E-03	3.01E-04
Ni	2.96E-03	6.33E-04	5.01E-03	1.07E-03	3.65E-03	7.82E-04	1.19E-03	2.54E-04
Cr	5.66E-04	1.21E-04	NIL	NIL	6.03E-04	1.29E-04	1.83E-04	3.91E-05
As	NIL	NIL	NIL	NIL	NIL	NIL	4.20E-04	8.99E-05

APPENDIX IX: Hazard Quotient of Heavy metals through the consumption of tilapia by Patrons from the local restaurants for Non-carcinogenic

	FISH FARM A		FISH FARM B		FISH FARM D		CONTROL	
METAL	**CHILDREN**	**ADULT**	**CHILDREN**	**ADULT**	**CHILDREN**	**ADULT**	**CHILDREN**	**ADULT**
Zn	1.26E-02	2.70E-03	1.30E-02	2.78E-03	1.11E-02	2.37E-03	5.93E-03	1.26E-03
Fe	1.89E-01	4.06E-02	2.54E-01	5.44E-02	2.01E-01	4.28E-02	5.64E-02	1.21E-02
Mn	4.45E-01	9.50E-02	2.30E-01	4.91E-02	3.13E-01	6.70E-02	1.01E-01	2.15E-02
Ni	1.48E-02	3.17E-03	2.51E-02	5.35E-03	1.83E-02	3.91E-03	5.95E-03	1.27E-03
Cr	1.89E-01	4.03E-02	NIL	NIL	2.01E-01	4.30E-02	6.10E-02	1.30E-02
As	NIL	NIL	NIL	NIL	NI	NIL	1.40	3.00E-01
HI	8.50E-01	1.82E-01	5.22E-01	1.12E-01	7.44E-01	1.59E-01	1.63	3.49E-01

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APPENDIX X: Cancer Risk Estimation of heavy metals in cage tilapia by the Patrons from the local restaurants

	FISH FARM A		FISH FARM B		FISH FARM D		CONTROL	
METAL	**CHILDREN**	**ADULT**	**CHILDREN**	**ADULT**	**CHILDREN**	**ADULT**	**CHILDREN**	**ADULT**
Ni	2.69E-03	5.76E-04	4.56E-03	9.74E-04	3.32E-03	7.12E-04	1.08E-03	2.31E-04
Cr	2.83E-04	6.05E-05	NIL	NIL	3.02E-04	6.45E-05	9.15E-05	1.96E-05
As	NIL	NIL	NIL	NIL	NIL	NIL	6.3E-04	1.35E-04