KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI

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PERSISTENT ORGANOCHLORINE POLLUTANTS IN LAKE BOSOMTWI AND WEIJA LAKE AND THEIR POTENTIAL TOXICOLOGICAL HEALTH IMPLICATIONS.

A THESIS PRESENTED TO THE DEPARTMENT OF CHEMISTRY, COLLEGE OF SCIENCE, IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF DOCTOR OF PHILOSOPHY DEGREE IN ENVIRONMENTAL CHEMISTRY.

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CERTIFICATION

I do hereby certify that this thesis was written by me, from the records of my research work, except portions which have been duly cited in the bibliography. The work has neither in part nor in whole been published by another person nor presented for any degree in this university or elsewhere.

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ABSTRACT

This research work focused on the assessment of organochlorine pollutants in two water bodies and their health implications on aquatic species and humans. The research involved conducting systematic assessment of occurrence and burden of indicator polychlorinated biphenyls and organochlorine pesticides in water, sediment and fish samples.The main objective focused on the determination of persistent organochlorine pollutants as well as their bioaccumulation in fish species and their toxicological risk assessment on human population via drinking of water and dietary intake of fishes from the two water bodies. Lake Bosomtwi and Weija Lake were the study areas and investigations started from January 2012 to June 2014. Instrumental Neutron Activation Analysis (INAA) was used for determination of extractable organochlorines (EOCs) and bound organochlorines (BOCs). The EOCs were further characterized with Capillary Gas Chromatography equipped with Electron Capture Detector (GC - ECD). Hexane was used as extraction solvent for the extraction of OC pollutants from the water samples whiles, the sediment and fish samples were sonicated on ultrasonic bath using hexane/acetone (3:1) solvent system. The extracts were then cleaned up on a combined florisil-silica adsorbent packed in glass column. Ecotoxicological impact of sediments on aquatic species was assessed using two sediment quality guidelines. The impacts of OC pollution on humans was assessed by estimating daily exposure and cancer and non cancer hazard ratios on consumption of the studied fishes. ANOVA was applied to determine the differences in the mean concentration. The average levels of extractable organochlorine were 0.71 mg/L and 0.39 mg/L for the water samples from the Weija and Bosomtwi respectively. The sediment compartments had average extractable organochlorine content of 3.57 mg/kg from the Weija while that from Bosomtwi was 3.28 mg/kg. The average BOC content in the sediments were respectively, 0.48 mg/kg and 0.46 mg/kg for Weija and Bosomtwi samples. In the fish compartments, EOC composition varied from 6.89 mg/kg to 9.02 mg/kg

for Weija species while those from Bosomtwi were from 3.99 mg/kg to 4.63 mg/kg. The concentrations range for the detected organochlorine pesticides (OCPs) were <0.01 µg/l to 4.30 µg/l, <0.01 µg/kg to 15.23 µg/kg, <0.01 µg/kg to 23.70 µg/kg for the water, sediment and fish samples respectively, while those for the PCBs were <0.01

µg/l to 4.72 µg/l for Lake water, <0.01 µg/kg to 7.55 µg/kg for sediments and <0.01 µg/kg to 32.40 µg/kg for the fish species. Statistically significant differences in the mean concentrations of the OCs were detected. The ecotoxicological impacts of measured organochlorine pollutants in the sediments to aquatic species showed that toxicity of ΣPCB, p,p'-DDT, P,P'-DDE and ΣDDT to aquatic species was below ERL Estimated daily intake (EDI) of organochlorine as a result of consumption of the studied fishes for children ranged from 0.002 µg/kg to 0.176 µg/kg and those for adults were from 0.0011 µg/kg to 0.0892 µg/kg. EDIs were however, far below reference doses (RFDs) recommended by United State Environmental Protection Agency (USEPA). Risk assessment in terms of carcinogenic and non-carcinogenic effects on humans on consumption of the fishes revealed that eating of *Tilapia zilli*, *Tilapia nile* and *Tilapia galilaea* from the Weija Lake present no risk of carcinogenic effect. However, more than one in a million of the consuming population on eating *Clarias gariepinus* can get cancer as a result of HCHs contamination. Consumption of fishes from the Lake Bosomtwi was found to present no carcinogenic effect. In general, the overall findings showed that levels of pollutants detected in the two water bodies posed minimum to no risk to communities that depend on the Lakes for livelihood.

TABLE OF CONTENTS

CHAPTER THREE

CHAPTER FOUR

LIST OF TABLES

CHAPTER TWO

CHAPTER FOUR

LIST OF FIGURES

CHAPTER TWO

CHAPTER THREE

CHAPTER FOUR

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TO GOD BE THE GLORY. This work is dedicated to my wife Victoria Afful and my children Josephine, Loretta, Lois and Samuel.

LIST OF ABBREVIATIONS

GHARR-1	Ghana Research Reactor One
AOAC	Association of Analytical Chemist
BC	Black carbon
BCF	Bio-concentration factor
CE	Capillary electrophoresis
CCME	Canadian Council of Ministry for Environment
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethene
DDT	Dichlorodiphenyltrichloroethane
DMDDE	Dimethoxydiphenyldichloroethane
DFs	Dibenzofurans
EDI	Estimated daily intake
EPA	Environmental Protection Agency
ERL	Effect range low
ERM	Effect range median

FAO	Food and Agricultural Organization
HCB	Hexachlorobenzene
HCHs	Hexachlorohexanes
HPTE	Hydroxyphenyl-trichloroethane
HPLC	High performance liquid chromatography
IARC	International agency for research on cancer
INAA	Instrumental neutron activation analysis
IUPAC	International union of pure and applied chemistry
LC	Liquid chromatography
LLE	Liquid-liquid extraction
LOD	Limit of detection
MAE	Microwave-assisted extraction
MRL	Maximum residue limit
NOAEL	No observable adverse effect levels
OC	Organochlorine
OCPs	Organochlorine pesticides
PCDDs	Polychlorinated dibenzo-*para*-dioxins
PCDF	Polychlorinated dibenzofuran
PCDFs	Polychlorinated dibenzofurans
POPs	Persistent organic pollutants
SBSE	Stir bar sorptive extraction
SDME	Single drop micro extraction
SFE	Supercritical fluid extraction

SLM	Supported liquid membrane
SPE	Solid phase extraction
SPME	Solid-phase microextraction
TCDD	Tetrachlorodibenzo-P-dioxin
TCDF	Tetrachlorodibenzofuran
TEQ	Toxicity equivalent
UHPLC	Ultra-high pressure liquid chromatography
USEPA	United States Environmental Protection Agency
UNEP	United Nation Environmental Program

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

Water pollution has negatively affected water supply in the world particularly in the developing countries. Unfortunately the outlook of the world's fresh water supply today is not very promising. Studies conducted by United Nations and International Joint Commission had revealed that many parts of the world would experience shortages of potable water in not too distance future (Enger and Smith, 1992). Fresh water supply is continuously being replenished by rainfall. However, the quality of rainfall depends largely on the environment, which is constantly being polluted through anthropogenic activities. Indeed, there have been great concerns over the degrading state of the world's fresh water resources as man continues to face explosive growth in the number of substances affecting the world water quality. The quest of the world's effort for economic advancement through industrialization and urbanization, with the objective of making life comfortable as well as poor environmental planning has negatively affected the purity of our waters. Therefore, studying and analyzing water ecosystem compartments have become a primary concern for the health of human beings. Information on water quality has become very important for policy makers, health and water resources managers.

Africa, in the past, was considered to be safe from water body pollution (Akpabli and Drah, 2001). However, the situation in contemporary times is different. The high population growth and its accompanied urbanization, increasing industrial activities, coupled with poor waste management practices have resulted in remarkable increase in the amount of potential pollutants that are

discharged into aquatic environments. In Africa today there is increasing deplorable worsening state and the death of water bodies. The Lagos lagoon in Nigeria (Okoye et al., 1991) and the Ebrie Lagoon in Cote d'Ivoire (Kouadio and Trefry, 1997) are typical examples of water bodies which have been polluted and are dying as a result of anthropogenic activities. In Ghana, the situation is not different; the Chemu and Korle Lagoons and the Odaw River are all in deplorable states (Akpabli and Drah, 2001). Many water bodies are dying as a result of the volume of domestic and industrial wastes reaching them. On 26th October, 2011, it was reported on the front page of Ghana's Daily Graphic that an unknown timber company had discharged toxic chemicals said to be used in the treatment of wood into the Butuah Lagoon, near New

Takoradi. This resulted in the death of over 40,000 fishes in the Lagoon and residents of New Takoradi who consumed the dead fish suffered from running stomach and dehydration and had to be rushed to nearby hospital for attention (Ghanaian Daily Graphic, 2011).

The effect of anthropogenic activities within the catchment of the Weija Lake and Lake Bosomtwi as well as other water bodies, for example, have culminated in poor quality of the water from these water bodies. This, as a result, has led to a ban on farming activities within the catchment of the Weija Lake by the Government of Ghana (Tay and Kortatsi, 2007). As a result of the growing public concern about the state of our water bodies some Governments in Africa including Ghana, signed a memorandum of understanding in 1999 with the United Nations

Centre of Human Settlements-Habitat to collaborate in a project on "Managing Water for African Cities". The primary aim of the project was to find solutions to the increasing water demand in fast growing African cities. All these confirm the fact that Africa has not been spared from water resource pollution.

Water body pollution may result from a variety of sources. Common sources of water body pollution include oil spillage, wastes dumped into water bodies, run off from agricultural and

industrial sites. There are also releases from manufacturing plants that produce toxic chemicals, some of which eventually are deposited into water bodies. Oil spillage harms living organisms in water bodies. Wastes including plastic bags, fishing nets and other trash items dumped can accumulate in an area within water bodies causing living organisms to be entangled and die.

Run-off from agricultural sites may introduce pesticides residues or fertilizers into water sources. Pesticides contamination can lead to fish kill, while fertilizer pollution leads to algal blooms that choke out naturally occurring plants. These eventually reduce the diversity of organisms in the water body (Kusimi, 2008).

In recent times persistent organic pollutants (POPs), of which organochlorines compounds are the dorminant, have generated international concern (Ritter, 2007). Persistent organohlorine pollutants are organic compounds that to a varying degree resist photolytic, biological and chemical degradation (Ritter et al., 2008). They are chlorinated compounds with carbon-chlorine bonds which are difficult to break. Exposure to persistent organochlorine compounds such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) has been linked to a wide range of conditions including reproductive toxicity, immunotoxicity, hepatoxicty, neurotoxicity, necrosis and endocrine abnormalities (Buah-Kwofie et al., 2010). They are semi-volatile, and this enables them to move long distances in the atmosphere before deposition (Ritter at al., 2008). The high lipid solubility and stability of organochlorine compounds have resulted in their widespread distribution in nearly all environmental compartments. They are therefore found in air, soil, water bodies, vegetation and rainfall. Although many different forms of organochlorine compounds may exist, those which are noted for their persistence and bio-accumulative nature include PCBs, organochlorine insecticides, toxaphenes and dioxins (Baird, 2007).

Persistent organochlorine compounds such as DDTs, HCHs, HCB, endosulfan and PCBs had been used in Ghana in the past but they are officially banned now. PCBs for example, had been used as dielectric fluid in transformers and capacitors by the Electricity Company of Ghana and the Volta River Authority while DDTs, HCHs, HCB, endosulfan and related agrochemicals had also been applied as pesticides in homes and agricultural fields. Other organochlorines are used in industrial processes and in the production of many goods (Ritter et al., 2008). Many congeners of PCBs are formed and released to the environment during various anthropogenic processes such as incineration, combustion, smelting and metal reclamation (Falandysz, 1998; Bullschmiter, 1987). Water body contamination with persistent organochlorine pollutants may be related to point sources or, more frequently, to diffuse sources (atmospheric transport and deposition). Indeed, although there are other pathways, atmospheric transport and deposition is the major pathway for the transfer of persistent organic pollutants to near and remote water bodies (Grimalt et al., 2004).

There is currently an international effort under the Stockholm Convention aimed at "total elimination" of persistent organochlorine compounds (Buah-Kwofie et al., 2010). Ghana being a signatory to the convention, therefore, has to develop a strategy of identifying and eliminating persistent organochlorine compounds from the environment. In the effort to "total elimination" of these pollutants from the environment, Ghana has banned the use of these chemicals in Ghana. There is, therefore, the need to assess the burden of persistent organochlorine pollutants in our environment in order to help establish a better picture of how the Ghanaian environment has been affected by these organic pollutants.

Water bodies such as the Weija Lake and Lake Bosomtwi are important natural resources of Ghana and therefore assessment of their persistent organochlorine pollution burden should be of prime importance in realizing the goals of the Stockholm Convention in Ghana.

1.2 Statement of problem

Persistent organic pollutants (POPs) of which majority are organochlorine compounds are known to be associated with a number of health related problems which include cancer (Giwercan et al., 1992; Davis et al., 1993; Barron et al., 1994; Hoyer et al., 1998; Moysich et al., 1998; Laden et al., 2001; Aronson et al., 2000; Cocco, 2002; Charlier et al., 2003; US EPA, 2008), neurological disorder (National Academies Press, 1999; US EPA, 2008), adverse effects on the immune system (US EPA, 2008), reproductive failures (Oliva et al., 2001; Andric et al., 2005; US EPA, 2008) and endocrine system disruptors (US EPA, 2008). As a result of significant concerns over their use due to their toxicity and their potential to induce toxicological impacts on both humans and wildlife (Jones et al., 1999), there is an intervention under the Stockholm Convention aimed at their elimination. The United Nation Environmental Programme (UNEP) has identified twelve (12) organochlorine compounds known as the "dirty dozen". These include nine organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), dioxins and furans. The nine OCPs are: aldrin, dieldrin, endrin, dichlorodiphenyltrichloroethane (DDT), chlordane, heptachlor, hexachlorobenzene (HCB), toxaphene and mirex. Hexachlorocyclohexanes (HCHs) were not included in the list, but due to their environmental concern and wide use as pesticides, HCHs are generally defined together as POPs by UNEP. An international ban on the use of lindane (γHCH), α-HCH, β-HCH was implemented in 2000 (UNEP, 2009). All state parties have pledged to ban the production, importation and the use of POPs on the red list. Ghana is a state party to the convention and it is therefore obligatory on Ghana to ensure their "total elimination".

In Ghana, and other neighbouring countries, body of evidence unfortunately, lends credence to the presence of organochlorine compounds in the environment (Darko et al., 2008, Ntow, 2007,

Fianko, 2010; Kuranchie-Mensah et al., 2012; Roche et al., 2007; Pazou et al., 2006). Several suggestions have been stipulated as to the origins of these pollutants but it is widely believed that they originated from agricultural, industrial and related use of organochlorine products. In Ghana the presence of persistent OCs has been attributed to historical use of OCs products and their presences have been reported in all environmental compartments including water bodies. Indeed, persistent organochlorines have been detected in water bodies such as Lake Bosomtwi, Volta and Weija Lakes (Darko et al., 2008, Ntow 2007, Kuranchie-Mensah et al., 2012).

1.3 Justification and relevance of the study.

The Weija Lake and Lake Bosomtwi are important water sources in Ghana. The two water bodies have played and will continue to play critical roles in the development of Ghana, particularly, for the many towns dotted around them. The Weija Dam on the Densu basin was built primarily for the supply of potable water to residents in the western parts of Accra in the Greater Accra Region. (Karikari et al., 2006). The Weija Dam is the restricted reservoir of the water body where the water is pumped and treated by the Ghana Water Company Limited. The damming has encouraged the fishing industry and boat transport on the Lake. Thus, the main economic activities in the catchment of the Lake are fishing and crop farming. In particular, vegetable farming at the catchment area of the Lake has been on the increase as farmers use water from the Lake to irrigate their fields. Other crops such as sugarcane, maize and cassava are cultivated along the banks of the Lake. Similarly, Lake Bosomtwi is the main source of livelihood for communities living around it. Each of the twenty four surrounding villages contributes about 50 fishermen to Bosomtwi fishery potential of 960 to 1200 fishermen (Dontwi et al., 2004). Besides fishing, the inhabitants depend on the water from the Lake for cooking and washing as well as for irrigation

activities. It is one of the major important tourist sites in Ghana. Other important activities around the Lakes include animal rearing. Thus, the economic importance of the two water bodies cannot be over-emphasized.

Environmental problems that may arise from the activities such as agrochemicals applications and other anthropogenic activities within the catchments of the two water bodies include pollution of water, sedimentation and population explosion of biota of the Lakes. There is no doubt that the water quality of the Lakes has been affected as a result of anthropogenic activities around the water bodies. So far, studies on water quality of the two Lakes, particularly, that of the Weija Lake had focused mainly on its physico-chemistry, nutrient burden, trace metals and pesticide residues contamination (Ameka et al., 2000; Debrah, 1999; Darko et al., 2008, Ntow, 2007; Fianko, 2010; Kuranchie-Mensah et al., 2012). Most studies on organochlorine pollution had focused mainly on organochlorine pesticides (Darko et al., 2008; Kuranchie-Mensah et al., 2012). Darko et al (2008) investigated organochlorine pollution in Lake Bosomtwi but focused on levels and occurrence of few OCPs while Kuranchie-Mensah et al (2012) also studied levels and effects of OCP residues in water and sediments from Weija Lake but sampled from only two points at Weija water works. Thus, previous studies on OC pollution in the two water bodies were limited in scope. There is, therefore, no data or very little information on the other typical organochlorine pollutants such as PCBs. In order to broaden the knowledge on organochlorine (OC) pollution, there is the need to assess bound organochlorines (non-extractable organochlorine) which always remained bound to some environmental matrices in addition to extractable organochlorine. Obviously, the formation of BOC reduces the amount of the OCs available for environmental re-cycling and potentially transfers into food chains. It ought to be stressed that there is little knowledge on bound OC composition of the two water bodies.

According to Chin-Chang et al (2006), significant organochlorine residues still exist in sediments. However, the distribution of organochlorine compounds in aquatic environments is still poorly understood. Organochlorines are organic compounds and are likely to interact with carbonaceous materials in sediments. Previous studies have shown that persistent organochlorine pollutants are strongly bound to organic matter (Jonker and Koelmans, 2002). The relationship between sediment carbonaceous materials and organochlorine residues in the environment is not well documented or understood. This, therefore, calls for the determination of the relationship, if any, between sediment carbonaceous materials and organochlorine availability.

It should further be stated that studies on organochlorine pollution in Ghana have focused mainly on measurement of levels. Risks assessments of OCs on humans have been limited to mainly comparing measured levels to maximum residue limits (MRLs). Thus, detailed human health implications as a result of exposure to organochlorine pollution have not been well documented despite their adverse health effects. Estimation of daily exposure of OCs to humans on consumption of contaminated food has not been well studied in Ghana. There is, therefore, the need to assess human health risks such as carcinogenic and non carcinogenic effects associated with drinking of water and dietary intake of fishes from the Lakes in terms of OC pollution.

Again, organochlorine pollution in water body sediment above certain threshold limits can pose threat to aquatic organisms including fishes. It is known that OC concentration in sediments above what is referred to as Effect Range Low (ERL) could pose danger to sensitive aquatic species (Wurl, 2006). Therefore, ecotoxicology impacts of sediments on aquatic species as a result of organochlorine pollutants in the sediment compartment as a matter of importance need to be investigated.

Analytical methods for the determination of OCs have well been established and documented. Determination of extractable organohalogen by instrumental neutron actvation analysis has been

reported (Kwablah Anim et al., 2010; Gustavson and Johnson, 1999). Characterization and quantification of extractable organochlorine using GC-ECD has witnessed numerous applications (Afful et al., 2010; Booij et al., 1998; Balinova and Balinov, 1991). However, to ensure the reproducibility, reliability and accuracy of results obtained from the study there is the need to validate the analytical methods being used for the investigation.

It is hoped that the present investigation will provide a clear picture of the nature and extent to which the two water bodies have been polluted by organochlorine pollutants. Analysis of the results would also provide information as to whether there has been fresh input of these chemicals after the EPA ban imposition. The study will also be helpful in mapping up strategy that ought to be formulated in protecting our water bodies against persistent organic pollution.

The Weija Lake and Lake Bosomtwi are being investigated as Weija is man-made and Bosomtwi is natural. The Weija Lake is part of the Densu basin that receives water from rivers running through areas of diverse land use while Bosomtwi is fed by groundwater which drains into it and rivers namely Aberewa and Konkoma as well as rainfall. (Dontwi et al., 2004).

1.4 Objective

1.4.1 Main objective

This research focuses on determination of Persistent Organochlorine Pollutants as well as their bioaccumulation in fish species and their toxicological risk assessment on human population via drinking of water and dietary intake of fishes from the two water bodies.

1.4.2 Specific objectives

The specific objectives of the research are

a. To validate analytical methods for the determination of organochlorine pollutants.

b. To determine extractable organochlorines in water, sediment and fish samples as well as bound organochlorine (non-extractable) in the sediment compartment.

c. To assess the extent of organochlorine pollution in the two water bodies. More specifically to

   i. Identify and quantify key organochlorine pesticides and indicator polychlorinated biphenyls.

   ii. Determine the potential sources of the identified organochlorines.

   iii. Establish whether there are statistical variations in the mean organochlorine concentrations.

   iv. To determine the bio-concentration factor (BCF) of the organochlorine pollutants.

d. To investigate the relationship between sediment carbonaceous materials and organochlorine availability with the view of

   i. Determining the correlation between organochlorine level and sediment total organic carbon. ii. Determining the correlation between organochlorine level and sediment total black carbon.

e. Assessing impacts of sediments on aquatic species using sediment quality guidelines with the view of deducing ecotoxicological effects to aquatic species due to OC pollution in the sediment compartment.

f. To determine the potential human's health risks associated with drinking of water and dietary intake of fish in terms of organochlorine pollution through

   i. Estimating daily intake of organochlorine as a result of dietary consumption of the studied fishes. ii. Estimating carcinogenic and non-carcinogenic effects on dietary intake of fishes from the Lakes.

1.5 Scope of study

The research involved conducting systematic assessment of occurrence and burden of indicator PCBs and OCPs in water, sediment and fish samples from different sampling points along the Lake Bosomtwi and Weija Lake. Extractable organochlorines in the water, sediment and fish

compartments as well as bound organochlorine of the sediment were measured. The extractable organochlorines were further characterized to ascertain the profile of organochlorine pollutants. Typical individual extractable organochlorine pollutants such as indicator PCBs and organochlorine pesticides that is, DDTs, HCHs, endosulfans, drins, heptachlor as well as their metabolites were studied. The bio-concentration factors (BCFs) which represent the equilibrium ratio of the concentration of a specific chemical pollutant in fish sample to its concentration in its immediate environment (water) were considered and computed. Data on organochlorine measured were further subjected to descriptive statistics and analysis of variance (ANOVA). Carcinogenic and non carcinogenic implications associated with dietary intake of fish from the water bodies were evaluated by using the estimated daily intake (EDI) and hazard ratios of the identified organochlorine pollutants in the fish species. Sampling was done in 2012 from January to February and September to October for the purpose of duplicating measurements. Sample preparation involving sample extraction, clean up and extract concentration were performed at the Nuclear Chemistry and Environmental Research Centre (NCERC) of Ghana Atomic Energy Commission. The Instrumental Neutron Activation analysis (INAA) at the Ghana Research Rector - 1 facility (GHARR-1) was used for measurement of extractable and bound organochlorine. The Varian Gas Chromatograph at Ghana Standard Authority and Shimadzu Gas Chromatograph at NCERC of GAEC were used for characterization and quantification of individual organochlorines in the extractable. Determination of organic carbon and black carbon were done at the Ecological Laboratory of University of Ghana.

1.6 Structure of the thesis

The thesis was organized into five (5) chapters as follows:

Chapter One deals with the introduction which comprises the background, statement of problem and project justification and relevance of the work. The objectives and scope of the study are also captured under Chapter One.

Chapter Two contains a literature review on persistent organochlorine compounds, their characteristics and mode of transfers into the environment and impacts on human health and environment. The scope of work previously, done on organochlorines has been reviewed together with instrumental methods for determination of organochlorines.

Chapter Three focuses on experimental methods. It describes the study areas, emphasizing on the topography and prevailing climatic conditions. Activities in the study areas are also discussed.

Sampling and analytical methods used for the study are presented. Notably analytical methods used involved sample extraction and clean-up methods, instrumental neutron activation analysis and gas chromatographic determinations.

In Chapter Four, results, observations and detailed discussion of results are presented. It entails discussion of data generated on organochlorine concentrations in the two water bodies. Data on statistical analysis of organochlorine concentrations are captured under this chapter. Data of impacts of organochlorine pollution on aquatic species as well as on humans as a result of drinking of water and eating of fishes from the water bodies are also presented and discussed.

Chapter Five deals with conclusions of the study and suggested recommendations for further studies.

Finally, there are six (6) Appendices of which Appendix six captures papers so far published from the study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Organochlorine compounds

Carbon forms many compounds with chlorine, some of these compounds are found in nature, though usually in very small amounts. Most of these carbon-chlorine compounds are however produced synthetically by the action of elemental chlorine on hydrocarbon obtained from petroleum. Carbon-chlorine bonds are typicall associated with persistent organochlorines (Afful et al., 2010). These synthetic organochlorines are mainly pesticides, toxaphenes, PCBs, and dioxins (Baird, 1997). The carbon-chlorine bonds are characteristically difficult to break, and the presence of chlorine atoms also lessens the reactivity of the other bonds in organic molecules. This lack of reactivity is a distinct advantage in many applications. However, this same property means that once organochlorines enter the environment, they are slow to degradation and instead tend to accumulate. Furthermore, most organochlorine compounds are hydrophobic. They therefore, do not readily dissolve in water but they are readily soluble in hydrocarbon – like media such as oils or fatty tissue. The lack of efficient sink for organochlorine compounds in addition to their hydrophobicity, has led to their accumulation in living organisms, including fish, humans and other animals. Indeed, the entire planet, including all living things are said to have undergone some level of contamination by these chemicals (Gribble, 1994). Organochlorines have been implicated in a broad range of adverse human effects including reproductive failures and birth defects, immune malfunction, endocrine disruption and cancer (Kwablah-Anim et al., 2010). Organochlorine compounds have long been recognized as potential threats to human health and, therefore, these compounds have been widely investigated in foods, vegetation and the atmosphere (Kwablah-Anim et al., 2010). In the past decades, much effort by Government agencies and environmental groups have involved in documentation of this contamination and the regulation of organochlorine use to prevent concentrations from reaching dangerous levels, particularly in the food supply chain

2.1.1 Organochlorine pesticides (OCPs)

The OCPs are synthetic organic insecticides which comprise predominantly of carbon, hydrogen, chlorine and sometimes oxygen as elements. The carbon-chlorine bonds constitute the essential structural feature. Some are produced naturally by certain species of plants. There are three main types of organochlorine insecticides (Agbeve, 2011). These are

1. Dichlorodiphenylethanes such as DDT, DDE, DDD or TDE, methoxychlor, methlochlor, 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. Many of these chemicals exist as isomers and some of them also have metabolites. Some of the isomers have insecticidal properties while others do not. For instance, there are five main isomers of technical mixture of HCH thus, alpha HCH, beta HCH, gamma HCH, delta HCH and epsilon HCH. However, it is only the gamma HCH that has insecticidal value.

Gamma HCH had been used as pesticide with a generic name gammalin 20 (lindane).

Many of the pesticides produced in the 1940s and 1950s by the chemical industries in North America and Western Europe were organochlorine pesticides (Ware, 1983). Most of these chemicals share notable properties such as stability against decomposition or degradation. They are low soluble in water, unless oxygen or nitrogen is present in the molecule. Again they are highly soluble in hydrocarbon-like environments, such as the fatty material of living matter and relatively high toxicity compared humans. Because of the persistence of organochlorine pesticides they have been phased out and have been replaced with less environmental persistence organophosphorus and carbamates pesticides.

2.1.1.1 Dichlorodiphenylethanes

These organochlorine pesticides have the dichlorodiphenyethane as a common unit structure for all the members in the family. The most popular and most extensively used dichlorodiphenylethane is the dichlorodiphenyltrichloroethane (DDT) whose structure is shown in Figure 2.1.

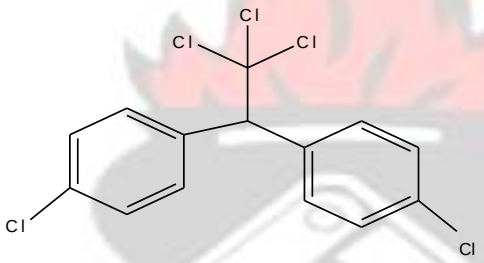
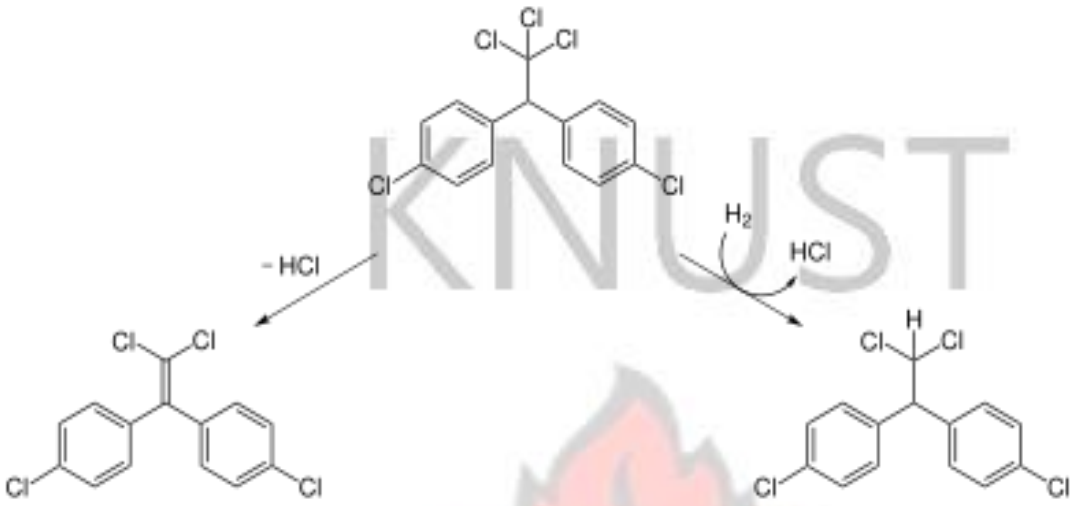


Figure 2.1: Dichlorodiphenytrichloroethane

Indeed, DDT has had a tumultuous history. It was discovered in 1939 by a Swiss scientist, Paul Muller as a very effective synthetic organic insecticide although it was first synthesized in 1874 by Othmar Zeidler (WHO, 1979). It quickly became the most widely used pesticide in the world and was hailed as "miraculous" by Sir Winston Churchill in 1945 because of its use in the war effort and being effective against body lice that transmit typhus, against plague-carrying fleas and mosquitoes that carry malaria and yellow fever (Dunlap and Thomas, 1981). WHO estimated that in malaria reduction programs, the use of DDT as a component in the applied chemical saved the lives of more than five million people (Baird, 1997; Gladwell and Malcolm, 2001). DDT was widely overused, particularly in agriculture, which consumed 80 % of its production. As a result, its environmental concentration rose rapidly and began to affect the reproductive abilities of birds which indirectly incorporated it into their bodies. By 1962, DDT was being called an "elixir of

death" by Rachel Carson in her influential book "silent spring" because of its role in decreasing the populations of the bald eagle, whose intake of the chemical was very high.

A number of molecules with the same general structure as DDT display similar insecticidal properties. The similarity arises from the mechanism of DDT action, which is due more to its molecular shape than from chemical interactions with specific species. The shape of a DDT molecule is determined by the fact that it contains two tetrahedral carbons in the ethane unit, and two benzene rings. Apparently in insects, DDT and other molecules with the same general size and 3-dimensional shape become wedged in the nerve channel that leads out from the cell of the nerve. Normally, this channel transmits impulses only as needed via sodium ions. But a continuous series of sodium ion initiated nerve impulses is produced when DDT molecule holds the channel open. The consequence is that the muscle of the insect twitch constantly, exhausting it with convulsions that lead to death. The same process does not occur in humans and other warm-blooded animals since DDT molecules do not exhibit any such binding action in nerve channels. DDD, dichlorodiphenyldichloroethane is an example of another molecule of DDT-like action. DDD is an environmental degradation product of DDT. They differ in that one chlorine atom from the $-CCl_3$ group in DDT is replaced by a hydrogen atom. Since the shapes and sizes of DDT and DDD are similar, their toxicity to insect is similar. Indeed, DDD has been used as an insecticide but its use has also been discontinued because of its bioaccumulation effect. Another environmental degradation product of DDT is dichlorodipheyldichloroethene (DDE). Unlike the DDT and DDD, DDE has a planar C=C unit rather than a C-C linkage with tetrahedral group at each end. Thus whereas DDD is DDT-like insecticide, DDE is not. Thus the 3-dimensional shape is very different. DDE is flat rather than propeller-shaped, and so it does not become wedged in the insect nerve channel. Environmental degradation pathway of DDT to DDD and DDE is as shown in Figure 2.2.



DDE DDD

Figure 2.2 Degradation pathway of DDT to form DDE and DDD

Analogs of DDT that have the same general size and shape and consequently possess the same insecticidal properties but are reasonably biodegradable and thus do not present the bioaccumulation problem associated with DDT has been developed. The best known of these analogs is methoxychlor, whose structure is shown in Figure 2.3

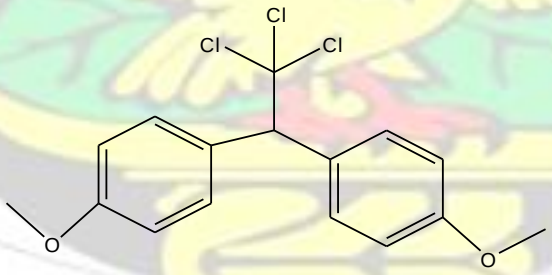


Figure 2.3: Molecular structure of Methoxychlor

Methoxychlor is used to protect crops, ornamentals, livestock, and pets against fleas, mosquitoes, cockroaches, and other insects. The major environmental degradation pathways of the chemical involve dechlorination and demethylation. Anaerobic biodegradation of methoxychlor results mainly in dimethoxydiphenyldichloroethane (DMDDE) as well as mono and dihydroxy or

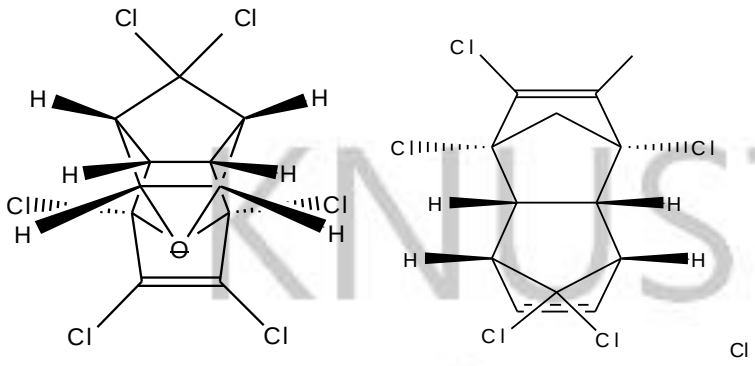
dimethylated derivatives of methoxychlor. Human exposure to methoxychlor occurs via air, soil, and water. In high doses the agent can lead to neurotoxicity as observed in animal experiments (ATSDR, 2005). One studied metabolite which is 2, 2-bis(p-hydroxyphenyl)-1,1,1trichloroethane (HPTE) is considered to have reproductive toxicity in the animal model by reducing testosterone biosynthesis (Cummings, 1997; Akingbemi, 2000). The USEPA also concludes that levels above the maximum contaminant level of 40 ppb can cause central nervous depression, diarrhea, and damage to liver, kidney, and heart while chronic exposure could lead to growth retardation (USEPA, 2006).

2.1.1.2 Chlorinated cyclodienes

Chlorinated cyclodienes are derivatives of hexachlorocyclopentadiene. Most of the cyclodiene pesticides that were commercially important have been branded as persistent organic pollutants by the United Nation Environmental Program. They arrived on the market in the 1950s and were used to control soil insects, cockroaches, termites, grasshoppers, locusts and other insect pests.

Like most chlorinated organics, these chemicals have low solubility in water but are fat-soluble. Typical cyclodiene pesticides are aldrin, dieldrin, endosulfan, endrin, heptachlor, chlordane and many others.

Aldrin and dieldrin are chemicals that were widely applied in agriculture throughout the world to control insects in soil and in public health to control mosquitoes and tsetseflies, the vectors that cause malaria and sleeping sickness (Baird, 1997; Nollet, 2000). These two insecticides have similar structure as shown in Figure 2.4 and therefore show similar chemical properties and toxicity (Baird, 1997). In soils, or in the digestive tracts of insects, aldrin degrades to the epoxide dieldrin, which has strong insecticidal value (Jubb, 1975).



Dieldrin Aldrin

Figure: 2.4: Structures of Dieldrin and Aldrin

They have been linked to health problems such as Parkinson's, breast cancer, reproductive failure, and nervous system damage. Aldrin does break down to dieldrin in living systems but dieldrin is known to resist bacterial and chemical breakdown processes in the environment

(Doyle et al., 1994; Orris et al., 2000).

Endrin has been used primarily as an insecticide on cotton as well as rodenticide and avicide. It is a colourless solid with the IUPAC name (1aR,2S,2aS,3S,6R,6aR,7R,7aS)-3,4,5,6,9,9hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimethanonaphtho[2,3-b]oxirene (ATSDR, 1996; Nollet, 2000; Metcalf, 2002) and its molecular structure is as shown in Figure 2.5. Like other organochlorine pesticides, it is lipophilic and thus tends to bioaccumulate in fatty tissues of living organisms and biomagnifies through the food chain. It is estimated that its half-life in soil is well over 10 years. Although it is very persistent, it partially decomposes to endrin ketone and endrin aldehyde when exposed to sunlight (Nollet, 2000). In comparison with dieldrin, endrin is less persistent in the environment. Endrin is toxic with an LD_{50} of 17.8 and 7.5 mg/kg. Acute endrin poisoning in humans affects the nervous system (Nollet, 2000; USEPA, 2006). Food contaminated with endrin caused several clusters of poisonings, especially in children. It is very toxic to aquatic organisms such as fish, aquatic invertebrates and phytoplankton. The USEPA has set a freshwater

acute criterion of 0.086 ug/L and a chronic criterion of 0.036 ug/L (USEPA, 2006). Endrin is a stereoisomer of dieldrin. It is hydrophobic and thus adsorbs strongly to soil particles and tends to be immobile.

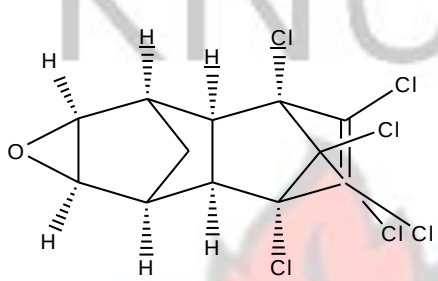


Figure 2.5: structure of Endrin.

Heptachlor is another well-known cyclodiene insecticide that was used extensively as a termiticide and pesticide in homes and on food crops. The chemical formula and the International Union of Pure and Applied Chemistry (IUPAC) name are $C_{10}H_5Cl_7$ and

4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methano-1*H* indene respectively and the structure is as indicated in Figure 2.6. Heptachlor epoxide is the main break down product of heptachlor and is more likely to be found in the environment than its parent compound. The epoxide also dissolves more easily in water than its parent compound and is more persistent. Heptachlor and its epoxide can adsorb to soil particles and evaporate (ATSDR, 2007). Soil microorganisms transform heptachlor by epoxidation, hydrolysis, and reduction. When the compound is incubated with a mixed culture of organisms, its precursor chlordene (hexachlorocyclopentadine) is formed, which could further metabolized to chlordene epoxide. Other metabolites include 1-hydroxychlordene, 1-hydroxy-2,3-epoxychlordene, and heptachlor epoxide. Soil microorganisms also hydrolyze heptachlor to ketochlordene (California EPA, 1999; Plimmer, 2003). Like any other OCs, it is hydrophobic and therefore poorly soluble in water (0.056

mg/L at 25 °C). Humans are exposed to heptachlor through drinking water and foods, including breast milk (ATSDR, 2007). It is still found in the environment particularly, soil and sediments. (Harmon and Katherine, 2010).

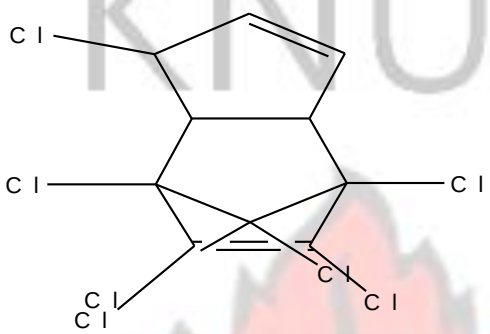


Figure 2.6: Molecular structure of Heptachlor

The chemical has been classified as a possible human carcinogen and was designated as a Class 2B. Animals exposed to heptachlor epoxide during gestation and infancy was found to have changes in nervous system and immune dysfunction (California EPA, 1999). Also, newborn animals exposed to higher doses of heptachlor decrease in body weight and eventual death (California EPA, 1999). The recommended USEPA maximum residue limit (MRL) for heptachlor in drinking water is 0.0004 mg/L. The United State Food and Drug Authority (FDA) limit on food crops is 0.01 ppm, 0.1ppm in milk and 0.3 ppm in edible sea foods (ATSDR, 2007).

Chlordane is a cyclodiene pesticide and was commonly used from 1948 to 1988, on corn and citrus crops as well as for termite control (Metcalf, 2002; ATSDR, 2007). Its chemical formula and IUPAC name are $C_{10}H_6Cl_8$ and Octachloro-4,7-methanohydroindane respectively. Its molecular structure is as shown in Figure 2.7. Technical grade chlordane consists of alpha or cis isomer and the gamma or trans isomer. Commercial formulations contain 10% heptachlor (Nollet, 2000).

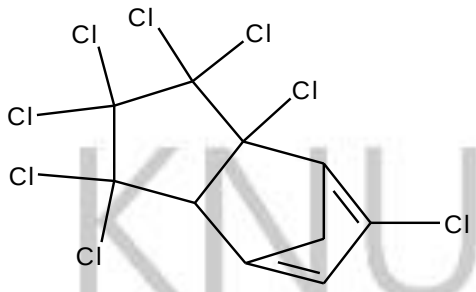


Figure 2.7: Molecular structure of Chlordane

Chlordane is highly hydrophobic and therefore adheres strongly to surface soil particles and can stay in the soil for 20 years. It does not easily dissolve in water or enters groundwater (Orris et al., 2000). Most chlordane leaves the soil by evaporation to the air, where it may be redistributed by air currents, contaminating areas far from their original application site (Orris et al., 2000). The USEPA recommends that children should not drink water with more than 60 ppb of chlordane for longer than 1 day. USEPA has therefore set a limit in drinking water of 2 ppb (USEPA, 2002). Currently, USEPA has defined chlordane concentration of 24 nanogram per cubic meter of air (ng/m^3) over a 20-year exposure period as the concentration that will increase the probability of cancer by 1 in 1,000,000 persons. This probability of developing cancer increases to 10 in 1,000,000 persons with an exposure of 100 ng/m^3 and 100 in 1,000,000 with an exposure of 1000 ng/m^3. The other health effects of chlordane compounds include migraines, respiratory infections, diabetes, anxiety, and depression (ATSDR, 2007).

Endosulfan was a very important and widely used cyclodiene insecticide. Its IUPAC name is 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzadioxathiepine-3-oxide and molecular formula $C_9H_6Cl_6O_3S$ (ATSDR, 1996; Pennington et al., 2004). The molecular structure of the chemical is as shown in Figure 2.8. Technical endosulfan is a 7: 3 mixture of two stereoisomers, designated α and β. Alpha-endosulfan is the more

thermodynamically stable of the two (Schmidt et al., 1997; Metcalf, 2002). Endosulfan is known to persist in the soil for lengthy periods of time, evaporating and breaking down very slowly (Nollet, 2000; USEPA, 2002). Endosulfan breaks down into endosulfan sulfate and endosulfan diol, both of which have structures similar to the parent compound and are therefore of toxicological concern. The estimated half-lives for the combined toxic residues of endosulfan plus endosulfan sulfate range from roughly 9 months to 6 years (USEPA, 2002). Endosulfan emerged as a highly controversial agrochemical due to its acute toxicity, potential for bioaccumulation and role as an endocrine disruptor (Colborn et al., 1996; Wilson and LeBlanc,

1998). Banned in more than 63 countries including the United States and Brazil (Australia Weekly Times, 2009), it is still used extensively in many other countries including India and China (Cone and Marla, 2010; USEPA, 2010). Because of this threat to the environment, a global ban on the use and manufacturing is being considered under the Stockholm Convention (US EPA, 2010). United State EPA's acute reference dose for dietary exposure of endosulfan is 0.015 mg/kg for adults and 0.0015 mg/kg for children. For chronic dietary exposure, the US EPA references doses are 0.006 mg/ kg per day and 0.0006 mg/kg per day for adults and children, respectively (US EPA, 2002).

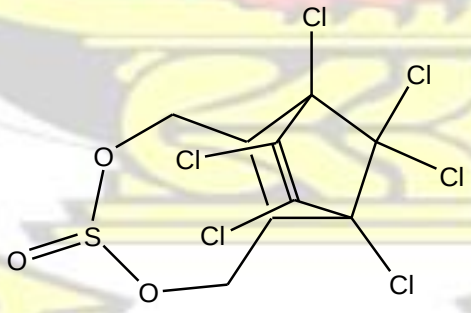


Figure 2.8: Molecular structure of Endosulfan

2.1.1.3. Chlorinated benzenes and cyclohexanes

Chlorinated benzene which had been used as pesticide is hexachlorobenzene (HCB). Indeed, it had been used as fungicide for seed treatment, especially on wheat to control fungal diseases. Its production and use has, however, been banned globally under the Stockholm Convention on persistent organic pollutants (POPs). HCB has a molecular formula of C_6Cl_6 and its IUPAC name is 1, 2 3, 4, 5, 6 hexachlorobenzene. The molecular structure of HCB is as shown in the Figure 2.9. HCB is a white crystalline solid that has negligible solubility in water but soluble in organic solvents.

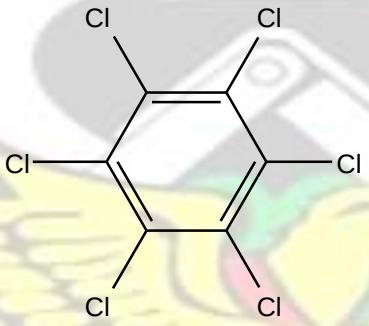
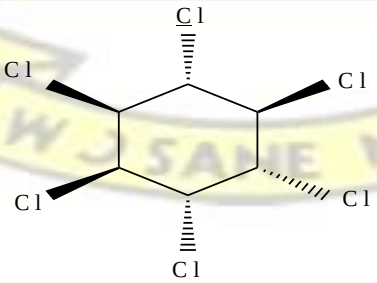
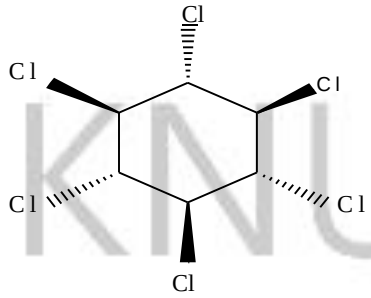


Figure 2.9: Structure of hexachlorobenzene

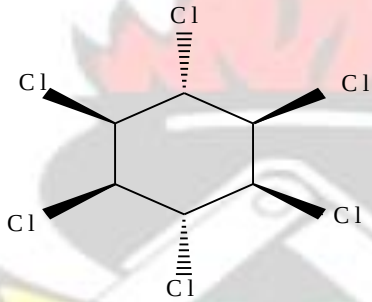
The chlorinated cyclohexane, (HCH) has the IUPAC name 1, 2, 3, 4, 5, 6hexachlorocyclohexane and molecular formula $C_6H_6Cl_6$. Hexachlorocyclohexane is a manufactured chemical that exists in eight isomeric forms. The structures of the first four isomeric forms are presented in Figure 2.10.



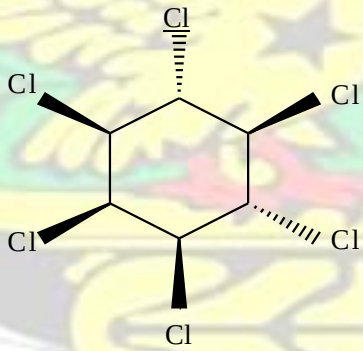
α – HCH



β - HCH



γ- HCH



δ – HCH

Figure 2.10: Structures of first four isomeric forms of HCH Research has shown that only one of the isomers, the gamma isomer, has insecticidal properties and is currently sold as insecticide under the trade name lindane (Baird, 1997; Nollet, 2000). Lindane is the active ingredients in several commercial medical

preparations, formulated as a shampoo or lotion used to rid children of lice and scabies (Baird, 1997; UNEP, 2002; USEPA, 2002). It has been used to treat food crops, forestry products, as a soil treatment, and also used to treat livestock and pets as well as seeds and seedlings. The chemical was originally synthesized in 1825, but its insecticidal action was discovered in 1942, and became widely used in the United Kingdom (USEPA, 2002; UNEP, 2002). It is estimated that between 1950 and 2000, around 600,000 tonnes of lindane were produced globally, and the vast majority of which was used in agriculture. Lindane has also been manufactured by several countries, including the United States, China, Brazil and several European countries and recently India and Russia (USEPA, 2006). Lindane is a persistent organic pollutant with relatively long half-life in the environment. It can be transported long distances by natural processes via global distillation, and as a result bioaccumulate in food chains, though it is rapidly eliminated when exposure is discontinued (UNEP, 2007; UNEP, 2009). Lindane eventually breaks down the environment into especially under aerobic condition and dependent on ambient environmental conditions (ATSDR, 2005). Volatilization is also very slow in water, although volatility represents the major source of release of lindane from soil (Nollet, 2000; US CDC, 2005). The USEPA and WHO have also classified lindane as moderately hazardous or acutely toxic. It has an oral LD_{50} of 88 mg/kg in rats and a dermal LD_{50} of 1000 mg/kg. Most of the adverse human health effects reported for lindane have been related to agricultural uses and occupational exposure of seed treatment workers (UNEP, 2007). Exposure to large amounts of lindane can harm the nervous system, producing a range of symptoms from headache and dizziness to seizures, convulsions and eventual death (ATSDR, 2005; US CDC, 2005). Prenatal exposure to β-HCH, an isomer of lindane, has been associated with altered thyroid hormone levels and could affect brain development. Studies have shown that all isomers of hexachlorocyclohexane may reasonably be anticipated to cause cancer in humans

(USEPA, 2002; ATSDR, 2005). An international ban on the use of lindane in agriculture was therefore implemented in 2009 under the Stockholm

Convention on Persistent Organic Pollutants (UNEP, 2009). Although the US has not ratified the Stockholm Convention, it has similarly banned agricultural use of lindane but allows its use as a second-line lice and scabies treatment (UNEP, 2009).

2.1.2 Polychlorinated biphenyl (PCBs)

PCBs are industrial organochlorine chemicals that became a major environmental concern in the 1980s and 1990s. PCBs found a wide variety of applications in modern society because of certain properties they possess. Since the late 1950s, over one million metric tons of PCBs have been produced. Like many other organochlorine compounds they are persistent in the environment and they bioaccumulate in living systems. As a result of careless disposal practices, they have become a major environmental contaminant in many areas of the world. In view of their own toxicity and that of their furan contaminants, PCBs have become a matter of concern because of their potential impact on human health, particularly, with regard to growth and development.

2.1.2.1 Chemical structure of PCBs

Benzene is a very stable compound; however, heating benzene to a very high temperature can disrupt the carbon-to-hydrogen bonds. This fact is exploited commercially when benzene is heated to about 750 ^{0}C in the presence of lead as a catalyst to form biphenyl, a molecule in which two benzene rings are linked by single bonds formed between two carbons that have each lost their hydrogen atoms. Equation for the transformation is as shown in Figure 2.11

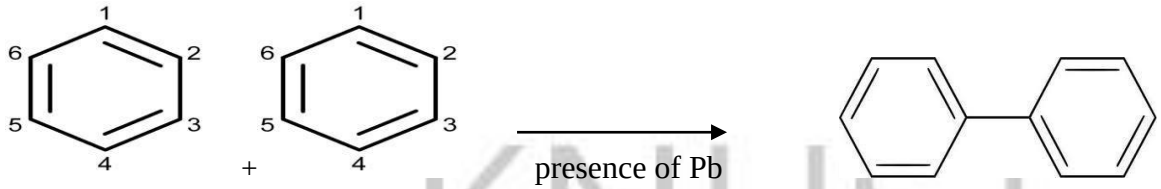


Figure 2.11: Transformation of two benzene rings to form biphenyl

Like benzene, biphenyl reacts with chlorine in the presence of a ferric chloride catalyst, in which some of the hydrogen atoms of the biphenyl become replaced with chlorine. The more chlorine initially present, and the longer the reaction is allowed to proceed, the greater the extent of chlorination of the biphenyl molecule. The products of this reaction are polychlorinated biphenyls (PCBs). The reaction produces a mixture of many of the known 209 congeners of the PCBs. Thus PCBs are class of organic compound with 1 to 10 chlorine atoms attached to biphenyls. Their individual structure formulae are based on the general molecular formula,

$C_{12}H_{10-x}Cl_x$

and that they differ from each other by the position and number of chlorine atoms attached to the biphenyl. The general structure formula of PCBs is shown in Figure 2.12.

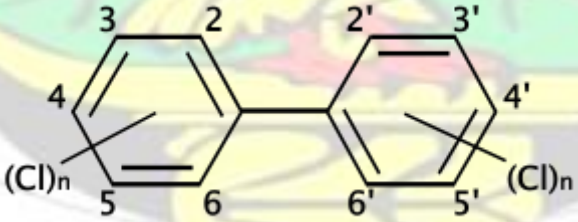


Figure 2.12: General structure of PCBs

The numbering scheme used for individual PCB congeners begins with the carbon of one ring that is joined to a carbon in the other ring. Those carbons joined are given number 1 and the other are numbered sequentially. As shown in Figure 2.12 the positions in the second ring are distinguished by primes.

2.1.2.2 The properties and uses of PCBs

They are odourless, clear to pale-yellow, viscous liquids. PCBs are practically insoluble in water but are soluble in most organic solvents, hydrophobic media such as fatty or oily substances. They have high dielectric constants, high thermal conductivity and are chemically inert. Indeed, they are extremely resistant to oxidation, reduction, addition, elimination and electrophilic substitution reactions, (Boate et al., 2004). Commercially, they were attractive because they are chemically inert liquids and are difficult to burn. They have low vapor pressures and are excellent electrical insulators. Because of these properties, they were used extensively as coolant fluids in power transformers and capacitors. They were also used as plasticizers, that is, agents used to keep other materials such as PVC products more flexible, in ‘’carbonless’’ copy paper, as deinking solvents for recycling newsprint, as heat transfer fluids in machinery, as water-proofing agents. The extensive usage of PCBs coupled with the inappropriate disposal practices, culminated in the widespread and environmental contamination of PCBs. When their accumulation and harmful effects were recognized concerns were raised regarding their production and usage. Indeed, North America production of PCBs was halted in 1977. However, the PCBs remain in use in many electrical transformers currently. Although the liquid in such transformers are mainly PCBs, other chemicals such as polychlorinated benzenes are also present. In the past PCB contained in decommissioned transformers were just damped into landfills and their PCB content was allowed to leak into the ground. However, nowadays, when these electrical units are decommissioned, their PCB contents are stored in order to prevent further contamination.

2.1.2.3 Indicator PCBs

The indicator PCBs are known to be persistent in the environment and bioaccumulate in the food chain, and they are assumed to be a suitable representative for all PCBs. They are the predominant congeners in biotic and abiotic matrices. Mixtures of PCBs are generally assessed on the basis of a chemical analysis of the sum of the seven so-called indicator PCBs. The amounts of chlorine atoms of these PCBs range from three to seven.

2.1.2.4 PCBs contamination by furan

PCBs when heated in the presence of oxygen can result in the production of small amounts of dibenzofurans. The basic furan ring contains five atoms, one of which is oxygen and the other four of which are carbon atoms that participate in the double bonds. Figure 2.13 is the structure of furan.

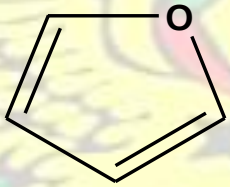


Figure 2.13: Molecular structure of Furan

The dibenzofurans (DFs) have a benzene ring fused to opposite sides of the furan ring as shown below in Figure 2.14

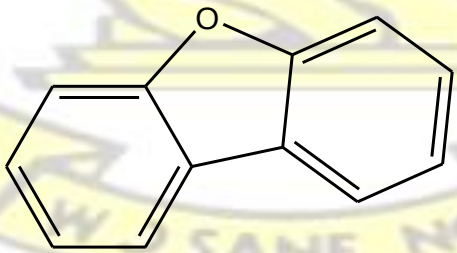


Figure 2.14: Structure of Dibenzofuran

Most of the chlorine in the original PCB molecule is still present in polychlorinated dibenzofuran (PCDF). Almost all commercial PCB samples are contaminated with some PCDFs. However, the level of contamination usually is only a few ppm of the original manufactured liquid. But if PCBs are heated to high temperatures and in the presence of oxygen, conversion of PCBs to PCDFs increases the level of contamination. Indeed, the furan concentration in used PCB cooling fluids is greater than in the virgin materials.

2.1.2.5 Environmental transport and transformations of PCBs

Due to their low vapour pressure, PCBs accumulate primarily in the hydrosphere in the organic fraction of soil and in organisms. Despite their hydrophobicity, the immense volume of water in the oceans is still capable of dissolving a significant quantity of PCBs. While the hydrosphere is the main reservoir, the atmosphere serves as the primary route for global transport of PCBs, particularly for those congeners with one to four chlorine atoms.

Atmospheric concentrations of PCBs tend to be lowest in rural areas, where they are typically in 10 times higher than the picogram per cubic meter range, higher in suburban and urban areas, and highest in city centres, where they can reach 1 ng/m^3 or more. In Milwaukee, an atmospheric concentration of 1.9 ng/m^3 has been measured, and this source alone was estimated to account for 120 kg/year of PCBs entering Lake Michigan (Wethington and Hornbuckle, 2005). Though USEPA guigeline is 3.4 ng/m^3, concentrations as high as 35 ng/m^3 have been found inside some houses in the U.S.A (Rudel et al., 2008)

In biosphere PCBs can be degraded by either bacteria or eukariotes, but the speed of the reaction depends on both the number and the disposition of chlorine atoms in the molecule. Less substituted meta-or para- substituted PCBs undergo biodegradation faster than more substituted congeners

2.1.3 General characteristics of persistent organochlorines compounds

The basic characteristics of persistent organochlorine compounds include persistence (long-half life), lipophilicity, toxicity, bioaccumulation as well as their long-range environmental transport.

2.1.3.1 Persistence

Persistence is the ability of a chemical to remain unchanged in the environment for a long period of time (Baird, 1997; Mukherjee, 2002; Ritter et al., 2007). This allows for their long range environmental transport and subsequent deposition and accumulation in the soil, sediments and in living systems. Most organochlorine compounds persist in the environment for up to 23 years or more. Organochlorine compounds such as DDT, mirex, endrin and PCBs have their half-lives ranging from 10 years to 23 years in the soil and in living tissues and they remain active and toxic for these years depending on environmental conditions. In general, the environmental persistence of some OCs makes it a long-term challenge for the international community to control and finally elimination from the environment. The physical factors that influence persistence include pH, light, moisture and temperature although some microorganisms may break down organochlorine compounds in the environment as well as in living tissues. The series of conversions, which finally lead to the breakdown of organochlorine compounds, is called degradation (Horvath et al., 1988). Such conversions may proceed on biotic pathway due to light, temperature and pH or chemical composition in the soil.

2.1.3.2 Toxicity

Toxicity can be defined as the harmfulness of a substance to an organism. But this effect is dose dependent (Baird, 1997; USEPA, 2006). The toxicity of persistent organochlorine compound is

expressed in terms of acute and chronic toxicity. An acute toxicity is the rapid onset of symptoms including death at the extreme limit following the intake of a dose of a substance. Acute exposures are usually characterized as lasting no longer than a day. The degree of acute toxicity highly depends on the route of entry of the chemical. The acute oral and dermal LD_{50} values for some selected organochlorines are shown in the Table 2.1 below (Porter, 1998; Jackai, 1995)

TABLE 2.1: The LD_{50} values (dermal and oral) of some organochlorine compounds in mg per kg (Porter, 1998; Jackai, 1995)

CHEMICAL	ACUTE ORAL	ACUTE DERMAL
Endosulfan	30	110
Hexachlorocyclohexane	88	1000
Methoxychlor	2820	5000

Chronic toxicity on the other hand is a long term exposure at relatively low dose of a toxic chemical that is present in the air, water, food, soil or medicinal plant materials. It may also be defined as continuous exposure to a toxin over an extended period of time, often measured in months or years which can cause irreversible side effects (Baird, 1997). Therefore the toxicity of OCs can either have acute or chronic effects on insect-pest, wildlife and humans to cause damage or death. Chronic exposure to organochlorines may induce rapid immediate effects (similar to those of acute toxicity) and long term chronic effects that build up gradually (Baird, 1997). For synthetic organochlorines that are not easily transformed, their residues remain stored in the fatty tissues of the exposed organism and cumulative quantities may eventually cause a chronic toxic effect.

Organochlorines that do not readily metabolise show severer penalty in the long term than those that metabolise with ease (Stocchi, 1990). Long term exposure to trace concentrations of OCs has been found to cause cancer, liver damage, immunotoxicity and birth defects (Adeola, 2004). The exposure to estrogenic compounds has also been associated with increased risk of breast and testicular cancers. This estrogen like effect is thought to be responsible for the weakening of birds' eggshells by DDT. Estrogenic organochlorine compounds in the environment have in more recent years been linked to a variety of reproductive malfunctions not only in birds but in humans (Wania and Mackay, 1996). The dose of the substance administered in toxicity tests is usually expressed as the mass of the chemical, usually in milligrams per unit of the test's animals body weight expressed in kilograms. The division by body weight is necessary because the toxicity of a given amount of a substance usually decreases as the size of the individual increases (Baird, 1997).

A substance is also described as hazardous if it does not easily breakdown, but rather accumulates easily in living tissues to cause harm to human health and produce degradation products that are themselves harmful and bioaccumulate in living tissues. Hazard caused to an organism by a chemical is considered as the product of exposure and toxicity. For a highly toxic organochlorine a small quantity or concentration may adversely affect an organism exposed to it while one with low toxicity would produce an effect only if exposure is to large quantities or concentration (Baird, 1997). Toxins such as OCPs react with specific cellular components to kill cells or alter their growth or development in a way that are often injurious, even in dilute concentrations (Baird, 1997). Toxicity of OCs is also expressed in terms of lethal dose (LD_{50}) value of the substance which is the dose that proved to be lethal to 50% of the population of test animals. The lesser the value of LD_{50}, the more potent or toxic is the chemical, since less of it is required to affect the animals (Baird, 1997).

2.1.3.3 Bioaccumulation and lipophilicity

One common notable property of organochlorine compounds is a generally high solubility in hydrocarbon-like environments, such as fatty material in living matter. This lipophilicity is expressed using the n-octanol-water partition coefficient which has been found experimentally to be an adequate surrogate for the fatty portions of the living matter. (Baird, 1997). The lipophilic tendency leads to higher concentration of organochlorine in fatty tissues of the organism and bioaccumulate up the food chain. Bioaccumulation results in higher concentration of a chemical in an organism than its immediate environment including food. This sort of process is called bioconcentration. The bioconcentration factor (BCF) represents the equilibrium ratio of the concentration of a specific chemical example in a fish (C_o) relative to that dissolved in the surrounding water (C_w) if the diffusion mechanism represents the only source of the substance to the fish (Baird,1997). BCF can be calculated by Eqn 2.1.

$$\mathbf{BCF} = \frac{\mathbf{concentration\ of\ pollutant\ in\ organism(Co)}}{\mathbf{concentration\ of\ pollutant\ in\ water\ (Cw)}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{Eqn\ 2.1}$$

BCF values occur over a very wide range, and vary not only from chemical to chemical but also to some extent from one type of fish to another, because of variations in the abilities of different fish to metabolize a given chemical. The BCF of a chemical can be deduced laboratory experiment by equilibrating the chemical between two phase system made up of water and 1octanol [$CH_3(CH_2)_6CH_2OH$]. Octanol has been found experimentally to be an adequate surrogate for the fatty portions of fish. The partition coefficient, K_{ow}, for a chemical S is defined as shown by Eqn 2.2

$$\mathbf{Kow} = \frac{[\mathbf{S}]\mathbf{octanol}}{[\mathbf{S}]\mathbf{water}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{Eqn\ 2.2}$$

where the brackets denote concentrations in molarities or ppm units. In general, the higher the octanol-water partition coefficient K_{ow}, the more likely a chemical is to be bound to organic matter in soil and sediment. A chemical whose concentration increases along the food chain is said to be biomagnified. In otherwise biomagnification result from a sequence of bioaccumulation steps that occur along the chain (Baird, 1997).

2.1.3.4 Long range environmental transport

With the evidence of long range environmental transport of organochlorine compounds to areas where they have never been used and the resultant threats they pose to the environment, the international community called for urgent global actions to reduce and eliminate the releases of these chemicals as an assurance of food safety (WHO 1996; Baird, 1997; Aguilar et al., 2002; Georke et al., 2004).

Despite the global attempts to eliminate or reduce the use of these organochlorine compounds there is still evidence of their presence in various matrixes from both abiotic and biotic components. For instance currently used organochlorine pesticides such as lindane and endosulfan have been detected in arctic samples where they have never been used (Tadeo, 2008).

They exhibit a phenomenon known as the ’’grasshopper effect’’ where the compounds move through cycles of volatilization and condensation. Indeed, there is evaporation of OCs into atmosphere in warmer climates and condensation and deposition in colder climates. These chemicals therefore tend to reach highest concentrations in the cooler regions of the globe (Colborn, 1996). There are scarcely any biomes or species including medicinal plants on earth left unaffected by OCPs. Virtually all living organisms in any parts of the globe have detectable levels

of persistent organic pollution in their tissue (WHO, 1996; Schafer et al., 2001; Mukherjee, 2002; Ballschmitter et al., 2002).

2.1.4 Toxicology of persistent organochlorine compounds.

Because organochlorines can bioaccumulate and magnify in the food chain, concerns have been raised and centered around their impact on top predator species, including humans. Probably the best documented and clearest evidence of effects have been in birds and marine mammals.

Indeed, Rachel Carson drew attention to declining bird populations in her classic book “Silent Spring" and this topic was addressed in the very first paper in Environmental Pollution in 1970

(Prest et al., 1970). Various papers have documented and reviewed how organochlorines, notably DDE, a metabolic breakdown product of DDT, can affect egg-shell thickness in birds (Ratcliffe, 1967, 1970; Pearce et al., 1979). These are amongst the classic ecotoxicological studies. Numerous subtle but far-reaching effects on the reproductive potential of fish-eating birds continue to be reported in the Great Lakes (Giesy et al., 1994) and in Europe (Bosveld and Van den Berg, 1994).

It is re-assuring to see how, as OC residues have declined in certain top predators in certain areas, populations of such predators have increased again. Examples include harbour seals in the Southeast North Sea (Reijnders et al., 1997), white-tailed eagles in the Baltic and piscivorous birds in the Great Lakes (Munro et al., 1994). Organochlorines, particularly,

PCBs, had been linked to reproductive impairment for seals in the Baltic Sea (Bergman and Olsson, 1985) and the Dutch Wadden Sea (Reijnders, 1986) and for Beluga whales in the St.

Lawrence sea way in Canada (Be’land et al., 1993), However, because an extensive array of OCs occur and accumulate simultaneously in biota it is very difficult to say conclusively that an effect is due to one particular chemical, a family of chemicals, their metabolites or indeed several

families of chemicals acting synergistically. This makes control of the problem difficult, because scientists and policy makers have been unsure which persistent organic pollutants require restriction or regulation.

Organochlorines are also amongst the many chemicals implicated in the current concerns over 'sex hormone' or endocrine disruption in humans and wildlife (Harrison et al., 1995; Kelce et al., 1995; Kavlock et al., 1996). In addition to reproductive effects, many OCs are known or suspected carcinogens. PCBs and PCDD/Fs are perhaps the most obvious examples. The health effects of PCDD/Fs have been the subject of a huge research and review effort, costing in excess of one billion dollars by the US EPA and various European government agencies. These compounds present particular challenges because they occur in mixtures and the 17 individual 2,3,7,8-substituted congeners act collectively on a range of biological end-points (Safe, 1994) and together with other compound classes (e.g. certain PCBs; polychlorinated naphthalenes, PCNs). These end-points include in vivo and in vitro effects. Current toxicological thinking is that the effects of these compounds are arylhydrocarbon receptor mediated and additive, so that toxicity equivalent factors and concentration data should be combined to determine the total toxicity equivalent (∑TEQ) loading present in the exposed tissue/target organism (Safe, 1994). These issues have led to a massive research effect from toxicologists over recent years, which will no doubt continue. Purported OCs effects also extend to damage to the immune system of top-predator species (Safe, 1994, Ross et al., 1995), enhancing their susceptibility to disease and effects on patterns of behaviour (De Swart et al., 1994; Leonards, 1997). Clearly, the concerns over adverse health effects in humans and wildlife provide the impetus for research on their sources, environmental fate and food chain transfer.

2.2 The Stockholm convention on persistent organic pollutants (POPs)

It is an international environmental convention which was signed on 23 May, 2001 in Stockholm, Sweden and became effective from 17th May, 2004. The convention aims at eliminating or restricting the production and use of persistent organic pollutants (POPs) which the convention defined as "chemical substances that persist in the environment, bio-accumulate through the food web, and pose a risk of causing adverse effects to human health and the environment"(UNEP, 2002). The Persistent organic pollutants referred to as the "dirty dozen" include the heterogeneous groups of compounds such as OCPs, PCBs and unintentional byproducts of chemical manufacturing and combustion processes such as dioxins and furans (UNEP, 2002; Fattore et al., 2002; Bouwman, 2004).

The convention which entered into full force on 17th May, 2004 with ratification by an initial 128 parties and 151 signatories, allows the co-signatories to eliminate or restrict the use of the dirty dozen chemicals, nine of which are organochlorine pesticides namely DDT, chlordane, aldrin, dieldrin, endrin, hexachlorobenzene, heptachlor, mirex and toxaphene. The convention also curtails the inadvertent production of dioxins and furans as well as PCB which is an industrial chemical and limits the use of DDT to malaria control (UNEP, 2002; Bouwman, 2004). Parties to the convention have also agreed to a process by which persistent toxic compounds can be reviewed and added to the convention, if they meet certain criteria for persistency and transboundary threat. The new chemicals to be added to the dirty dozen chemicals were agreed at a conference in Geneva on 8th May, 2009. Signatory countries are also obliged to take strong measures to control or prevent the release of persistent organic pollutants formed as a result of various industrial combustion processes and to ensure proper and safe disposal of such substances when they become waste. Provisions were also made for information exchange and public awareness creation about the adverse health effects of persistent organic pollutants, besides ensuring the implementation of various articles of the convention. As of January 2011, there are 172 parties to the Convention

(UNEP, 2002; Adeola, 2004). Ghana signed and adopted the convention on 23rd May, 2003 and was ratified on 30th May, 2003.

2.3 Historical use of organochlorines in Ghana

The most widely used pesticide among farmers is the OC insecticides because of their effectiveness and their broad spectrum activity (Bempah et al., 2010).

In Ghana, DDT was used in the form of an emulsion spray in 1948 for the control of pests and disease pathogens of cocoa and also for the control of mosquito vector for transmission of malaria parasite (Ntow, 2001). Even though DDT is banned from importation, sales and use, third world countries continue to use them. For example in Ghana there were evidence of their continued application to crops, vegetables and fruits (Ntow, 2005; Amoah et al., 2006; Darko et al., 2008). Its use today had been outlawed by Environmental Protection Agency of Ghana (Agbeve, 2011). Lindane was used extensively by the Ghana Cocoa Board in the cocoa industry for treatment of swollen shoots disease that affected the cocoa tree. In the early 2000, the Cocoa Board stopped its use because of high lindane residues in the cocoa beans. Despite the ban farmers continued to use the chemical in vegetable cultivation. Its use in Ghana has, however, been discontinued by Ghana EPA. Endosulfan on the other hand, was used extensively in the cotton industry and as insecticide for control pests in vegetables cultivation. When Ghana signed the Stockholm Convention it use was restricted only to the cotton industry by Ghana EPA (Afful et al., 2010). Ghana has now officially banned the use of the chemical. Again, aldrin had been used extensively to control pests on cocoa as well as termites under the trade name Aldrex 40.

PCB oil had historically been used as dielectric fluid in electrical transformers and capacitors by the Volta River Authority and Electricity Company of Ghana. The Ghana Environmental Protection

Agency has now banned the use of PCBs as dielectric fluid in transformers and capacitors. Transformers and capacitors which are imported are now tested to ensure that the oils are PCBs free.

2.3.1 Previous studies on organochlorine pollution in Ghana

Organochlorine pollution studies in Ghana have focused mainly on persistent organochlorine pesticides such as DDTs, lindane, endosulfan (Appoh et al., 1995; Antwi-Boasiako 1996; Ntow 2005). Very little data are available on other typical organochlorine compounds such as PCBs and dioxins despite the threat they pose to the environment. These studies have focused mainly on determination of levels of individual organochlorine compounds in various compartments in the environment. There is therefore very little or no information on bound organochlorine (non extractable organochlorine) composition in our environment. Knowledge of extractable bound organochlorine will broaden our understanding of organochlorine pollution in the environment.

Appoh et al (1995) studied persistence of γ-HCH (lindane) in Ghanaian coastal savannah top soil using a radiotracer technique. They reported that dissipation of the chemical in the soil favours a second order kinetics. They further indicated that dissipation from all the soils exhibited a biphase nature with more rapid dissipation occurring within the first 2 – 6 days after application followed by relatively, slower phase. Persistence was also observed to be dependent on the organic matter content of the soil. Antwi-Boakye (1996) studied persistence of lindane and endosulfan in two soil ecosystems under laboratory conditions, and established that the degradation pattern of the chemicals in both soil ecosystems was similar. However, after six weeks of incubation, endosulfan had degraded more than lindane. He further indicated that soil moisture facilitated the degradation process.

Ntow (2005) investigated levels of organochlorine pesticide residues in water and sediments from the Volta Lake and detected residues of gamma HCH (lindane) and endosulfan from water samples. He also reported levels of HCB, p,p'-DDE and heptachlor epoxide in the sediments.

Ntow (2006) further studied organochlorine pesticide residues in vegetables at Akomanda in Ashanati Region of Ghana, noted for cultivation of tomatoes. His investigation revealed heptachlor epoxide residues as dominant residue in the vegetables. Other organochlorine residues of endusulfan, lindane and DDTs were detected in insignificant amount.

Darko et al (2008) studied organochlorine pollution in the Lake Bosomtwi and reported organochlorine residues in water, fish and sediment samples. However, most of the organochlorine pesticides residues were in the fish and sediment samples. They reported a mean concentration of 0.126 μg/kg of gamma HCH.

Afful et al (2010) determined the spectrum of organochlorine pesticide residues in the six fish species sampled from Nsawam and Weija village of the Densu basin. They detected fourteen individual OCPs namely, p,p'-DDT p,p'-DDE, α-endosulfan, dieldrin, aldrin, endrin, endrinaldehyde, endosulfan sulfate, endrin ketone, endrin aldehyde, γ-HCH, δ-HCH, heptachlor, and γchordane. They concluded that the concentrations of the organochlorines were below the stipulated Australian Maximum Residue Limits (MRL) of 50 μg/kg to 1000 μg/kg stipulated for fresh water fish.

Kwablah Anim et al (2010) applied neutron activation analysis to investigate the burden of total chlorine and extractable organochlorine in fish species sampled at Nsawam and Weija from the Densu river. Concentrations of total chlorine and extractable organochlorine were in the range of

77.70 mg/kg to 1123.59 mg/kg and 150.00 mg/kg to 350.40 mg/kg respectively. They therefore stated that most of the chlorine content was non extractable and concluded that the non extractable chlorine could either be organic bound chlorine or inorganic chlorine.

Buah-Kwofie et al (2010) determined levels of polychlorinated biphenyl (PCB) in transformer oil sampled from Grreater Accra Region and concluded that all the samples that tested positive with the PCB test kit on analysis with INAA showed PCB contamination with total chlorine exceeding 50 μg/g.

Kuranchie-Mensah et al (2011) assessed polychlorinated biphenyl levels in fishes from Volta Lake and reported the presence of the six indicator PCBs. PCB 180 was, however, not detected in the samples. They also reported PCB 28 and PCB 52 as the the most predorminant congeners.

Asante et al (2010) studied PCBs in cow milk samples from Ghana and reported that the presence of PCBs in the milk could be attributed to dust-infested food, and any electronic and electrical equipment or their wastes which are sometimes found at dumping site where the cow grazed.

2.4 Analytical procedures for analysis of organochlorine compounds

Regardless of the analytical methods used, the procedures for analysis of organochlorines follow the following steps.

1. Sampling and sample preparation

2. Sample extraction

3. Extract clean-up
4. Determination of organochlorines in the extract

2.4.1 Sampling and sample preparation

The importance of careful, unbiased and representative sampling in the field cannot be overemphasized. It should always be remembered that chemical residue analyses are usually time consuming as well as expensive and therefore the minimum sampling to obtain reasonable validity is of paramount importance. Samples collected must have the following characteristics (Van Middelem, 1963).

1. Sample must be accurate. The final accuracy of the residue determination depends on the original field sample. Data obtained may be precisely determined but woefully inaccurate due to inadequate field sampling.

2. The sample must be valid. A valid sample is the one that is selected in a manner that ensures that each unit of material in the batch being sampled has an equal chance of being selected for the extraction and ultimate test.

3. The sample must be representative. A representative sample is not only a random sample but the proportion of each type of the sample material should be identical to that of the gross sample from which it was originally selected.

2.4.2 Sample extraction

2.4.2.1 Pre-analysis

Once a valid, representative field and sub-sample have been selected for eventual analysis, the next major problem for the analyst is to quantitatively remove the organochlorine or its metabolites from the surrounding biological environment. Extraction techniques must be adequate to yield

extract which accurately reflect the toxicant level. Bann (1957) reviewed three basic extraction procedures for organic pollutants removal.

1. the whole crop surface rinsed with a suitable solvent

2. maceration of sample with crystalline anhydrous sodium sulphate and extraction with suitable solvent

3. maceration of the sample in the presence of a suitable solvent or solvents combination.

2.4.2.2 Solvent extraction

The first step in the analysis of organic pollutant is usually separation of the pollutant from the environmental sample by solvent extraction. For efficiency, the solvent must remove the pollutant in a reproducible manner without removing large amount of co-extractives from the sample. Many specialized solvent have been developed for extraction of organochlorines from agricultural and related samples. The analyst must consider the method of analysis before extraction is begun. For instance to analyse for γ-HCH in a sample using Schechter-Hornstein procedure (Schechter et al., 1952), sample should not be extracted with benzene, since benzene is the material to be detected in the final step of analysis.

Unless adequate experimental data concerning the solvent purity is known the solvent should be distilled before use. This is especially important in the case of chlorinated solvents such as chloroform, methylene chloride and carbon tetrachloride. These solvents often form phosgene on standing, which not only produce negative analytical results, but may be hazardous to the analyst. Before unstable pesticides were developed, samples were often dried, ground and extracted in soxhlet or some other type of continuous extractor. However, drying was soon found to cause loss of many organic pollutants.

2.4.2.3 Liquid-liquid extraction (LLE)

Analytes in solutions or liquid samples can be extracted by direct partitioning with an immiscible solvent. Liquid-liquid extraction (LLE) is based on the relative solubility of an analyte in two immiscible phases and is governed by the equilibrium distribution/partition coefficient. Extraction of an analyte is achieved by the differences in the solubilising power (polarity) of the two immiscible liquid phases. LLE is traditionally one of the most common methods of extraction, particularly for organic compounds from aqueous samples. Typically a separating funnel is used and the two immiscible phases are mixed by shaking and then allowed to separate. To avoid emulsions, in some cases, a salt may be added and centrifugation can be used if necessary. Alternatively a matrix solid-phase dispersion (MSPD) approach can be used to avoid emulsions. Both layers can be collected for further analysis. To ensure the complete extraction of an analyte into the required phase, multiple extractions may be necessary. Due to the limited selectivity, particularly for trace level analysis, there is a need for clean up or analyte enrichment and concentration steps prior to instrumental analysis. In the case of multi residue methods, the extracting solvent has to be suitable for the extraction of compounds within a wide polarity range from a variety of matrices containing different amounts of water, fats, sugars and other substances. The usual way for extracting organic pollutants from the sample is by thorough disintegration of the matrix in a high speed homogenizer in the presence of the solvent or solvent mixture. In this way, even the Association of Analytical Chemist (AOAC) method, which is one of the most commonly instituted methods, has been modified. The original methods which were extraction with acetonitrile, followed by liquid-liquid partitioning with petroleum ether/dichloromethane and a laborious florisil column cleanup, were modified in 1985 to include acetone instead of acetonitrile (Torres et al., 1996). Acetone extraction is usually preferred since it is suitable for both non-polar and polar chlorinated compounds, as has been demonstrated in many comparative

studies performed by GC and HPLC. In addition, acetone has low toxicity, is easy to purify, evaporate and filter and is inexpensive. Fruit and vegetable extracts in acetone are usually cleaner than those obtained with other solvents of similar polarity (Torres et al., 1996). A rapid and efficient multi residue extraction procedure using ethyl acetate and sodium sulphate, followed by GPC on an SX-3 column, was first reported by Roos et al (1987). Recoveries better than 90% were obtained for organochlorine (OC) pesticides, and chlorobiphenyls. In another study, Castro et al (2002) developed a rapid LLE method for the determination of endosulfan isomers and endosulfan-sulfate in plant samples. Tomato leaf samples were homogenized with ethyl acetate and extracts cleaned-up on an aluminium oxide column. The compounds were eluted with a hexane-ethyl acetate (80:20, v/v) mixture. Recoveries obtained from plant samples were higher than 78% with relative standard deviation (RSD) lower than 14% and detection limits were 0.02 μg/g for both endosulfan isomers and endosulfan sulfate.

2.4.3. Current trends in liquid-liquid micro extraction and other methods.

2.4.3.1 Single drop micro extraction (SDME)

Single-drop micro extraction was first introduced, in 1996, by Liu & Dasgupta (1996). They extracted sodium dodecyl sulphate ion pairs by a micro drop (1.3 μL) of a water-immiscible organic solvent, suspended in a larger aqueous drop. In the same year, Jeannot and Cantwell (1977) introduced a technique that they termed as solvent micro extraction in which the extraction medium was a droplet (8 μL) of 1-octanol held at the end of a Teflon rod and

suspended in a stirred aqueous sample solution. After extraction for a prescribed time, the Teflon rod was withdrawn from the aqueous solution and the organic phase collected with a micro syringe and injected into a GC system. In this work, the authors also proposed equilibrium and kinetic

theories to explain this micro extraction procedure. Subsequently, the technique was changed to allow simultaneous extraction and injection of analytes, by introducing as support a micro syringe, where the organic phase was suspended at the needle tip (Jeannot and Cantwell, 1997) (Figure 2.16).

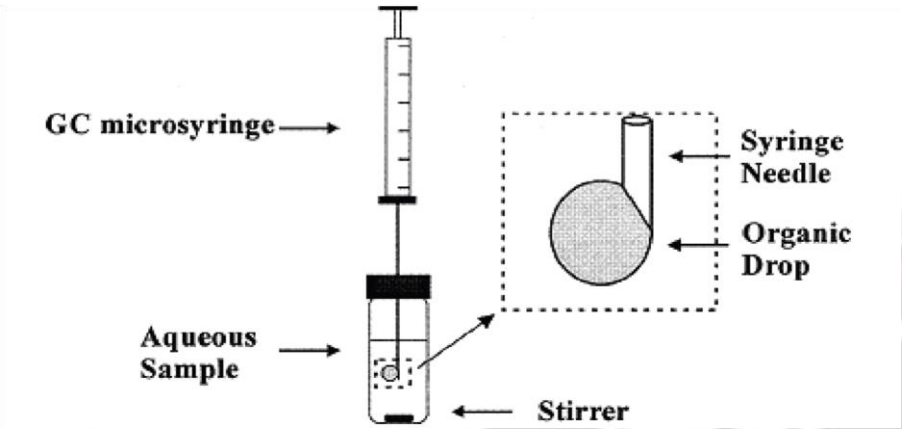


Figure 2.16: Illustration of direct immersion single-drop micro extraction (Xu et al., 2007).

One advantage of SDME over other liquid extraction techniques is the small volume of organic solvent required. Additionally, in this technique, analytes with high partition coefficient can reach high concentrations, since they are transferred by diffusion from a significant volume of sample (1-5 mL) to a small micro-extract (5-50 µL). Since its introduction, different modes of SMDE have been developed, in order to improve extraction efficiency, such as direct SDME, headspace SDME (HS-SDME) and continuous flow micro extraction (CFME). Direct SDME consists of suspending a micro drop of organic solvent at the tip of a syringe, which is immersed in the aqueous sample. An alternative approach was described as dynamic technique by He and Lee (1997), in which organic solvent repetitively forms a film inside the syringe barrel by continuously pulling and pushing of the syringe plunger. Extraction takes place between the sample solution and the organic film. Direct SDME has extensively been used for the direct extraction of pesticide residues from

aqueous samples (Table 1). Xiao et al (2006) evaluated two types of SDME, static and dynamic, in extraction of six organophosphorus compounds

(dichlorvos, phorate, fenitrothion, malathion, parathion, quinalphos) from water and fruit juice. Significant parameters affecting SDME performance such as extracting solvent, solvent volume, stirring rate, sample pH and ionic strength were evaluated. The authors verified that static SDME procedure allowed an enrichment factor of the six compounds nearly 100 fold The potential of SMDE was also investigated by Liu et al (2006) in the extraction of four fungicides from water and wine samples. Additionally, SDME has been applied in the extraction of organochlorine pesticides (OCPs) in various matrices.

Qia and He (2006) introduced a funnel from SDME to extract 11 OCPs and 2 pyrethroid pesticides from tea samples and analyzed by GC-ECD. More recently, Cortada et al. (2009a) proposed a SDME procedure comprising a 2 μL toluene micro drop exposed for 37 min to 10 mL aqueous sample without salt addition and stirred at 380 rpm to extract eight OCPs from wastewater followed by GC-MS analysis. Contrary to the aqueous samples, vegetable and fruits, being mostly in solid or heterogeneous form do not allow direct extraction with SDME.

However, it is possible to use SDME after a previous pretreatment. Nine OCPs (β-,λ-,α-, σ- BHC, dicofol, dieldrin, DDD, DDE, and DDT) were extracted with SDME from fresh vegetable (cabbage, cauliflower, Chinese cabbage) after an adequate mixture of sample aliquots with acetone using a ultra-sonic vibrator.

2.4.3.2 Stir-bar sorptive extraction (SBSE)

Stir bar sorptive extraction (SBSE) was developed by Baltussen et al (1999) to overcome the limited extraction capacity of SPME fibers. A glass stirrer bar is coated with a potentially thick

bonded absorbent layer (polydimethylsiloxane – PDMS) to give a large surface area of stationary phase, leading to a higher phase ratio and hence a better recovery and sample capacity. The advantages of sorptive extraction using PDMS include predictable enrichment, the absence of displacement effects, inertness, and rapid thermal desorption at mild temperature. Stir bar sorptive extraction of a liquid sample is performed by placing a suitable amount of sample in a headspace vial. Normally, SBSE is applied to the extraction of aqueous samples containing low concentrations of organic compounds. For samples containing high concentrations of solvents, the solutions should be diluted before extraction. For the extraction of highly non polar solutes, an organic modifier is added to minimize wall adsorption. Thus, the optimization of the organic modifier concentration is necessary. After extraction, the stir bar is removed, then placed on a clean tissue paper, rinsed with distilled water to remove water droplets, and introduced in a thermal desorption unit. This step will avoid the formation of non-volatile material during the thermal desorption step. Rinsing would not cause any solute loss, because the adsorbed solutes are present inside the PDMS phase. After thermal desorption, the stir bars can be reused.

Typically, the lifetime of a single stir bar is approximately 20 to 50 extractions, depending on the matrix (David and Sandra, 2007). Sandra et al (2003) used SBSE with thermal desorption capillary GC-MS for the screening of OCPs pesticides in fruits, vegetables and baby food. A 10 mm stir bar coated with 0.5 mm PDMS was used. The recoveries for spiked samples ranged between 43-75%. The coupling of SBSE with RTL-GC-MS operated in the scan mode could monitor simultaneously about 300 pesticides present in fruits, vegetables and baby food. The detection limits from mg/kg to the µg/kg levels were obtained.

2.4.3.3 Extraction by sonication

Sonication is the act of applying sound energy to agitate particles in a sample, for various purposes. In the laboratory, it is usually applied using an ultrasonic bath or an ultrasonic probe, colloquially

known as a sonicator. Sonication has numerous effects, both chemical and physical. The chemical effect of sonication is concerned with understanding the effect of sonic waves on chemical systems. The chemical effects of ultrasound do not come from a direct interaction with molecular species. Studies have shown that no direct coupling of the acoustic field with chemical species on a molecular level can account for sonochemistry. Sonication can be used to speed dissolution, by breaking intermolecular interactions. Shin et al(2004) in the determination of persistent organochlorine pollutants in Rat hair by gas chromatography-mass spectrometry extracted the organochlorine pollutants by sonication the samples using in an ultrasonic bath (Branson 5210, Branson Ultrasonic Cleaner, USA) for 3 hr at 40 ºC with 2 mL of 3 M HCl. The solution was extracted 3 times with 2ml of hexane/methylene chloride (4:1). PCBs in sediments sampled from European high altitude mountain Lakes were determined by extraction through sonication with methanol for 20 mins (Grimalt et al., 2004).

2.4.3.4 Soxhlet extraction

A soxhlet extractor shown in Figure 2.20 is a piece of laboratory apparatus (Harwood et al., 1988) invented in 1879 by Franz Von Soxhlet was originally designed for the extraction of a lipid from a solid material. However, a soxhlet extractor is not limited to the extraction of lipids. Today, soxhlet extraction is applied for extraction of many organic compounds from solid materials. Typically, a soxhlet extraction is only required where the desired compound has a limited solubility in a solvent, and the impurity is insoluble in that solvent. If the desired compound has a significant solubility in a solvent then a simple filtration can be used to separate the compound from the insoluble substance (Jensen, 2007). Normally a solid material containing some of the desired compound is placed inside a thimble made from thick filter paper, which is loaded into the main chamber of the soxhlet extractor. The soxhlet extractor is placed onto a flask containing the

extraction solvent. The soxhlet is then equipped with a condenser. The solvent is heated to reflux. The solvent vapour travels up a distillation arm, and floods into the chamber housing the thimble of solid. The condenser ensures that any solvent vapour cools, and drips back down into the chamber housing the solid material.

The chamber containing the solid material slowly fills with warm solvent. Some of the desired compound will then dissolve in the warm solvent. When the soxhlet chamber is almost full, the chamber is automatically emptied by a siphon side arm, with the solvent running back down to the distillation flask. This cycle may be allowed to repeat many times, over hours or days. During each cycle, a portion of the non-volatile compound dissolves in the solvent. After many cycles the desired compound is concentrated in the distillation flask. The advantage of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled. After extraction the solvent is removed, typically by means of a rotary evaporator, yielding the extracted compound. The non-soluble portion of the extracted solid remains in the thimble, and is usually discarded.

Figure 2.20: A set up of soxhlet extraction with the sample placed in thimble.

2.4.4 Storage of extracts

Afful (2002) has shown that stripping or extracting solutions should be stored under conditions that will permit no change in the analyte until analysis is performed. If delay is unavoidable, a recovery can be made under the same condition of extraction, and stored along with the sample extracts. Even under optimum conditions, however, prolonged storage of extracts is not advisable. Extract should be near 0 ^{0}C in screw-cap bottles with aluminium liners in the caps. Liners of waxed paper should be avoided. Since the wax is usually dissolved by the solvent. Even at low temperatures, organic pollutants in extract may be lost. Extracts should therefore be analyzed as soon as possible after extraction unless there is considerable experimental evidence showing that the pollutant is stable in the solvent.

2.4.5 Concentration of extracting solution

After extracting of an organic pollutant from a sample material, the pollutant is usually at such a low concentration that direct measurement is not likely to yield the desired result. The extracting solution must therefore be concentrated by removal of the extracting solvent. Concentration or removal of solvent may be achieved in several ways, but distillation or evaporation of the solvent is most practical.

2.4.5.1 Air evaporation

In most cases, evaporation is achieved either by blowing warm air over the extract in a beaker or blowing filtered dry air or nitrogen over the extract held in a warm bath. If the sample is being evaporated by stream of air from the laboratory line, it is well to filter the air just before use. A convenient air filter with replaceable cartridge is satisfactory to remove water, oil and rust particles. The temperature usually should not be over 50 ^{0}C, must be lower since at higher temperatures most of the organic pollutants will be lost through evaporation. In the determination of organochlorine pesticide residues in *Sardinella auritus* from the coastal waters of AccraTema, and their potential health risks the cleaned up extracts were concentrated by blowing in gentle streams of nitrogen gas (Nyarko et al., 2011).

2.4.5.2 Concentration using vacuum

Vacuum can be often be used in concentrating extract solutions that are sensitive to heat. A rinco evaporator utilizes the principle of spreading a thin film of solution over a large rotating surface area and subjecting it to negative pressure. This is a convenient method for vacuum concentration of extracts containing persistent organic pollutants. Kuranchie-Mensah et al (2011) applied rotary

vacuum evaporator for concentration of the extracts in the extraction of organochlorines from fish samples.

2.4.6 Clean up or purification of extract

Usually, one day prior to laboratory analysis, the frozen extracts are removed from freezer and allowed to thaw at room temperature, and then purified. In order words, the pollutant of interest must be isolated from the previous environment by suitable solvent. Thus, a clean up procedure must be devised to quantitatively separate the pollutants of interest from the associated interfering materials co-extracted from the original biological environment. Gunther and Blinn (1955), Schecter and Hornstein (1952) discussed a detailed clean up and isolation of chemical residues from accompanying interfering extractants. The extracted toxicant must be free of most accompanying extractants before precise and valid chemical analyses can be achieved. Most clean up procedures are based on

a. chromatographic separation with materials exhibiting a selective adsorption for compound being determined.
b. chemical removal of interference through oxidation, reduction, saponification or hydrolysis without detrimental effect on the compound itself.
c. physical separation by solvent partition, steam distillation, freezing.

2.4.6.1 Solvent partitioning

An example of clean up by solvent partitioning is the preferential solubility of chlorinated compounds in acetonitride. Thus, following partitioning of butter fat containing organochlorines between petroleum ether and acetonitrile, the organochlorines in the butter will be concentrated in the acetonitrile while the fat is retained in the non polar petroleum ether solvent.

2.4.6.2 Acid clean up

Strong acids such as fuming sulphuric acid could be used to clean extracts which have greater proportion of fat and oil. Many organochlorines are stable in strong acid medium. Indeed, treatment of fats and oil with fuming sulphuric acid will remove the fats and oil while leaving the organochlorine in the solvent phase. Acid clean up is typically used for toxaphenes.

2.4.6.3 Column chromatography clean up

Column clean up is probably the most widely used but least understood clean up procedure. Adsorbents normally used are alumina, silica, charcoal, diatomaceous earth, C-18 and florisil. Solid phase extraction (SPE) is the most widely used column chromatographic clean up. Solid phase extraction is relatively new technology that is gaining popularity, where low concentrations of analyte can be concentrated from large sample volume. Analytical laboratories use solid phase extraction to concentrate and purify samples for analysis. Solid phase extraction can be used to isolate analytes of interest from a wide variety of matrices, including urine, blood, water, beverages, soil, and animal tissue (supelco, 1998). Solid phase extraction cartridges and disks are available with a variety of stationary phases, each of which can separate analytes according to different chemical properties. Most stationary phases are based on silica that has been bonded to a specific functional group. Some of these functional groups include hydrocarbon chains of variable length for reversed phase SPE, quaternary ammonium or amino groups for anion exchange, and sulfonic acid or carboxyl groups for cation exchange (supelco, 1998). A typical solid phase extraction involves four basic steps.

1. Conditioning the sorbent beds with solvent to improve the reproducibility of the analyte retention and to reduce the concentration of any contaminant present in the extract.

2. Sorbing the analytes on the bed, together with the undesirable matrix constituents.

3. Rinsing the column with weak solvent to remove undesirable matrix component.

4. Eluting the analyte with a sufficiently strong solvent, while leaving the undesirable components on the bed. Useful adsorbents (stationary phase) in the extraction of organochlorines include diatomaceous earth, C-18, florisil, alumina, silica gel and silica support bonded with ethyl, octyl, octadecyl, cyclohexyl and cyanopropyl functionalities. SPE is mostly used off-line, the adsorbent being packed in disposable columns or cartridge. Kuranchie-Mensah et al (2011) applied SPE equipped with alumina for the cleanup of the extracts. The extracts were then fractionated over silica. The first fraction was eluted with 10 ml hexane for the PCBs. The second fraction was eluted with hexane:ether (8.5:1.5 v/v) for the OCPs. Ho-Sang et al (2004) in the determination of persistent organochlorine pollutants in rat hair by gas chromatography-mass spectrometry also used SPE column consisting of 2.5 g silica gel, 2.5 g of florisil and 2.0 g of sodium sulphate for the extracts clean up. The SPE column was washed with 10 ml of hexane at a rate of 10ml/min. The POPs were then eluted with 8 ml of methylene chloride.

2.5 Instrumental analysis of organochlorine compounds.

2.5.1 Instrumental neutron activation analysis (INAA)

Neutron activation is one of the most powerful analytical techniques for multi-elemental analysis. It is an excellent tool for the determination of halogens such as Cl, Br and I (Gustavson and Johnson, 1999). Thus INAA is very useful for the determination of total halogen, extractable organohalogen and total organically bound halogen compounds. Neutron interacts with elemental nuclei over a wide range of incident energies. The neutron having no charge can penetrate the coulomb field surrounding the nuclei. When neutrons are captured compound nuclei are formed. When a sample is exposed to a flux

of thermal neutrons **(Φ)** for a period of time **t,** small fractions of the various stable isotopes of the elements present will capture some of the neutrons and the mass number of the element will be increased by one and the element get to the excited state and when it de-excites emit gamma ray (γray) of characteristic energies. Thus elements have their characteristic γ energies. This can be represented by hypothetical Eqn 2.3

$$ {}_{Z}X + {}_{10}n \rightarrow {}_{A+1}ZY + \gamma \quad \text{.....Eqn 2.3} $$

The product Y is radioactive and therefore the nuclei will decay. Thus at the end of irradiation, the product nuclides decay to their half-lives. The decay time is termed the ***cooling time.*** If the cooling time is t_d and the irradiation time is t_i, then the number of product nuclides N_1 which is a function of t_i and t_d is given by Eqn 2.4.

$$ N_1 = k / \lambda_1 (1 - e^{-\lambda_1 t_d}) e^{-\lambda_1 t_i} \quad \text{.....Eqn 2.4} $$

In NAA a spectrum is obtained with a multi-channel analyzer. Each peak in the spectrum is the characteristic γ-energy of the product nuclide which is used for identification of the nuclide. The area under the peak is proportional to the amount of the radioactive nuclide.

A simpler method has been developed that avoids errors implicit in the uncertainties. The unknown and a known standard are irradiated and counted in an identical fashion. A direct comparison can then be made according to the Eqn 2.5

$$ \frac{\text{Weight of standard}}{\text{Weight of sample}} = \frac{\text{Activity of sample}}{\text{Activity of standard}} \quad \text{..... Eqn 2.5} $$

This method is called the comparator method.

2.5.2 Gas chromatography (GC)

Gas chromatography equipped with electron capture detector is an excellent tool for characterization and quantifying of extractable organohalogens including organochlorines. Gas chromatography is a separation science technique applied to separate components in a mixture. It consists of an injector, a column, a detector and a recorder or an electronic integrator. A few of micro liters of the sample are injected into the injector. The sample is then vaporized in the injector and carried through the column by means of a carrier gas which serves as mobile phase. GC achieves separation of components in a sample by partition of the components between the mobile and stationary phases. The components are selectively retarded by the stationary phase as components interact with the stationary phase. This therefore causes the components to leave at different times depending on both the volatility of the compound and the affinity for the stationary phase. The time spent in the column is characteristic for each component under a specific set of operating conditions. This time is referred to as ***retention time***. As the components of the sample emerge from the column, the detector sends a signal proportional to the ***concentration*** of the component to the recorder. Each component is registered as a peak or chromatogram and is identified by means of the ***retention time*** and quantified by the ***peak area*** or ***peak height***.

To a large extent, the choice of column determines the success of separation. The two types of columns used are packed and capillary. Packed columns are cheaper, easier to handle and are often used where high resolution is not required. Capillary columns are expensive but very good separation is achieved if handled correctly. The selection of column length depends on the required resolution and analysis time. Short columns (10 – 25 m) are useful for samples containing relatively smaller compounds. Intermediate column length of 25 – 30 m, provide sufficient separation power simultaneously with reasonable analysis time, are most cases used for many separations analysis (Kostiainnen, 2000)

The success of GC in residue analysis is based on the sensitivity and selectivity of wide range of detectors. The critical properties of detectors are sensitivity, selectivity, linearity of response, reproducibility and reliability of operation. Currently the flame ionization detector (FID) is the most popular universal detector for GC Analysis. Selective detectors, such as flame photometric detector (FPD), nitrogen-phosphorus detector (NPD), and electron capture detector (ECD) are available. Electron capture detector is used exclusively for determination of halogenated compounds. ECD has been used widely for determination of organochlorine compounds in many matrices (Balinova and Balinov, 1991; Afful et al., 2010; Kuranchie-Mensah et al., 2011; Nyarko et al., 2011).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

This chapter deals with the steps involved in sample collection, sample preparations and analyses of samples in order to obtain the concentrations of organochlorine pesticides and indicator polychlorinated biphenyls present. Methods used for risk assessments of measured organochlorine pollutants on aquatic species and humans are captured. Equipment, chemicals, reagents and other consumables used for the study are also presented under this chapter. Quality assurance and quality control measures taken to ensure the reliability and reproducibility of the analytical data and statistical analysis of the data are also presented. Sampling sites are also described here.

3.2 Geographical description of the study areas.

The study areas were aquatic environments of two important water sources, the Weija Lake in the Greater Accra Region and Lake Bosomtwi in the Ashanti Region of Ghana. Figure 3.1 is a map of Ghana showing where Ashanti and Greater Accra Regions are located. The figure also shows where Lake Bosomtwi and Weija Lake are located in their respective regions.

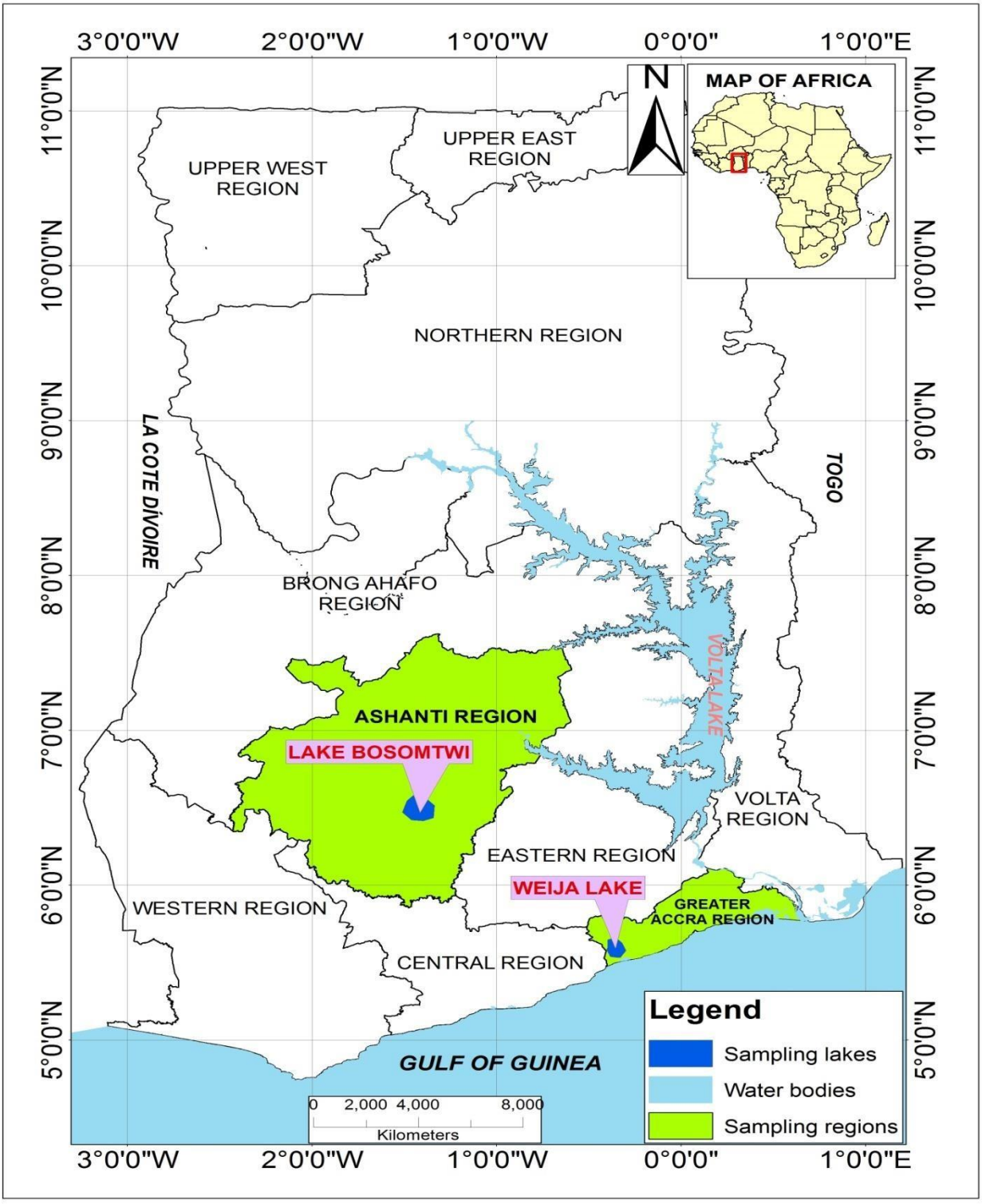


Figure 3.1: Map of Ghana showing the the sampling regions.

3.2.1 Weija Lake.

Weija Lake shown in Figure 3.2 lies 17 km west of Accra between $5^0\,33^{'}$ to $5^0\,40^{'}$ N and $0^0\,20^{'}$ to $0^0\,24^{'}$ W in the coastal savannah thicket and grassland vegetation zone in southern Ghana. The Weija Lake was created by damming the Densu River at Weija with the main objective of providing potable water for the residents of western Accra in the Greater Accra Region of Ghana. It was also created for irrigation purposes and to increase the fishery potential of the river system. The Lake is shallow with a maximum water level of 15.3 m during the peak of the rainy season and covers an area of about 33.6 km^2. Area of water shed is 2264 km^2 with mean surface water level of 14.3 m. Principally, the vegetation in the catchment of the Lake is densely thickets interspersed with patches of grasses. The nature of the soils in the catchments have been reported to be well drained, friable, porous loam savannah ochrosols which are low in nutrients especially phosphorus and nitrogen (Boateng, 1970; Dickson and Benneh, 1970). Also, the soils in the catchment are sodium uleisols and lithosols (Ayibotele and Tuffour-Darko, 1979). Generally, erratic and low rainfall, averaging 840 mm a year is recorded with major rains occurring mainly from May to June and in October (Boateng, 1970). Some catchment areas of the Weija Lake, however, enjoy much higher rainfall as experienced in other areas in the country (Hall and Swaine, 1981). The hottest months are in February to April with the highest mean monthly temperature of 32 ^oC occurring in March, whilst the lowest mean monthly temperature of 21.7 ^oC occurs in August. The main economic activities of the people in the catchment of the Lake includes fishing (small-scale canoe fishing), animal rearing, stone quarrying and crops farming. The normal surface elevation is estimated at 14.37 km with maximum of 15.24 km (Nukunya and Boateng, 1979). As a result of availability of water for irrigation, vegetables cultivation in the catchment of the Lake has become lucrative. Thus, communities dotted around the Lake are therefore engaged in vegetable and other crops cultivation. In their effort to fight the menace of insects, organochlorine pesticides such as DDT, lindane, endosulfan etc in the past were used by the

farmers to spray their crops. Residues of these pesticides obviously washed into the Lake through run-off from the farm lands. It should however, be indicated that persistent OCPs are no longer used in Ghana. The indiscriminate dumping of electrical and electric waste materials in the Weija catchment could be linked to the presence of PCBs in the Weila Lake

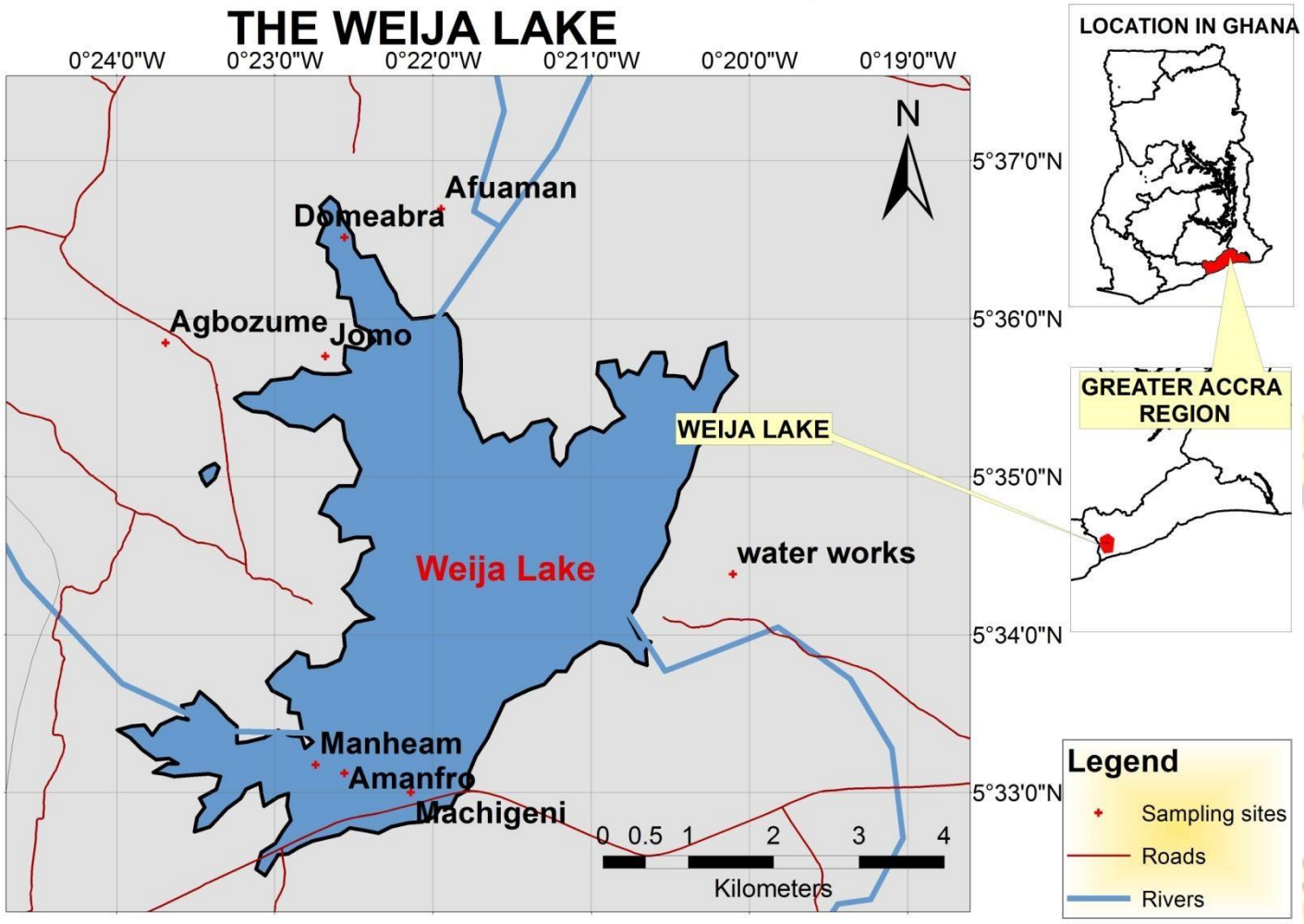


Figure 3.2: Map of Weija Lake showing the sampling locations.

3.2.2 Lake Bosomtwi

Lake Bosomtwi, shown in Figure 3.3, is situated within an ancient meteorite impact crater. It is approximately 8 km across and the only natural Lake in Ghana (Koeberl et al., 2007). It is situated about 30 km south-east of Kumasi in the northern tip of the Adansi mountains in the forest zone of Ghana and is a popular recreational area. The Lake has a coordinate of $6^{o}\,30.3^{'}\ 1^{o}\,24.5'$ with a catchment area of 400 km^2. Lake Bosomtwi has maximum length of 8.6 km, maximum width of 8.1 km and surface area of 49 km^2. There are about 24 villages dotted around the Lake, with a combined population of about 70,000 people (Ghana Statistical Service, 2010). The Ashantis consider Bosomtwi a sacred Lake. According to traditional belief, the souls of the dead come here to bid farewell to the Twi god. Because of this, it is considered permissible to fish in the Lake only from wooden planks. Lake Bosomtwi is a natural inland freshwater Lake in the Ashanti Region of Ghana. The Lake exhibits a radial drainage system of 106 km^2, a diameter of about 11 km at its widest part and a maximum depth of 78 m. Lake Bosomtwi covers an area of about 52 km^2 (Turner et al., 1995). The Lake has no outlet, although it has apparently overflowed in recent geologic past (Turner et al., 1996a). Lake Bosomtwi is fed by ground water which drains into it, by ranfall and run-off. It is also believed to be fed by river Aberewa.

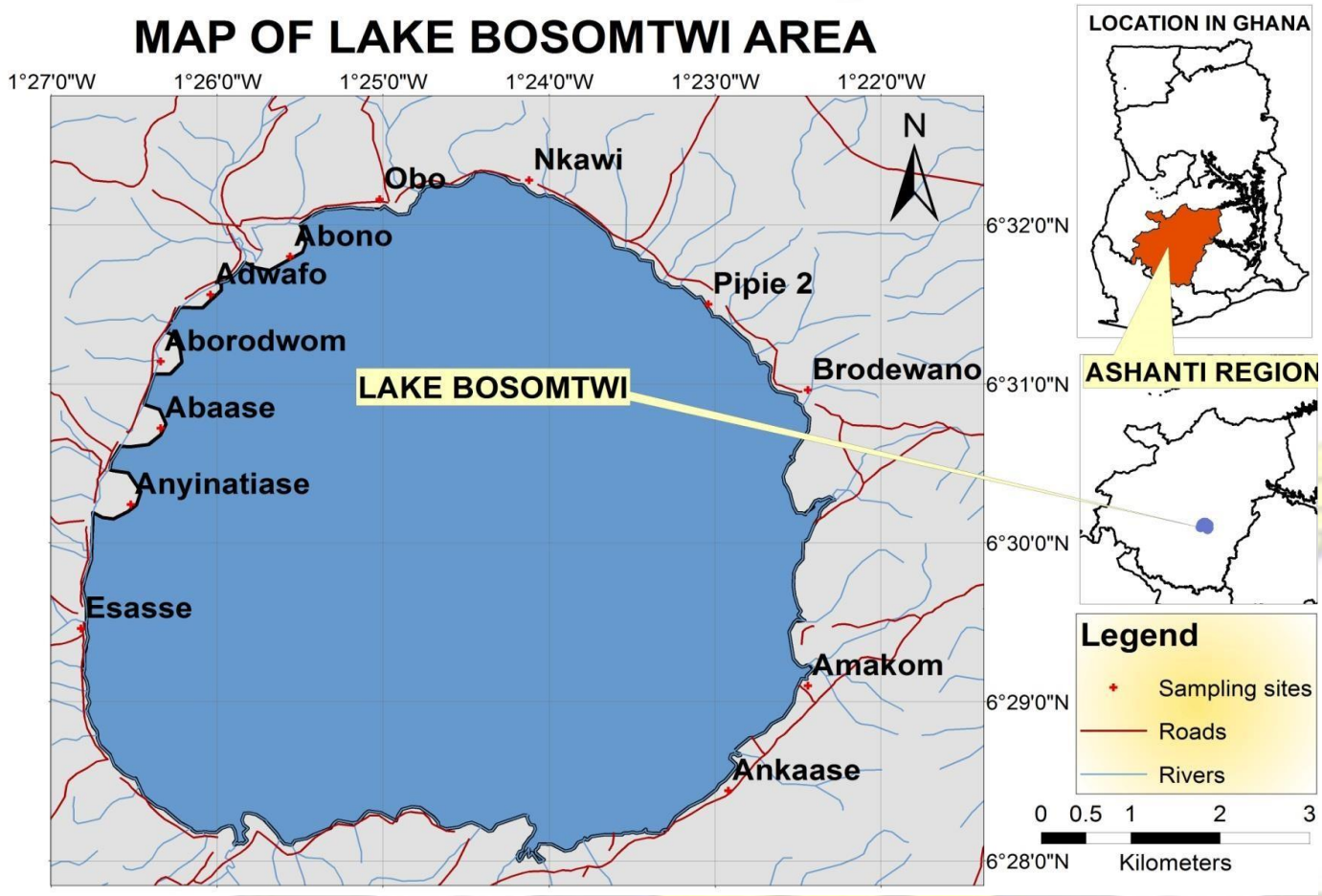


Figure 3.3: Map of Lake Bosomtwi showing the sampling locations

3.3 Chemicals and reagents

The chemicals and reagents used for the experiments were obtained from BDH, England, and Sigma-Aldrich Germany, unless otherwise stated. The extraction solvents (hexane, acetone, ethyl acetate) were of pesticide grade with purity ranging from 99.0 % to 99.8 %. The 60 -100 mesh size florisil and silica adsorbent materials used for the clean-up of extracts were obtained from Hopkin and Williams Limited, England. The organochlorine standards were from Cambridge Isotope Laboratories, incorporated and they were supplied by United Nation Environmental Program (UNEP) in Sweden in sealed ampoules. They were of 98 % to 99.5 % purity and were used without further purification. The standard reference materials, NIST-SRM 1566b (Oyster tissue) and NIST-SRM 1547 (Peach leaves), were supplied by International Atomic Energy Commission (IAEA).

3.4 Equipment and tools

Ekman grab – This is a metallic implement with a metallic chain handle which was used to sample sediments from the water bodies.

FRITSCH mortar grinder P-2 – This was used to grind the sediments and fish samples.

500 µm mesh-size sieve - This was used to screen the sediment samples to remove stones and other debris

Jaytec 100 ml separating funnel – A separating funnel used for the liquid-liquid extraction of the water samples.

AB 204-S Toledo weighing balance – For weighing of chemicals, reagents and samples.
Food Alyt RS 60 soxhlet extractor – A soxhlet extractor used for sample extraction.

Bransonic 220 ultra sonic – A sonication extractor equipment used for sample extraction.

Buchi rotavapor R – 200 – This is a rotary evaporator used for concentration of sample extracts.

GHARR-1 – Ghana Research Reactor-1 used for sample irradiation.

Gamma-ray spectroscopy system – A spectrometer with High Purity Gemanium Detector system used for counting of gamma ray emitted from irradiated samples.

Varian GC – ECD CP -3800 model and Shimadzu 2010 series GC - ECD – Gas chromatographic tools equipped with Electron Captured Detector used for the analyses of organochlorine extracts.

3.5 Cleaning of laboratory glass ware

All the sampling bottles and laboratory glass wares were washed with warm water with detergent and rinsed with deionised water. They were sealed tightly with pre-cleaned aluminum foil (Ntow, 2001). In most cases the bottles and the glass wares were cleaned immediately before use.

3.6 Sample collection

Sampling was done in 2012 from January to February and from September to October for the purpose of duplicating measurement. Fish samples used for the investigation were bought from fishermen at the sampling locations. Between twelve to fifteen samples of each fish species were bought from the fishermen as composite fish samples. Pictures of the fishes used for the study are shown in Appendix 1. The intestines

and scales of the fish were removed at the sample point to prevent decay. The fish samples were wrapped in precleaned aluminium foil and packed in ice thermo insulator box. Surface water samples were collected into 500 ml high-density polyethylene containers. At sampling point, the sampling bottle with the lid on was lowered into the water and then opened while under the water to fill the bottle and covered with the lid immediately. Sediment samples were collected at various points in the neighborhood where the water samples were collected using Ekman grab from a depth of about 20 cm. Sediment samples were wrapped in precleaned aluminium foil to prevent cross contamination and then bagged in polyethylene bags. At each sampling location, three water samples were collected as composite sample. All the samples were labeled before transportation to the laboratory.

3.6.1 Samples treatment

In the laboratory the water samples were kept in a freezer at a temperature below 0 ^{0}C, while the fish samples were first washed with deionized water then wrapped in pre-cleaned aluminium foil and stored in deep freezer. Before the fish samples were kept in the deep freezer, two samples of each species were selected for identification at the Department of Oceanography of the University of Ghana. The sediment samples were air dried and milled with pestle and mortar and sieved using 500 μm mesh size sieve to remove stones and other debris. The sieved samples were then wrapped in aluminium foil and kept at room temperature in a clean cupboard.

3.7 Preparation of powdered fish samples

Fish samples were removed from the deep freezer to thaw and rinsed several times with deionised water. Biometric data of the fish samples were taken by weighing them with electronic balance

and measuring their lengths with a ruler. Representative samples of each fish species were selected and the muscle tissues cut into pieces and subjected to freeze drying for 72 hrs. After freeze drying samples were homogenized in a warring stainless blender to obtain a homogenous dry fish sample.

3.8 Determination of sediment carbonaceous materials

Sediment carbonaceous materials, that is total organic carbon and black carbon were determined with the objective of studying the relationship between the carbonaceous materials and organochlorine availability.

3.8.1 Determination of organic carbon and organic matter of sediments

Analysis of organic carbon was based on the method of Walkley and Black modified by Page (Page, 1982). About 1 g of the sediment sample was weighed into 250 ml conical flask and 10 ml of 1 M $K_2Cr_2O_7$ solution was added to the sample in the flask and shaken to disperse the sample. Twenty milliliter (20 ml) of concentrated H_2SO_4 was then added and the content of the flask was shaken for about one minute. After allowing the mixture to stand for about thirty minutes, 10 ml of distilled water and 10 ml orthophosphoric acid were added. Finally, 2 ml barium diphenyl amine was added as indicator. The content was titrated against 0.2 M ammonium ferrous sulphate $[Fe(NH_4)_2(SO_4)_2.H_2O]$ solution until the colour changed to green. Blank determination was carried out similarly, but without the sample. Percentage organic matter was obtained by multiplying the percentage of organic carbon by the Van Bemmelen factor, 1.724. Van Bemmelen factor is used because organic matter contains 58 % carbon. The method is basically

the reduction of $Cr_2O_7^{2-}$ by organic carbon and subsequent reduction of unreduced $Cr_2O_7^{2-}$ by redox titration with Fe^{2+}. The reaction involved is as shown by the Eqn 3.1

$$2Cr_2O_7^{2-} + 3C + 16H^+ + Fe^{2+} \rightarrow 3CO_2 + Fe^{3+} + 8H_2O + 4Cr^{3+} \quad \text{.....Eqn 3.1}$$

The percentage organic carbon was calculated using Eqn 3.2 below

$$\% \text{ Organic carbon} = \frac{Vb - Vs \times M \times 0.39}{\text{Weight of sample}} \quad \text{.....Eqn 3.2}$$

V_b = titre volume (ml) of blank, V_s = titre volume (ml) of sample.

M = molarity of hydrated ferrous ammonium sulphate.

The factor 0.39 = 3 x 10^{-3} x 100 x 1.3. 3 is the equivalent weight of carbon, 1.3 is the due to 77 % recovery of carbon.

3.8.2 Black carbon

Black carbon (BC) contents were determined by treating 1 g of the sediment thrice with 2 M HCl solution to remove any inorganic carbon, after which the sample was heated at 400 ^oC for 18 hours using Thermo Scientific Furnace (Gustafsson et al., 2001). Thermally labile organic matter is removed during heating and the remaining fraction of organic carbon (OC) is recognized as BC (Zhang, 2013).

3.9 Validation of INAA method

The INAA method was validated by determining the precision and accuracy of the method using two certified standard reference materials, NIST – SRM 1547 (peach leaves) and NIST – SRM 1556^b (oyster tissue).

3.9.1 Determination of precision and accuracy of INAA

Accuracy and precision of the INAA method were determined by analyzing the two standard reference materials, NIST – SRM 1547 (peach leaves) and NIST – SRM 1556^{b} (oyster tissue). Accuracy was calculated as percentage relative error while, precision was computed as percentage relative deviation. Two hundred milligram (200 mg) of the SRM was weighed unto polyethylene sheets, wrapped and heat sealed. Samples were irradiated in the Ghana Research Reactor – 1 (GHARR-1) at the Ghana Atomic Energy Commission, operating at a power of 15 KW at a neutron thermal flux of 1 x 10^{11} ncm^{2} S^{-1}. Samples were transferred into irradiation sites via pneumatic transfer system at a pressure of 60 psi. The irradiation was categorized according to the half-life of the element of interest. The reaction of interest for this work is as presented by Eqn 3.3

$$^{37}Cl + ^{1}n \rightarrow ^{38}Cl + \gamma \quad \text{.....Eqn 3.3}$$

^{38}Cl is a short lived radionuclide with half-life of about 37.3 minutes; samples were therefore irradiated for 120 seconds after which radioactivity measurement of induced radionuclide was performed by a PC-based γ -ray spectrometry and counting was done for 10 minutes.

3.9.2 Counting of irradiated samples

The irradiated certified SRM were counted by using a computer based gamma-ray spectroscopy system, consisting of an N-type High Purity Germanium (HPGe) Detector model GR 2518 mounted on liquid nitrogen as a coolant, high voltage power supply model 3103, spectroscopy amplifier model 2020, ACCUSPEC multi-channel analyzer simulation software card (all manufactured by Canberra industries inc.), and a micro computer for data acquisition, evaluation

and analysis. The qualitative and quantitative analysis of the Cl nuclide was achieved using the ORTEC MAESTRO 32 and spreadsheet based program developed based on the relative comparator method as described by Eqn 3.4 below.

$$\rho sam = \frac{\left[\left(\frac{PA}{tc}\right)CD\right]sam[\rho W]std}{\left[\left(\frac{PA}{tc}\right)CD\right]std.Wsam} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eqn 3.4}$$

3.10 Determination of total chlorine of Lake water, sediment and fish samples

About 2 ml of the water sample was filtered using Whatman No. 42 into 10 ml cleaned glass container of which 200 mg was weighed into vial and the vial was placed in a capsule and heat sealed. For the sediment and fish samples, 200 mg was weighed into polyethylene sheets, wrapped and heat sealed and irradiation for the determination of total chlorine content by instrumental neutron activation analysis (INAA). Samples were irradiated in the Ghana Research Reactor (GHARR-1) at the Ghana Atomic Energy Commission as described per section 3.9.1 and irradiated samples counted as described per section 3.9.2.

3.11 Determination of extractable organochlorine in water

Liquid-liquid extraction with as solvent was used for the extraction of the extractable organochlorine (EOC) from the water samples. Twenty milliliter portion each water sample was shaken with 20 ml of hexane as extraction solvent in 100 ml separating funnel. The hexane extract (organic layer) was separated from the aqueous layer. Extraction was repeated three times and the

organic layers were then put together. Extract was then concentrated to about 5 ml and quantitatively transferred into 10 ml vial for INAA analysis as described in sections 3.9.1 and 3.9.2.

3.12 Optimization of sonication method of extraction

The sonication method for extraction of OCs was optimized by determining the optimum sonication time. This was done by determining the corresponding yield of organochlorines on sonicating for 0.5, 1.0, 2.0, 3.0, 4.0 and 5 hours. The time of sonicating which gave optimum yield of the tested organochlorines was then selected. Figure 3.4 shows fume hood containing the 220 Bransonic ultra sonic bath that was optimized.

Figure 3.4: Fume hood containing the Bransonic 220 ultra sonic bath and Alyst Rs 60 soxhlet extractor used for extraction.

3.13 Determination of extractable organochlorine in sediment and fish samples

Extractable organochlorine (EOC) in samples waa extracted by sonicating 2.5 g of the sample for 3 hours at 40 ^{o}C with 50 ml of 3:1 hexane/acetone solvent system after. The residual sediment and fish samples after filtration were dried at room temperature and packed in precleaned aluminium foil for determination of bound organochlorine (BOC). Extracts were subjected to INAA as described per section 3.9.1 and 3.9.2 for determination of EOC.

3.14 Determination of bound organochlorine (BOC)

The samples that were kept for determination of BOC were washed several times with distilled water and 0.1 M $NaNO_3$ solution (Ivanora and Aneva, 2008) to remove any residual inorganic chlorine which might be present in the samples. The samples were then dried at room temperature and then subjected to irradiation and neutron actvation analysis as per sections 3.9.1 and 3.9.2.

3.15 Validation of GC-ECD methodology

3.15.1 Precision and accuracy

The precision and accuracy of the GC method were determined by analyzing 10 ng/ml of organochlorine standard. A 1µl of standard was injected for each measurement and

concentrations of the OCPs in the injected standard as reported by the GC were recorded. Four independent runs were carried out. Precision and accuracy were computed as percentage relative deviation and percentage relative error respectively.

3.15.2 Linearity (working range)

Calibration curves for the oganochlorines were developed by analyzing mixed standard of OCs in concentration range of 0.01 µg/ml to 0.30 µg/ml. Regression lines involving the peak area of the organochlorine compounds and corresponding concentrations were made. Sample calibration curves are presented in Appendix 3.

3.15.3 Minimum detectable quantities (MDQ)

Minimum detectable quantity considered as the smallest quantity of the standard material resulting in definite peak three times the baseline peak was obtained by analyzing various amount of OCs standard in a range of 0.1 – 0.001 ng. The amount of OC whose chromatogram was equal to three times the signal to noise peak was considered as the MDQ.

3.16 Analysis for organochlorine pollutants

Analysis of individual OCps and indicator PCBs was done by first extracting the OCs from the samples followed by extract clean up and final determination by the GC-ECD method.

3.16.1 Extraction of organochlorine pesticides and polychlorinated biphenyls

Hexane as solvent was used for extraction of OCs from the water samples as described per section 3.11 while the sediment and fish samples were sonicated on ultra sonic bath as described per section 3.13. After extraction and concentration, extracts were cleaned up to remove coextractives.

3.16.2 Combined florisil-silica clean up of extracts

Florisil-silica clean up columns were prepared by packing 1.5 g and 0.5 g pre-activated florisil and silica adsorbent material respectively with 1.0 g anhydrous sodium sulphate packed on top of the adsorbents in glass column (Figure 3.5). The packed columns were each conditioned with 10 ml of hexane prior to clean up after which the extracts were passed through the columns and the eluate collected into 50 ml conical flask. The column was further eluted, first with 15 ml hexane followed by 5 ml of 2:1 hexane/diether.

Figure 3.5: Set up for the clean up of extracts.

3.16.3 Gas chromatography analysis

The GC-ECD was Shimadzu 2010 series (Figure 3.6) was used for analysis. The operation conditions were; capillary column: Restek Rtx, 30m x 0.25mm x 0.25µm, temperature programme: 80^0C (2min) to 200^0C (15 min) at 4^0C/min, injector temperature: 225^0C, detector temperature: 300^0C, carrier gas: nitrogen at 1.0ml/min, make up: nitrogen at 29ml/min. The organochlorines were identified quantified by external standard method.

Figure 3.6: Shimadza 2010 series GC-ECD facility in the organic laboratory of NCERC, GAEC.

3.17 Risk assessment of organochlorine pollution

Risk assessment of organochlorine pollution was achieved by determining ecotoxicological impact of sediment to aquatic species and health implications to humans on drinking of water and eating of fishes from the water bodies based on the measured organochlorines.

3.17.1 Ecotoxicology impact of sediment to aquatic species

Ecotoxicological impact of sediment to aquatic species due to OC pollution was assessed by using two sediment quality criteria specified by United State Environmental Protection Agency (USEPA, 1997) and Canadian Council of Ministry for Environment (CCME, 2002). The sediment quality guidelines were Effect Range Low (ERL) and Effect Range Median (ERM).

ERL is the value at which toxicity will begin to be observed in sensitive aquatic species, while ERM is the value above which adverse effect will be noticed in aquatic species. Average OC concentrations in the sediments were then compared to ERL and ERM values.

3.17.2 Impact of organochlorine pollution to humans.

The impact of organochlorine pollutants to human was studied by comparing measured OCs to maximum residue limits and estimating daily intake or exposure of OCs as a result of consumption of the fishes as well as estimating carcinogenic and non carcinogenic hazard ratios.

3.17.2.1 Comparison of organochlorine to maximum residue limits.

Mean individual organochlorine concentrations computed in the water and fish compartments were compared to maximum residue limits (MRLs) of international bodies such as World Heath

Organization (WHO), European Union (EU), Austrian and Food and Agricultural Organization (FAO).

3.17.2.2 Estimated daily intake (EDI) of organochlorines through eating of the studied fishes.

The dietary intake of OCs through consumption of the fish samples were computed by multiplying the individual organochlorine concentration in each fish species by the rate of fish consumption which is estimated at 68.5 g/day (Global Fish Alliance, 2010). Mean organochlorine concentrations recorded were used in the computation. Daily exposure to organochlorine through consumption of fish was computed by the Eqn 3.6 described below

$$\text{EDI} = \text{mean OC concentration x rate of fish consumption} \quad \text{Eqn 3.6}$$

EDI through consumption of studied fishes is in µg/kg body wt, mean OC concentration in µg/g and rate of fish consumption in g/kg body wt/day.

The following assumptions were adopted from the U.S Environmental Protection Agency's guidelines (USEPA, 1998, USEPA, 1996).

1) A hypothetical body weight of 30 kg for children (2 - 11 yrs) and 70 kg for adults.

2) Maximum absorption rate of 100% and a bioavailability rate of 100%.

The estimated daily intake or exposures computed were then compared to available USEPA reference doses.

3.17.2.3 Carcinogenic hazard ratio.

Cancer hazard ratios (HRs) for the organochlorine pollutants in the fish investigated were calculated by dividing the average daily intake (EDI) or exposure by the cancer benchmark concentrations (Dougherty et al., 2000; Jiang et al., 2005). Cancer HR and cancer benchmark concentrations were calculated by the equations 3.7 and 3.8 respectively.

$$\text{Carcinogenic HR} = \frac{\text{average daily exposure}}{\text{cancer benchmark conentration}} \quad \text{Eqn 3.7}$$

$$\text{Cancer benchmark concentration} = \frac{\text{cancer risk x body weight}}{\text{rate of fish consumption x cancer slope factor}} \quad \text{Eqn 3.8}$$

where risk is the probability of lifetime cancer risk, which has been put to one in one million (1/1,000,000) of the population by USEPA (Dougherty et al., 2000). the estimated cancer benchmark concentrations, carcinogenic HRs were estimated for the pollutants in the fish species.

3.18 Data analysis

Statistical analyses used for the data analysis include subjecting the measured organochlorine data to descriptive statistics for the deduction of minimum, maximum and mean concentrations of detected organochlorines. Data was further subjected to variance to determine the differences in organochlorine compounds detected.

3.19 Analytical quality assurance/control.

In an effort to obtain results that are accurate and reproducible in these analyses, a number of quality control measures were ensured; from the initial sampling process to the final analyses of

the samples using INAA and GC-ECD equipment. Precautions were taken to reduce contamination during the handling and preparation of samples. As mentioned earlier in this work, all reagents were of analytical grade and sample containers and apparatus were washed and rinsed thoroughly prior to their use. Since reagents could be reliable sources of contamination in analytical work, high purity reagents and distilled water were used in this work. Again, reagent blanks were analyzed where appropriate. The concentrations reported in this work were thus actual concentrations of the samples relative to the reagent blanks. Internal standards, thus PCB 18 for PCBs, and lambda cyhalothrin for OCPs were spiked into samples before extraction for recovery evaluation during the whole analytical procedure. Recovery was calculated using Eqn 3.9

$$\text{Recovery} = \frac{\text{concentration of internal standard recovered}}{\text{level of spiking}} \text{ x } 100 \ldots\ldots\ldots\ldots\ldots \text{Eqn 3.9}$$

Blank samples were prepared and analyzed in the same manner as the samples in each batch of analysis in order to check the possibility of interference or contamination. Sampling and sample analyses were performed in duplicate, unless otherwise specified. In some cases, batches of samples were analyzed two to three times in order to assess the homogeneity of samples. The INAA was validated by analyzing standard reference materials (SRMs), NIST – SRM 1547 (peach leaves) and NIST – SRM 1556^{b} (oyster tissue) and the accuracy and precision of the INAA method were then computed as percentage relative error and percentage relative deviation respectively. For the GC- ECD method standards were run to check column performance and resolution. The GC-ECD method was tested by analysis of soil samples which had been fortified with OCs standards.

3.20 Safety and good laboratory practice.

Organochlorines are toxic to human health and potentially carcinogenic. All standards containing organochlorines and sample extracts were kept in sealed glassware in a freezer dedicated for chemical and sample storage. Organochlorines standards, sample extracts, solvents and any other harmful chemicals were handled under a fume hood with good ventilation. Personal protection, including laboratory coat and gloves and safety goggles were worn in the laboratory where necessary.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

The results obtained from the validation of Instrumental Neutron Activation Analysis (INAA) and GC-ECD methods as well as results of analyses of water, sediment and fish samples from the study areas for indicator polychlorinated biphenyls and organochlorine pesticides are presented and discussed in this chapter. Results of risk assessment of OC pollution to aquatic species and humas are also presented and discussed.

4.2 Biometric data and feeding habits of the fish species.

The biometric data on the fish species used for the investigation as well as their feeding habits are presented in Table 4.1. In all seven fish species, three species from Lake Bosomtwi and four from the Weija Lake were analyzed. The species from Lake Bosontwi were all tilapia while for those from the Weija Lake, three were tilapia and the other one was a catfish. The fish species from Lake Bosomtwi were identified to be *Tilapia busumana, Hemischromis faciatus* and *Sarotherodon galileu*, while those from Weija Lake were *Tilapia Zilli, Tilapia galilaea, Tilapia nile* and *Clarias gariepinus*. The average lengths of the species from Bosomtwi were almost the same. However, in terms of average weight *Hemischromis faciatus* were quite bigger than *Sarotherodon galileu*. *Tilapia busumana,* also from Lake Bosomtwi, was however, bigger compared to the other two species, thus *Hemischromis faciatus* and *Sarotherodon galileu*. The length and weight of fish

species from Lake Bosomtwi ranged from 9.50 cm to 17.50 cm and 14.80 g to 64.30 g respectively. The average length and weight of the species from Weija Lake on the other hand, ranged respectively, from 12.35 cm to 42.73 cm and 36.56 g to 231.50 g. The species, *Clarias gariepinus* were longer and heavier than the other three tilapia species from the Weija Lake. Anim (2008) reported an average length and weight in a range of 24.30 cm to 46.70 cm and 216.00 g to 712.80 g, respectively, for fish samples collected from Manheam in the

Weija Lake. Obviously, the sizes of the fishes used for this study are smaller than those of Anim (2009). This to an extent confirms report of fishermen on the Weija Lake about fish size reduction over time. In general, however, fish samples from the Weija Lake were far bigger than those from Bosomtwi. Indeed, the average weight difference between species from Weija and Bosomtwi was about 99.16 g. The general decline in the sizes of the fish from the water bodies over time may be attributed to over fishing.

Table 4.1: Biometric data of the fish species and their feeding habits.

	Average length (cm)	Range(cm)	Average weight(g)	Range (g)	Feeding habits
Bosomtwi species					
Tilapia busumana	16.80±1.22	17.50 – 15.90	68.0±5.22	64.30 – 71.40	Feed on phytoplankson, algae, destritus[1]
Hemischromis faciatus	11.60±0.52	10.90 – 12.90	23.6±1.67	19.50 – 28.60	Feed on blue green algae, green algae, diatom[2]
Sarotherodon galileu	10.60±0.56	9.50 – 11.50	18.3±1.34	14.80 – 22.50	Feed on phytoplankson, diatom
Weija species					
Tilapia zilli	12.35±0.78	11.2 - 13.2	36.58±2.88	22.65 - 43.02	Feed on phytoplankton, detritus, algae[1]
Tilapia galilaea	17.73±1.52	16.10 - 19.70	126.63±16.18	110.57 - 152.82	Feed on phytoplankton, algae, destritus[3]
Tilapia nile	20.10±1.66	20.10 - 21.22	148.35±17.44	140.58 - 157.60	Feed on phytoplankson, zooplankton zoobenthos, detritus
Clarias gariepinus	42.73±5.36	41.50 - 47.50	231.50±20.48	221.70 - 242.80	Zoobenthos, insects, crustaceans, mollusk,worms, rotifers, detritus[1]

[1]Kuranchie-Mensah et al (2011), [2]Onyeche et al (2013), [3]Spataru (1976)

4.3 Sediment carbonaceous materials

Table 4.2 presents the results of the studied carbonaceous materials, that is total organic carbon (TOC) and black carbon (BC) contents in the sediments. Total organic carbon reported in percentages ranged from 0.43 to 4.43 and 0.05 to 2.11 in the Weija and Bosomtwi sediments respectively, with the corresponding black carbon were 0.04 to 0.49 and 0.01 %to 0.23 . The maximum TOC value, 4.43 % was recorded in sediment from Manheam, a fishing community in the catchment of the Weija Lake. Analyses of the results showed that the ratios of TOC to BC in the sediments were in the range of 5.0 to 11.25 with an average value of 9.37 and 9.03 in Weija and Bosomtwi sediment compartments respectively. Thus, on the average the composition of TOC in the sediment was about 9.00 times higher than the corresponding BC content. In general, the results suggest that the higher organic carbon composition, the higher the corresponding black carbon ccontent.

Table 4.2: Organic carbon and black carbon compositions in sediments

Sampling sites	Total organic carbon (TOC) (%)	Organic matter (%)	Black carbon (BC) (%)	TOC/BC
Weija				
water works	2.07±0.32	3.57	0.22±0.08	9.41
Machigeni	2.41±0.12	4.16	0.26±0.06	9.25
Amanfro	1.88±0.33	3.25	0.21±0.06	8.95
Manheam	4.43±0.52	7.63	0.49±0.09	9.04
Domeabra	1.42±0.16	2.45	0.15±0.03	9.47
Afuaman	1.63±0.59	2.81	0.18±0.05	9.06
Agbozume	0.45±0.09	0.78	0.05±0.02	9.00
Jomo	0.43±0.05	4.43	0.04±0.07	10.75
Bosomtwi				
Esasse	1.00±0.22	1.72	0.12±0.09	8.33
Anyinatiase	1.82±0.45	3.14	0.19±0.05	9.58
Abaase	0.52±0.08	0.89	0.05±0.08	10.40
Aborodwom	0.45±0.10	0.78	0.04±0.02	11.25
Obo	0.35±0.07	0.60	0.04±0.01	8.75
Nkwi	0.05±0.02	0.09	0.01±0.00	5.00
Pipie 2	2.11±0.19	3.64	0.23±0.03	9.17
Brodekwamo	0.57±0.10	0.98	0.06±0.03	9.50
Abonu	0.63±0.11	1.09	0.06±0.02	10.50
Adwafo	0.39±0.08	0.67	0.05±0.02	7.80
Amakom	0.19±0.06	0.33	0.02±0.00	9.50
Ankaase	0.26±0.05	0.45	0.03±0.01	8.66

4.4 Validation of Instrumental Neutron Activation analysis (INAA) method for determination of extractable and bound organochlorine

The results obtained from the validation of INAA method by analysis of certified standard reference materials are presented in Table 4.3. Validation of the INAA method was achieved by analyzing two certified reference materials and computing for the precision and accuracy. Uncertainties

associated with the measurements are mean deviations based on replicate determination of each certified standard reference material (SRM). Results of the present study were compared with the reported values for the two standard reference materials. The reported and the measured values within the limit of experimental errors agreed favourably (Table 4.3) The accuracy of the method for the determination of chlorine nuclide was computed as percentage relative error and was within 4 % while that of the precision calculated as percentage relative deviation was within 3 %. The method was, however, more precise for determination of chlorine content in NIST-SRM (Oyster tissue) with 1.35 % precision compared to NIST-SRM

1547 (Peach leaves) with 2.80 % precision. The nuclear data for determination is presented in Appendix 2.

Table 4.3 Analysis of SRM for determination of precision and accuracy of INAA

Reference material	Measured (mg/kg)	Reported (mg/kg)	Precision (%)	Accuracy (%)
NIST-SRM 1566b (Oyster tissue),	0.494±0.007	0.514±0.01	1.35	3.89
NIST-SRM 1547 (Peach leaves),	366.3±8.060	360.0±19	2.80	- 1.75

4.5 Validation of GC – ECD methods for the determination of organochlorine compounds.

4.5.1 Linear (working) range data for the organochlorine compounds.

Table 4.4 shows the data obtained for the linear (working) range determination of the organochlorines compounds. The data shows the linear range, the regression equation and the coefficient of correlation (R^2) between the concentrations and the peak areas. The coefficient of correlation (R^2) between the concentration and peak area were greater than 0.90. Thus, R^2 varied from 0.955 for heptachlor to 0.999 for PCB 28, and these indicate good correlation between concentrations and peak areas in the linear or working range. In all, the linear range concentrations were between 0.01 – 0.25 μg/ml. The difference in the linear range for the compounds shows the differences in the electron capture detector (ECD) response factors to the individual compounds. The linear range (0.01 μg/ml to 0.25 μg/ml) obtained for the compounds suggests that ECD has quite wide linearity. This result does not confirm or support the findings of Booij et al (2008). Booij et al (2008) reported that electron capture detectors (ECDs) have limited linear calibration range. Sample calibration curves for the determination of the OCs indicating the linear range, regression equation and correlation between concentration and peak area are presented in Appendix 3.

Table 4.4: Data for the linear range determination of the organochlorine compounds

Compounds	Linear range (µg/ml)	Calibration equation	Coefficient of correlation (R^2)
PCB 28	0.01 - 0.25	y = 10.87x+ 1.136	0.999
PCB 52	0.01 - 0.10	y = 5.150x+ 1.041	0.998
PCB 101	0.01 - 0.10	y = 9.505x+ 1.114	0.981
PCB 153	0.01 - 0.20	y = 19.99x+ 2.310	0.997
PCB 138	0.01 - 0.20	y = 13.19x+ 2.320	0.985
PCB 180	0.01 - 0.15	y = 36.42x+ 2.429	0.998
γ-HCH	0.01 – 0.15	y = 23.36x+ 0.254	0.985
β-HCH	0.01 – 0.15	y = 0.363x+ 0.005	0.993
δ-HCH	0.01 – 0.15	y= 13.41x+ 0.233	0.995
α-endosulfan	0.01 - 0.20	y= 1.768x+ 0.041	0.993
β-endosulfan	0.01 - 0.20	y= 0.449x+ 0.015	0.985
Endosulfan sulfate	0.01 - 0.20	y= 10.91x+ 0.218	0.968
Aldrin	0.01 – 0.10	y= 13.18x+ 0.434	0.980
Heptachlor	0.01 – 0.15	y= 7.865x+ 0.355	0.955
P,P^1-DDT	0.01 – 0.20	y= 9.157x+ 0.443	0.968
P,P^1-DDE	0.01 – 0.20	y= 5.820x+ 0.191	0.985
Methoxychlor	0.01 – 0.15	y= 6.230x+ 0131	0.987

4.5.2 Minimum Detectable Quantities

The Minimum Detectable Quantity (MDQ) is considered as the smallest quantity of the standard material resulting in a definite peak or chromatogram three times the baseline peak (Afful et al, 2010). The results, which suggest the suitability and sensitivity of the GC method for the dare presented in Table 4.5. Minimum Detectable Quantity obtained for the compounds ranged from 0.0005 ng to 0.008 ng. The results (Table 4.5) suggest that the detector relatively detected small quantities of polychlorinated biphenyl (PCBs) compared to the persistent organochlorine pesticides. For the organochlorine pesticides, detectability of 0.004 ng was achieved for γ-HCH, α-HCH, aldrin and dieldrin. It is obvious that the method could detect small quantities of the PCBs as the number of chlorine atoms bonded to the biphenyl increases. For example, the detector could respond to small quantity of PCB 180 with seven chlorine atoms compared to PCB 153 and 138, both with 6 chlorine atoms. PCB 18 and PCB 28 both with three chlorine atoms attached to the biphenyl had MDQ of 0.002 ng. When the results of this study were compared to those of Balinova et al (1996), this method is more detectable to the organochlorines. The differences could be attributed to the use of different columns. In this investigation, separation was achieved by Restek Rtx capillary column whereas, Balinova et al

(1996) used packed column containing 3 % OV-225 + % % SE -52 on chromosorb W AW DMCS 80 – 100 mesh. Capillary columns are generally, more sensitive than packed columns.

Table 4.5: Minimum detectable quantities for the OCs measured with Shimadzu 2010 GC-ECD with capillary column, Restek Rtx, 30m x 0.25mm x 0.25µm, temperature programme: 80^0C (2min) to 200^0C (15 min) at 4^0C/min, injector temperature: 225^0C, detector temperature: 300^0C.

Organochlorines	Amount (ng)	Balinova et al (1996)
γ-HCH	0.004	0.01
α-HCH	0.004	0.01
Aldrin	0.004	
Dieldrin	0.004	
α-endosulfan	0.002	
β-endosulfan	0.002	
p,p' DDT	0.008	0.02
p,p' DDE	0.005	0.02
Heptachlor	0.002	
PCB 18	0.002	
PCB28	0.002	
PCB 52	0.002	
PCB 101	0.001	
PCB 138	0.001	
PCB 153	0.001	
PCB 180	0.0005	

4.5.3 Precision and accuracy for GC – ECD determination of the organochlorines

Table 4.6 shows the results of precision and accuracy of the GC-ECD method. For four independent determinations at spiking levels of10.0 μg/kg, the precision and accuracy calculated

as percentage relative deviation and percentage relative error respectively varied from 3.4 % to 9.5 % and -9.0 % to 4.0 % . The low precision of 9.5 % was obtained for α – endosulfan and p,p' -DDE, while the low accuracy of -9.0 % was recorded for p,p'-DDE. The accuracy of -9.0 % means that the mean value of 10.9 µg/kg estimated for p.p'-DDE is 9.0 % higher than the spiking level of 10.0 µg/kg. The coefficient of variation (CV) for determining the compounds ranged from 0.06 to 0.16. The results of the CV suggest that for instance, there was smaller variation in the determination of dieldrin (CV of 0.06) compared to α- HCH (CV of 0.16). Figure 4.1 illustrates the correlation between the precision of the method and the coefficient of variation while Figure 4.2 also shows the correlation between accuracy and coefficient of variation. Correlation between precision and coefficient of variation yielded R^2 of 0.8014 (Figure 4.1). On the other hand correlation between accuracy and coefficient of variation gave R^2 of 0.093 (Figure 4.2). Margin of errors associated with the mean of the measured organochlorines ranging from 0.42 to 1.06 are standard deviations.

Table 4.6: Precision and accuracy of GC method for the determination of OCPs

Compounds	mean(ng/g)	CV	precision (%)	accuracy (%)
α - HCH	10.4±1.06	0.10	4.6	-4.0
γ - HCH	10.1±0.88	0.09	3.9	-1.0
heptachlor	10.6±0.94	0.09	6.4	-6.0
aldrin	10.1±0.84	0.08	5.2	-1.0
α-endosulfan	9.9 ± 1.36	0.14	9.5	1.0

β-endosulfan	10.7±0.83	0.08	5.8	-7.0
dieldrin	10.5±0.58	0.06	3.8	-5.0
p,p-DDT	10.4±0.78	0.08	5.3	-4.0
p,p-DDE	10.9±1.55	0.14	9.5	-9.0
PCB 28	10.5±0.80	0.10	8.3	-5.0
PCB 52	9.6± 0.42	0.07	3.4	4.0
PCB 101	9.8±0.49	0.07	3.8	2.0
PCB 138	10.8±1.02	0.11	9.0	-8.0
PCB 153	10.4±0.84	0.12	8.4	-4.0
PCB 180	10.3±0.81	0.09	7.5	-3.0

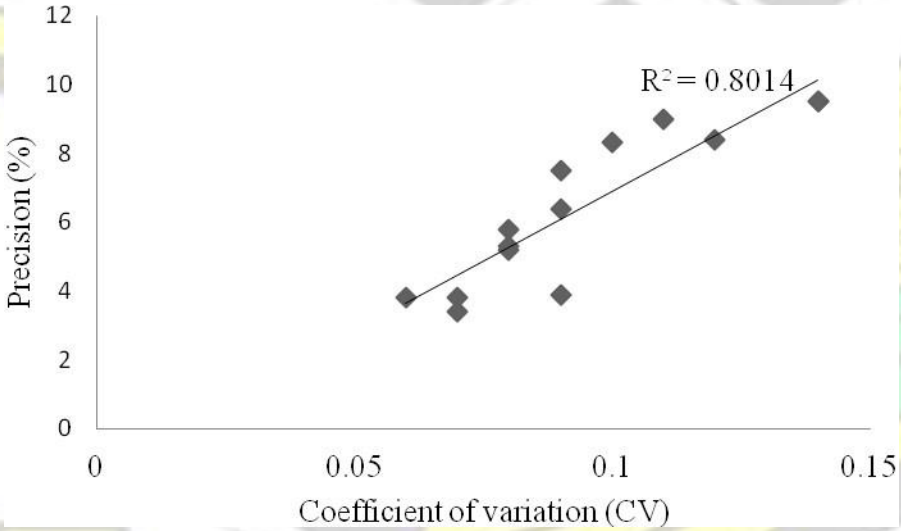


Figure 4.1: Correlation between precision and coefficient of variation for GC-ECD determination of the compounds.

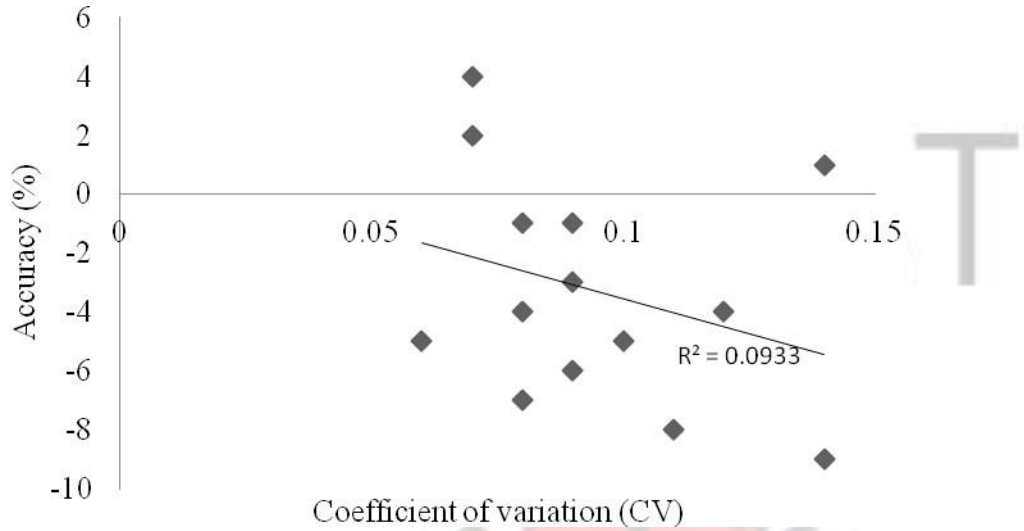


Figure 4.2: Correlation between accuracy and coefficient of variation for GC-ECD determination of the compounds.

4.6 Optimization of the sonication method

Figure 4.3 shows the results when the sonication method was optimized by varying the sonicating times between 0.5 hours to 4 hours. The results as presented in Figure 4.3 indicated that generally, higher yield was obtained when the organochlorines in fortified samples were sonicated for 3 hours at 40ºC. The yields of almost all the OCs begin to decline after three hours of sonication. Therefore, sonication time of three hours was therefore adopted.

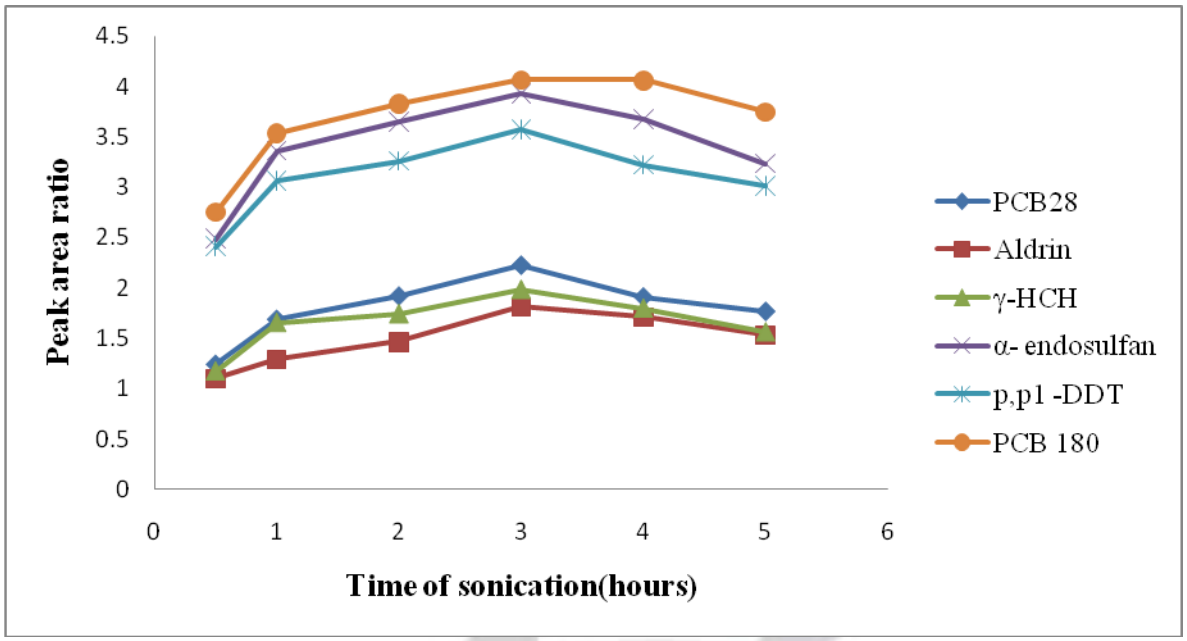


Figure 4.3: Yields of organochlorines by sonicating on ultrasonic bath at 40^0 C

4.7 Extractable and bound organochlorine.

Table 4.7 shows the results obtained when the INAA method was applied to determine extractable organochlorine in the water and sediment samples. Also presented in Table 4.7 are the mean concentrations of bound organochlorine in the sediments. The level of extractable organochlorine ranged from 0.53 mg/L to 0.97 mg/L averaging 0.71 mg/L and from 0.08 mg/L to 0.56 mg/L averaging 0.39 mg/L in Weija and Bosomtwi water compartments respectively. In the case of the sediment compartments, the average extractable organochlorine contents from the Weija and Bosomtwi were respectively, 3.57 mg/kg and 3.28 mg/kg. The average bound organochlorine content in the sediments from Weija Lake was 0.48 mg/kg while those from Lake Bosomtwi averaged 0.46 mg/kg. Bound organochlorine compositions in the sediments from the two water bodies were, therefore, almost the same. Figures 4.4 and 4.5 compare the EOC in the water and

sediment compartments as well as the BOC in the sediment compartments. Clearly, EOC was highest in the sediment compartments in both Weija and Bosomtwi. In Weija, EOC in the water was slightly higher than BOC in the sediments. However, in Bosomtwi, the two were almost the same as shown in Figure 4.5.

Table 4.8 also presents the extractable, bound (unxetractable) and total organochlorine content of the fish samples. Organochlorine content in the fish species from the Weja Lake varied from 6.89 mg/kg to 9.02 mg/kg for extractable organochlorine and 0.22 mg/kg to 0.34 mg/kg for the bound organochlorine. On the other hand, extractable and bound organochlorine compositions in the fish species analyzed from Lake Bosomtwi ranged from 3.99 mg/kg to 4.63 mg/kg and 0.10 mg/kg to 0.13 mg/kg respectively. The results, therefore, show that levels of extractable and bound organochlorine in the fish species sampled from Weija Lake were quite higher compared to those from Lake Bosomtwi. The difference could be attributed to the difference in size of the fish species. In terms of size, species from Weija Lake were bigger than those from Bosomtwi. Bigger fish samples in Weija Lake are likely to have higher fatty content and are therefore, susceptible to bioaccumulating more OCs than those from Bosomtwi as evident in a correlation plot of fish size and OC concentration (Figure 4.10).

Table 4.7: Extractable OC in water and sediments as well as bound OC in sediments

Sampling locations	Extractable OC in water (mg/L)	Extractable OC in sediment (mg/kg)	Bound OC in sediment (mg/kg)
Weija			
water works	0.84±0.03	4.36±0.33	0.63±0.02
Machigeni	0.67±0.02	3.22±0.31	0.39±0.02
Manheam	0.97±0.11	4.39±0.29	0.57±0.03
Amanfro	0.83±0.14	4.57±0.42	0.61±0.02
Domeabra	0.57±0.03	2.60±0.22	0.31±0.04
Afuaman	0.64±0.03	2.75±0.45	0.37±0.03
Agbozume	0.53±0.04	2.66±0.38	0.23±0.02
Jomo	0.63±0.05	3.99±0.44	0.63±0.04
Bosomtwi			
Esasse	0.48±0.03	2.47±0.23	0.48±0.04
Anyinatiase	0.51±0.03	2.44±0.21	0.39±0.04

Abaase	0.34±0.02	2.83±0.36	0.47±0.03
Aborodwom	0.20±0.02	8.18±0.56	0.33±0.02
Obo	0.20±0.01	3.88±0.34	0.53±0.08
Nkowi	0.19±0.02	2.37±0.29	0.36±0.06
Pipie 2	0.56±0.04	1.71±0.22	0.31±0.02
Brodekwamo	0.11±0.01	2.83±0.25	0.44±0.04
Abonu	0.32±0.01	3.02±0.32	0.39±0.05
Adwafo	0.26±0.01	2.96±0.25	0.69±0.06
Amakom	0.31±0.02	3.59±0.37	0.56±0.05
Ankaase	0.08±0.01	3.05±0.33	0.63±0.05

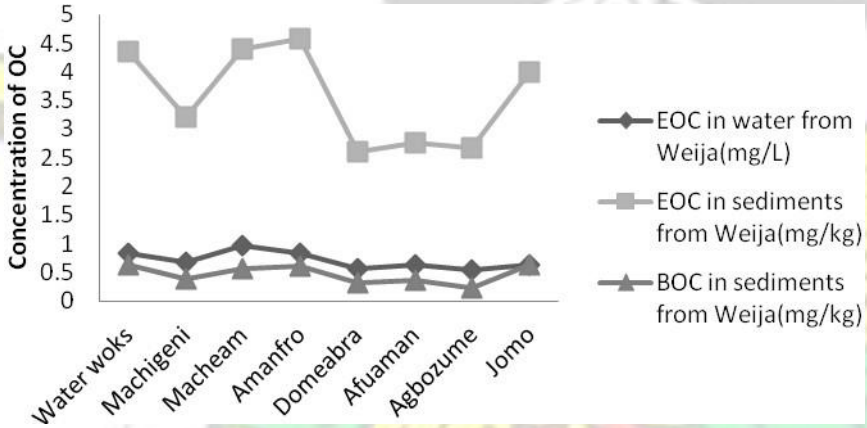


Figure 4.4: Comparison of OC types in water and sediment compartments in Weija

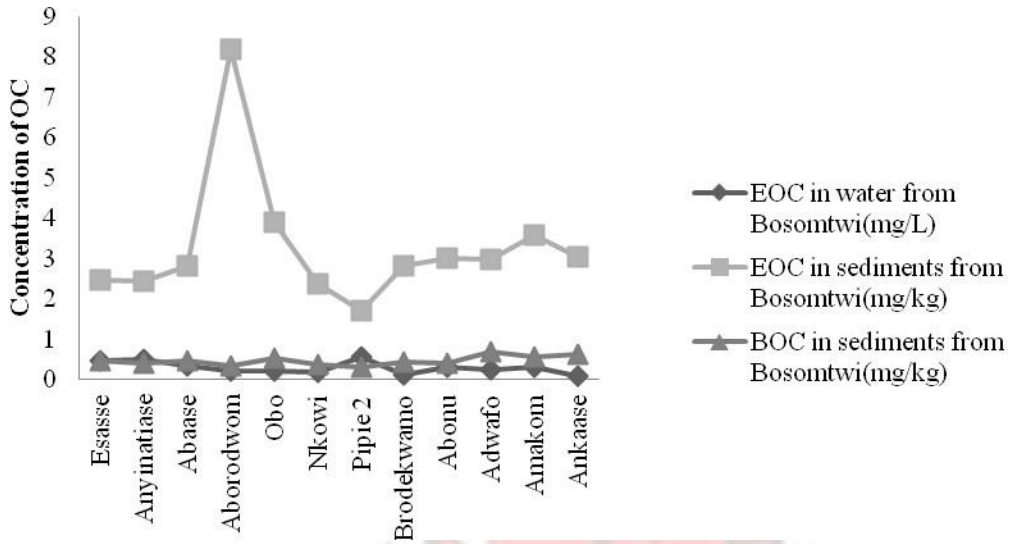


Figure 4.5: Comparison of OC types in water and sediment compartments in Bosomtwi Table 4.8: Extractable, bound (unextractable) and total organochlorine (mg/kg) in fish samples

Fish samples	Extractable organochlorine	Bound organochlorine	Total organochlorine
Weija species			
Tilapia zilli	8.93±0.32	0.25±0.05	9.18±0.37
Tilapia galilaea	9.02±0.20	0.34±0.03	9.36±0.23
Tilapia nile	7.82±0.13	0.25±0.03	8.07±0.16
Clarias gariepinus	6.89±0.22	0.22±0.02	7.11±0.24
Bosomtwi species			
Tilapia busumana	4.63±0.20	0.12±0.03	4.75±0.23
Hemischromis faciatus	4.87±0.22	0.13±0.02	5.00±0.24
Sarotherodon galileu	3.99±0.24	0.10±0.02	4.09±0.26

4.8 Variation of extractable and bound organochlorine in the sediments

Figures 4.6 and 4.7 present the percentage composition of extractable and bound organochlorine in the sediment compartments of the two Lakes. Extractable organochlorine in the sediments accounted for between 82.0 to 91.0.0 % of total organochlorine in the samples while bound organochlorine composition on the other hand, accounted for between 9 to 17.2 % of the total organochlorine content. The trend for extractable and bound organochlorine compositions in the sediments from the two Lake is quite the same. Thus, there was more extractable organochlorine than bound (unavailable) organochlorine. The maximum extractable organochlorine composition of 91.0 % was recorded in sediments from Agbozume in the Weija Lake while, Lake Bosomtwi registered maximum extractable organochlorine content of 90.1 % from Aborodwom sediment samples. On the other hand, maximum bound organochlorine composition of 17.2 % in the study areas was obtained in sediments from Ankaase in Lake Bosomtwi. The significance of the bound organochlorine composition in the sediment compartment is that this percentage of OC may not be available for environmental recycle and may not enter the food chain.

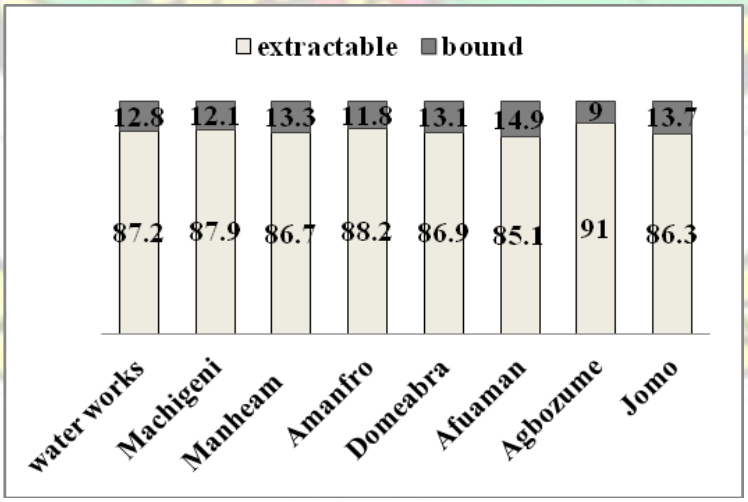


Figure 4.6: Percentage composition of extractable and bound organochlorine in sediments from sampling locations along Weija Lake

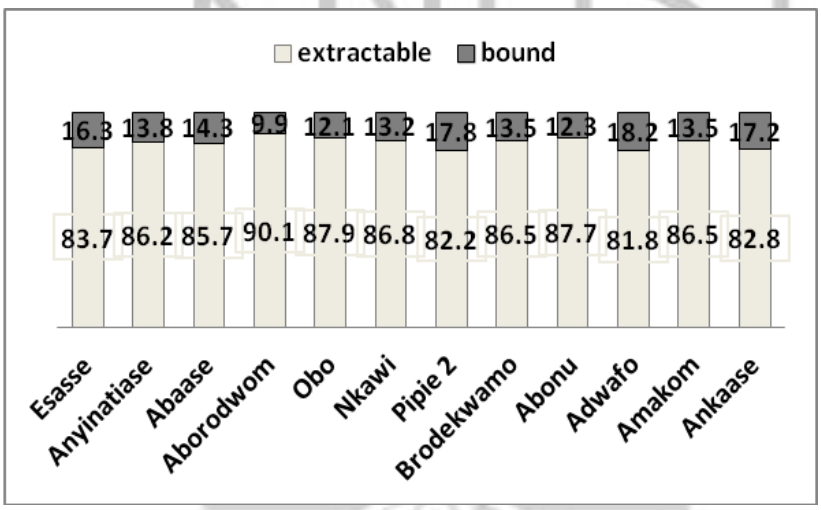


Figure 4.7: Percentage composition of extractable and bound organochlorine in sediments from sampling locations along Lake Bosomtwi.

4.9 Variation of extractable and bound (unextractable) organochlorines in fish samples.

Figures 4.8 and 4.9 show the variation of extractable and bound organochlorine compositions in the fish species. Bound organochlorine accounted for between 2.7 % to 3.8 % of the total organochlorine in Weija Lake species whereas for those from Lake Bosomtwi, values were from 2.4 % to 3.4 %. In all the fish samples the extractable organochlorine accounted for more than 95.0 % composition of total organochlorine load. This means that in aquatic environment apart from sediments bound organochlorine could also be found in aquatic species. It must, however, be stressed that this percentage of bound or unextractable OC in the fish samples was far negligible compared to those in the sediments. This variation could be due to the fact that sediment with its abundance organic matter content can facilitate in formation of bound OC.

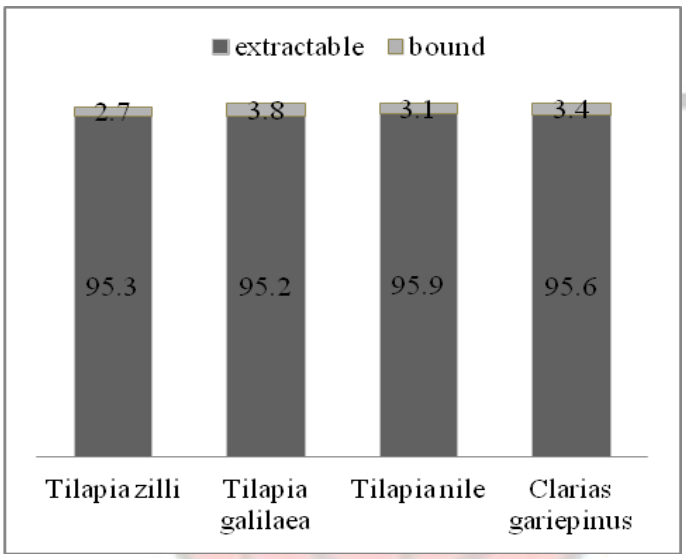


Figure 4.8: Percentage composition of extractable and bound OC in fish species from Weija

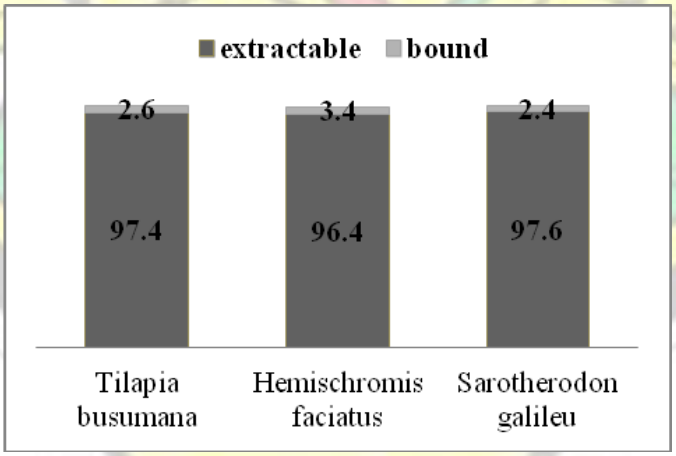


Figure 4.9: Percentage composition of extractable and bound OC in fish species from Lake Bosomtwi.

4.10 Characterization and quantification of the extractable organochlorine

Extractable organochlorine was characterized and quantified with the validated GC-ECD method. Results obtained are presented in Table 4.9 to Table 4.14.

4.10.1 Organochlorine compounds in the water samples.

Table 4.9 and Table 4.10 show the concentrations of persistent organochlorine compounds in the water samples. Margins of errors associated with the concentrations are standard deviations.

Analysis of the water samples revealed the presence of nine and ten OCPs residues in Lake Bosomtwi and Weija Lake, respectively. The detected OCPs in the water samples from both study areas were δ-HCH, γ-HCH, heptachlor, α-endosulfan, β-endosulfan, dieldrin, endrin, p,p'DDE, p,p'-DDD, P,P'-DDT, endosulfan sulfate and methoxychlor. Alpha-endosulfan was however, not detected in Bosomtwi. As at December 2008, the organochlorine pesticides namely: aldrin, chlordane, DDT, endrin, dieldrin, lindane, and heptachlor were among the banned pesticides by Environmental Protection Agency of Ghana (Afful et al., 2010). With respect to the PCBs, five and four indicator PCB congeners were, respectively, detected in the waters of Weija and Bosomtwi. These were PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180. PCB 28 was, however, not detected in water from Lake Bosomtwi. The concentrations of the OCs; β-HCH, α-HCH, aldrin, δ-chlordane, α-endosulfan, o,p-DDE, o,p-DDD, PCB 28 and PCB 153 in the water samples were below detection limit at most of the sampling locations. The mean concentration of OCPs and PCBs in the Lake water ranged from <0.01 μg/l to 4.35 μg/l and <0.01 μg/l to 4.72 μg/l, respectively. The highest organochlorine concentration of 4.72 μg/l, was measured for PCB 52 in Lake Bosomtwi at Brodekwano. Analyses of the organochlorine concentrations in the water

compartments generally, revealed the following pattern: ΣPCBs (sum of PCB 28, 52, 101, 138, 153 and 180)> ΣHCHs (sum of α-HCH, β-HCH, γ-HCH and δ – HCH)> heptachlor> Σendosulfans (sum of α, β endosulfan, and endosulfan sulfate) > ΣDDTs (sum of p,p' –DDT, p,p' DDE, p,p'-DDD)> drins (sum of aldrin, dieldrin, and endrin)> methoxychlor> γ-chlordane.

Table 4.9: Concentration (µg/l) of organochlorine pesticides in the waters of the two Lakes

Sampling locations	α-HCH	β-HCH	δ-HCH	γ-HCH	heptachlor	aldrin	γchlordane	α-endosulfan	βendosulfan	dieldrin	endrin	p,p-DDT	p,p-DDE	p,p-DDD	endosulfan sulfate	methoxychlor
Weija																
water works	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05±0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05±0.01	0.05±0.02	<0.01
Machigeni	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Manheam	<0.01	<0.01	<0.01	0.45±0.12	0.55±0.10	<0.01	<0.01	0.15±0.01	0.30±0.01	<0.01	1.30±0.08	<0.01	0.25±0.02	<0.01	<0.01	0.05±0.01
Domeabra	<0.01	<0.01	0.10±0.03	0.30±0.02	0.20±0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.15±0.02	0.20±0.04	<0.01
Afuaman	<0.01	<0.01	<0.01	0.15±0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.10±0.02	<0.01	<0.01
Agbozume	<0.01	<0.01	0.05±0.01	0.15±0.05	0.70±0.04	<0.01	<0.01	<0.01	0.11±0.05	<0.01	0.50±0.11	<0.01	<0.01	<0.01	<0.01	<0.01
Jomo	<0.01	<0.01	<0.01	<0.01	0.33±0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Amanfro	<0.01	<0.01	<0.01	0.22±0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04±0.01	<0.01	<0.01
Bosomtwi																
Esasse	<0.01	<0.01	<0.01	0.15±0.01	0.85±0.03	<0.01	<0.01	<0.01	<0.01	0.05±0.01	<0.01	<0.01	<0.01	0.35±0.11	<0.01	<0.01
Anyinatiase	<0.01	<0.01	<0.01	<0.01	0.30±0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	1.30±0.08	<0.01
Abaase	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.25±0.04	<0.01	0.65±0.21	<0.01
Aborodwom	<0.01	<0.01	<0.01	0.30±0.011	0.25±0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Obo	<0.01	<0.01	0.15±0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	3.20±0.03	0.50±0.02	0.10±0.02
Nkowi	<0.01	<0.01	0.40±0.10	0.05±0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	4.30±0.11	<0.01	<0.01
Pipie 2	<0.01	<0.01	0.15±0.01	<0.01	0.15±0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.15±0.02	<0.01
Brodekwamo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.15±0.02	<0.01
Abonu	<0.01	<0.01	<0.01	0.05±0.02	0.50±0.10	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	2.55±0.50	<0.01	<0.01
Adwafo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Amakom	<0.01	<0.01	0.05±0.01	0.05±0.02	<0.01	<0.01	<0.01	<0.01	0.45±0.12	<0.01	<0.01	<0.01	<0.01	<0.01	0.05±0.01	<0.01

Ankaase	<0.01	<0.01	0.10±0.02	0.15±0.03	0.25±0.11	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.15±0.2	<0.01	<0.01

Table 4.10: Concentration (μg/l) of indicator PCBs in water of the two lakes

sampling locations	PCB 28	PCB 52	PCB 101	PCB 153	PCB 138	PCB 180
Weija						
water works	<0.01	1.09±0.20	<0.01	<0.01	1.43±0.44	nd
Machigeni	<0.01	0.75±0.06	<0.01	<0.01	<0.01	0.65±0.03
Manheam	2.50±0.42	1.68±0.40	<0.01	<0.01	<0.01	<0.01
Domeabra	<0.01	1.81±0.11	<0.01	<0.01	<0.01	1.08±0.66
Afuaman	<0.01	1.38±0.41	<0.01	<0.01	<0.01	1.05±0.41
Agbozume	1.20±0.22	1.99±0.13	<0.01	<0.01	<0.01	<0.01
Jomo	1.32±0.30	1.62±0.61	0.28±0.08	<0.01	<0.01	0.50±0.08
Amanfro	<0.01	0.50±0.04	<0.01	<0.01	<0.01	<0.01
Bosomtwi						
Esasse	<0.01	4.47±0.55	<0.01	<0.01	<0.01	<0.01
Anyinatiase	<0.01	1.09±0.20	<0.01	<0.01	<0.01	<0.01
Abaase	<0.01	3.62±0.61	<0.01	<0.01	0.12±0.02	<0.01
Aborodwom	<0.01	4.13±0.99	<0.01	<0.01	<0.01	3.06±0.81
Obo	<0.01	1.68±0.40	<0.01	<0.01	<0.01	<0.01
Nkowi	<0.01	0.75±0.06	<0.01	<0.01	<0.01	0.51±0.03
Pipie 2	<0.01	1.99±0.13	0.02±0.01	<0.01	<0.01	<0.01
Brodekwamo	<0.01	4.72±0.30	<0.01	<0.01	1.15±0.02	<0.01
Abonu	<0.01	4.26±0.33	<0.01	<0.01	<0.01	<0.01
Adwafo	<0.01	1.81±0.11	<0.01	<0.01	<0.01	<0.01
Amakom	<0.01	3.21±0.02	<0.01	<0.01	<0.01	<0.01
Ankaase	<0.01	2.37±0.42	<0.01	<0.01	<0.01	<0.01

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4.10.2 Organochlorine compounds in the sediment samples

Tables 4.11 and 4.12 present the detected organochlorine pesticides and indicator PCBs in the sediments from the two Lakes. In all a total of sixteen organochlorine pesticides and five indicators PCB congeners were detected in the sediments. Five and four indicator PCB congeners were respectively detected in the sediment compartments in Weija Lake and Lake Bosomtwi. The trends of persistent organochlorine compounds distribution in the samples indicate higher organochlorine

concentrations in sediments than in the water compartments. In an aquatic medium, persistent organochlorine compounds being hydrophobic tend to settle more in sediments than remaining in the overlying water. Sediments, therefore, serve as sink for persistent organochlorine compounds. The organochlorine pesticides namely, α – HCH, β – HCH, aldrin, δ – chlordane, p,p'- DDT and p,p'- DDE were those that were detected in the sediments but not in the water samples. Though the concentrations of organochlorine pesticides detected in the sediment compartments were largely comparable in the two study areas, sediments from Weija reported slightly higher concentrations than those from Lake Bosomtwi. This variation could be attributed to the fact that the communities in the catchment of Lake Bosomtwi keep the Lake neat because of its sacred nature. The concentrations of organochlorine pesticides in the sediments ranged from <0.01µg/kg to 15.25 µg/kg and <0.01 to 7.25 µg/kg at Weija and Bosomtwi, respectively. Compared to other study, Chin-Chang et al (2007) reported lower OCPs concentrations (not detected to 3.57µg/kg) in sediments from Danshui River estuary of Taiwan. Meanwhile, the concentrations of indicator PCBs were more significant in Lake

Bosomtwi than Weija. For instance, whereas PCB 101 was detected only in the sediment from Agbozume in Weija, the compound was prominent in most of the sediment samples from Bosomtwi. The concentrations of indicator PCBs ranged from <0.01 µg/kg to 7.05 µg/kg dry

weight and <0.01 µg/kg to 7.55 µg/kg dry weight at Weija and Bosomtwi, respectively. Despite the high PCB concentrations, the values did not exceed the sediment quality guideline value of 22.7 µg/kg dry weight (Mohebbi Nozar et al, 2013). Therefore, the levels of PCBs in the sediment do not pose adverse health effects to sensitive aquatic species. Analysis of the sediment samples showed the following pattern of concentrations: ΣPCBs> ΣEndosulfans> ΣDDTs> ΣDrins>

Heptachlor> ΣHCHs> γ-chlordane> Methoxychlor in Weija. The pattern in Bosomtwi sediments followed same order except that mean methoxychlor concentration was higher than that of γ-chlordane.

Table 4.11: Mean concentrations (μg/kg) of organochlorine pesticides in the sediments.

Samplng locations	α-HCH	β-HCH	δ-HCH	γ-HCH	heptachlor	γ-endosulfan	α-endosulfan	βaldrin dieldrin	chlordane	endosulfan endrin	p,p-DDT	p,p-DDE	p,p-DDD	endosulfan sulfate
Weija														
Weija works	0.22±0.02	0.50±.02	1.50±0.13	1.15±0.12	0.60±0.04	<0.01	0.50±0.04	1.00±0.03	5.60±0.22	0.95±0.08	0.90±0.22	0.50±0.55	0.65±0.03	3.60±0.10	4.50±0.33
Machigeni	0.15±0.01	1.02±0.04	1.21±0.05	0.31±0.03	6.86±0.22	<0.01	0.63±0.04	0.63±0.06	0.50±0.06	0.84±0.15	0.73±0.10	0.78±0.21	0.90±0.23	10.20±0.33	15.23±1.01
Manheam	<0.01	0.40±0.06	1.33±0.22	0.35±0.06	6.55±0.25	2.63±0.15	0.84±0.06	0.84±0.03	0.61±0.02	3.05±0.33	0.67±0.08	0.84±0.09	3.09±0.21	1.59±0.24	11.42±0.84
Domeabra	<0.01	0.72±0.04	1.29±0.08	0.33±0.02	1.53±0.07	2.69±0.25	0.69±0.08	0.69±0.07	0.58±0.08	3.78±0.16	<0.01	<0.01	1.49±0.10	3.12±0.19	<0.01
Afuaman	<0.01	<0.01	0.40±0.03	0.60±0.05	0.45±0.04	<0.01	0.25±0.02	4.63±0.30	1.05±0.07	<0.01	0.75±0.09	0.10±0.02	<0.01	2.00±0.12	<0.01
Agbozume	<0.01	0.58±0.05	1.03±0.05	0.25±0.02	1.47±0.12	1.45±0.22	1.84±0.10	0.19±0.01	0.50±0.04	1.55±0.07	0.56±0.04	1.25±0.11	2.34±0.22	1.90±0.12	4.22±0.30
Jomo	<0.01	0.35±0.02	<0.01	0.44±0.03	0.77±004	1.35±0.10	<0.01	<0.01	0.55±0.15	0.50±0.12	0.60±0.04	<0.01	0.95±0.10	<0.01	4.63±0.35
Amanfro	<0.01	<0.01	<0.01	0.53±0.06	3.64±0.25	<0.01	2.55±0.16	1.25±0.14	<0.01	0.55±0.06	0.66±0.03	0.72±0.07	0.50±0.03	0.60±0.04	7.55±0.56
Bosomtwi														
Esasse	0.15±0.02	<0.01	<0.01	0.60±0.02	<0.01	<0.01	0.25±0.01	0.15±0.02	1.05±0.04	0.90±0.20	0.75±0.11	0.10±0.01	<0.01	2.00±0.21	5.23±1.04
Anyinatiase	1.15±0.03	0.05±0.01	0.22±0.04	1.15±0.09	0.60±0.11	<0.01	0.05±0.03	0.10±0.02	5.60±0.25	0.95±0.15	0.90±0.15	<0.01	3.60±0.27	0.65±0.07	4.50±0.32
Abaase	<0.01	0.05±0.01	0.40±0.01	1.10±0.3	<0.01	<0.01	0.05±0.01	<0.01	2.05±0.22	0.50±0.09	0.95±0.16	<0.01	<0.01	0.30±0.02	<0.01
Aborodwom	<0.01	<0.01	1.29±0.25	0.75±0.03	2.40±0.13	0.25±0.08	0.25±0.03	<0.01	1.25±0.05	0.60±0.01	1.20±0.09	<0.01	1.25±0.06	3.01±0.41	<0.01
Obo	0.50±0.02	<0.01	<0.01	1.05±0.04	2.40±0.06	1.20±0.07	0.05±0.01	<0.01	1.25±0.03	0.60±0.01	1.20±0.07	1.79±0.07	<0.01	0.25±0.01	0.65±0.05
Nkowi	<0.01	<0.01	0.40±0,02	0.60±0.04	0.45±0.03	<0.01	0.25±0.04	0.25±0.04	1.05±0.04	0.90±0.22	0.75±0.22	0.10±0.03	<0.01	2.00±0.07	<0.01
Pipie 2	0.22±0.04	0.50±0.02	1.50±0.72	1.15±0.09	0.60±0.02	<0.01	0.50±0.02	1.00±0.05	5.60±0.77	0.95±0.06	0.90±0.07	0.10±0.01	3.60±0.36	0.65±0.04	4.50±0.46
Brodekwamo	<0.01	0.05±0.01	0.40±0.02	1.10±0.21	0.55±0.03	<0.01	0.05±0.01	<0.01	2.20±0.08	0.50±0.03	0.95±0.12	<0.01	1.50±0.07	0.30±0.03	0.15±0.05
Abonu	<0.01	<0.01	0.22±0.03	0.75±0.03	0.12±0.01	<0.01	0.25±0.01	<0.01	7.25±0.88	0.70±0.02	1.20±0.04	<0.01	4.75±0.55	0.25±0.05	6.65±0.55

Adwafo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05±0.01	<0.01	1.25±0.40	0.60±0.02	1.20±0.05	<0.01	0.50±0.06	2.90±0.43	<0.01
Amakom	<0.01	<0.01	0.60±0.07	0.30±0.05	0.25±0.02	<0.01	<0.01	<0.01	0.95±0.08	1.05±0.10	0.20± 0.01	0.45±0.05	<0.01	2.40±0.08	0.15±0.02
Ankaase	<0.01	<0.01	0.50±0.05	0.45±0.07	0.10±0.04	<0.01	<0.01	0.22±0.01	<0.01	1.05±0.08	0.30±0.03	0.55±0.06	<0.01	0.25±0.03	0.20±0.05

Table 4.12: Mean concentrations (μg/kg) of indicator PCBs in the sediments of the two Lakes.

Sampling locations	PCB 28	PCB 52	PCB 101	PCB 153	PCB 138	PCB 180	∑PCBs
Weija							
water works	1.73±0.12	1.68±0.47	<0.01	<0.01	<0.01	1.32±0.20	4.73±0.79
Machigeni	3.21±0.35	3.20±0.47	<0.01	<0.01	0.99±0.06	2.08±0.53	9.48±1.38
Manheam	2.32±0.40	4.14±0.52	<0.01	<0.01	0.12±0.02	2.37±0.41	8.95±1.35
Domeabra	1.59±0.31	1.71±0.22	<0.01	<0.01	<0.01	<0.01	3.30±0.53
Afuaman	2.88±0.33	5.05±0.83	1.21±0.05	<0.01	<0.01	<0.01	9.93±1.16
Agbozume	1.38±0.11	2.41±0.31	1.20±0.05	<0.01	<0.01	<0.01<0.01	4.99±0.47
Jomo	2.10±0.41	5.77±0.88	<0.01	<0.01	<0.01	3.06±0.69	10.93±1.98
Amanfro	1.55±0.35	1.88±0.25	0.59±0.03	<0.01	<0.01	<0.01	4.02±0.63
Bosomtwi							
Esasse	<0.01	5.79±1.23	0.78±0.61	<0.01	<0.01	<0.01	6.57±1.83
Anyinatiase	<0.01	5.51±1.34	1.14±0.55	<0.01	<0.01	<0.01	6.65±1.89
Abaase	<0.01	4.87±1.53	1.06±0.09	<0.01	<0.01	<0.01	5.93±1.62
Aborodwom	0.55±0.22	5.45±0.15	1.37±0.04	<0.01	<0.01	5.03±0.12	12.40±0.53
Obo	<0.01	5.43±0.96	<0.01	<0.01	<0.01	<0.01	5.43±0.96
Nkowi	0.91±0.31	<0.01	1.10±0.22	<0.01	<0.01	2.07±0.43	4.07±0.96
Pipie 2	5.90±1.05	4.85±1.20	<0.01	<0.01	0.95±0.10	7.08±1.23	18.78±3.58
Brodekwamo	3.53±0.90	4.26±1.12	0.16±0.02	<0.01	<0.01	7.55±1.33	15.50±3.37
Abonu	5.25±0.74	5.24±1.92	0.33±0.08	<0.01	3.90±0.63	<0.01	14.72±3.37
Adwafo	<0.01	5.74±1.81	<0.01	<0.01	<0.01	<0.01	5.74±1.81
Amakom	<0.01	3.56±0.75	<0.01	<0.01	<0.01	<0.01	3.56±0.75
Ankaase	<0.01	3.88±0.60	1.43±0.04	<0.01	2.30±0.10	5.65±1.06	13.26±1.80

∑PCBs is listed as sum of the entire detected indicator PCBs in the sample at a particular location.

4.10.3 Organochlorine compounds in the fish samples

Tables 4.13 and 4.14 respectively present mean concentrations of detected OCPs and PCBs in the fish samples. In all, a total of seventeen organochlorine pesticides and six indicator PCBs were detected in the fish species. In general terms, the concentrations of OCs detected showed slightly

higher levels in the fish compartment compared to those in the sediment compartment but significantly higher than the concentrations in the water compartment. The negligibility of OC residues in water was due to the fact that organochlorines are scarcely soluble in water (Imo et al. 2013). Veljanoska-Sarafiloska et al (2013) similarly, reported higher OCPs concentrations in the muscle tissue of fish than in water and sediment compartments. This trend of result was anticipated as organochlorines are hydrophobic in nature and therefore in an aquatic environment they are prone to concentrating in fatty tissues of living systems like fishes and other related aquatic organisms. Sediment plankton and microflora are used as a main source of food for young fishes, which are eaten by larger fishes, which are then used by humans. In this cycle, the repetitive accumulations of such compounds increase the rate of breast cancer in the female population that live near the coastal areas and these compounds will be subsequently transferred to new generations via mother's milk as a result of their high lipophilic storage (Iscan et al., 2002; Alpay et al., 2008). The concentrations of organochlorine pesticides varied from <0.01 µg/kg to 23.74 µg/kg and <0.01 µg/kg to 10.70 µg/kg in fish samples from Weija and Bosomtwi, respectively. The highest concentrations (23.74 µg/kg and 10.70 µg/kg), were, respectively recorded for γ-HCH in *Clarias gariepinus* and p,p$^{'}$-DDE in *Tilapia busumana.* The pesticide loads (sum of all detected pesticides) in Weija fish species were from 82.38 µg/kg to 107.96 µg/kg while those from Bosomtwi were from 58.21 µg/kg to 78.67 µg/kg. The highest pesticide load of 107.96 µg/kg was obtained for *Clarias gariepinus* while the lowest load of 58.21 µg/kg was also recorded for *Sarotherodon galileu.* The highest pesticide load recorded for *Clarias gariepinus* could be linked possibly to its large size as bigger fishes due to their high lipid content are susceptible to bio-accumulating more organochlorine residues. This result is supported by Figure 4.10 which showed correlation analysis of pesticide load and fish size. The analysis yielded coefficient of

correlation of 0.8618 between pesticide load and fish weight. Thus, the fish size strongly correlated with total pesticide load. Again, *Clarias gariepinus* are sediment bound fish species and are likely to accumulate more OCs in sediment environment as sediments serve as sink for OCs.

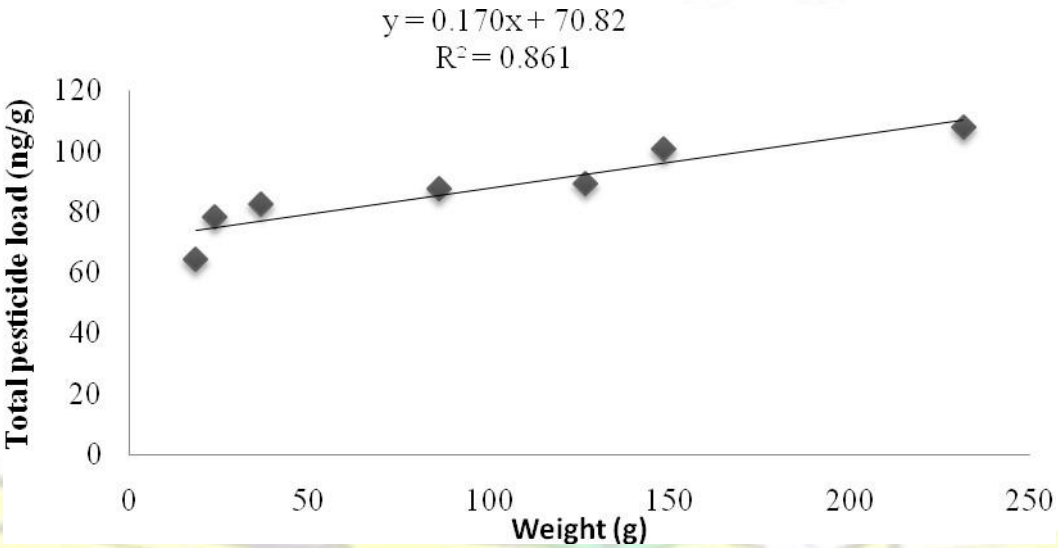


Figure 4.10: Plot of total pesticide load against mean weight of fish

With regard to the PCBs, the mean concentration ranged from <0.01 µg/kg to 32.40 µg/kg for species from Weija Lake while those from Bosomtwi ranged <0.01 µg/kg to 18.43 µg/kg. Total PCB load on the other hand, was from 13.99 µg/kg (*Tilapia zilli*) to 78.07 µg/kg (*Clarias gariepinus*) for Weija species and 23.81µg/kg (*Sarotherodon galileu*) to 44.56 µg/kg (*Tilapia busumana*) for the Bosomtwi fish species. The highest PCB load was also recorded for *Clarias gariepinus* while the lowest load 13.99 µg/kg was measured for *Tilapia zilli*.

Figure 4.11 shows the relationship between the fish size and total PCBs load in the fish samples. Correlation analysis yielded R^2 which is approximately 0.5. A correlation analysis therefore indicates that fish size and PCBs concentrations fairly correlated by about 50 %.

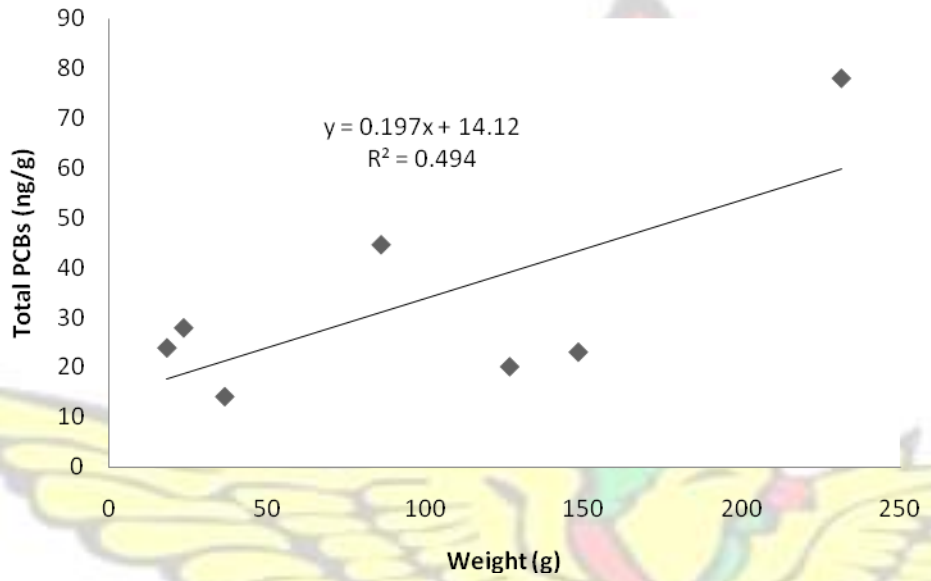


Figure 4.11: Correlation plot of total PCBs against mean weight of fish.

Table 4.13: Mean concentration (μg/kg) of organochlorine pesticides in the fish samples

Organochlorines	Weija species				Bosomtwi species		
	Tilapia zilli	*Tilapia galilaea*	*Tilapia nile*	*Clarias gariepinus*	*Tilapia busumana*	*Sarotherodon galileu*	*Hemischromis faciatus*
α - HCH	1.29±0.40	4.82±0.06	0.88±0.04	10.27±0.81	3.42±0.50	3.58±0.64	3.90±0.55
β - HCH	3.21±0.43	16.85±0.28	10.72±0.55	11.69±0.66	5.42±0.22	5.79±0.66	4.40±0.07
γ - HCH	9.53±0.99	13.24±1.29	7.28±0.50	23.70±0.76	7.27±0.58	7.04±0.50	7.28±0.57
δ - HCH	12.24±0.55	6.61±0.47	8.03±0.09	12.20±0.90	1.18±0.42	1.39±0.08	5.83±0.88
Heptachlor	<0.01	4.21±0.15	19.02±0.55	21.91±0.07	7.30±0.10	8.08±0.89	8.46±0.45
aldrin	4.84±0.08	8.06±0.70	0.93±0.04	8.14±1.01	5.87±0.33	3.04±0.41	5.03±0.09
γ-chordane	<0.01	4.16±0.05	5.83±0.70	<0.01	7.18±0.80	0.66±0.03	0.99±0.08
α-endosulfan	4.30±0.05	<0.01	2.32±0.03	<0.01	3.64±0.11	<0.01	6.88±0.63
β-endosulfan	2.64±0.03	<0.01	<0.01	<0.01	<0.01	5.90±0.07	<0.01
dieldrin	12.49±0.11	5.19±0.96	9.59±0.77	3.36±0.43	10.70±0.86	4.90±0.44	7.36±0.65
endrin	6.42±0.12	5.08±0.12	3.33±0.62	4.96±0.22	9.21±0.47	<0.01	<0.01
p,p-DDT	<0.01	<0.01	0.93±0.13	2.44±0.01	<0.01	1.09±0.02	<0.01
p,p-DDE	2.44±0.75	2.75±0.89	1.85±0.33	6.94±0.54	8.40±0.91	10.09±0.45	4.73±0.07
p,p-DDD	3.50±0.07	10.46±1.14	8.77±0.66	5.70±0.06	3.62±0.83	0.53±0.66	5.62±0.95
Methoxychlor	<0.01	5.62±0.09	<0.01	<0.01	<0.01	<0.01	5.76±0.47
Endosulfan sulfate	8.31±0.06	<0.01	10.53±0.80	6.65±0.52	4.47±0.77	5.22± 0.75	<0.01
Total OCPs load	**82.38**	**89.43**	**100.54**	**107.96**	**77.67**	**58.21**	**78.11**

Table 4.14: Mean concentration (μg/kg) of indicator PCBs in the fish samples.

	Weija species				Bosomtwi species		
PCBs	*Tilapia zilli*	*Tilapia galilaea*	*Tilapia nile*	*Clarias gariepinus*	*Tilapia busumana*	*Hemischromis faciatus*	*Sarotherodon galileu*
PCB 28	3.54±0.22	8.41±0.51	3.36±0.11	30.66±1.08	5.30±0.31	7.63±0.37	6.46±0.40
PCB 52	2.32±0.14	<0.01	10.01±0.58	32.40±1.13	3.12±0.25	11.28±0.87	4.35±0.28
PCB 101	3.46±0.27	6.46±0.36	4.82±0.38	13.32±0.70	7.76±0.44	6.26±0.38	5.08±0.97
PCB 118	3.67±0.11	5.05±0.27	3.67±0.37	<0.01	<0.01	2.65±0.15	7.72±0.45
PCB 153	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PCB 138	<0.01	<0.01	<0.01	0.96±0.05	18.43±0.75	<0.01	0.20±0.05
PCB 180	<0.01	<0.01	<0.01	0.73±0.030	9.85±0.86	<0.01	<0.01
Σ PCBs	**13.99**	**20.02**	**22.95**	**78.07**	**44.56**	**27.82**	**23.81**

ΣPCBs is listed as sum of the entire indicator PCBs in a particular fish.

4.11 Comparison of profile and levels of OCs measured to other studies.

Table 4.15 compares the results of the current study to those of Darko et al (2008) and Kuranchie-Mensah et al (2012) and other studies. Studies carried out by Darko et al (2008) and Kuranchie-Mensah et al (2012) in terms of organochlorine pollution studies were limited in scope as their investigations focused on few OCPs. The current study has filled vital gaps as far as organochlorine pollutants in the study areas are concerned. Indeed, this study has revealed useful information on the profile of indicator polychlorinated biphenyls in the study areas. On the other hand, in terms of levels, concentrations of organochlorines reported in this study are comparable to those reported by Darko et al (2008) but higher than those of Kuranchie-Mensah et al (2012). Kuranchie-Mensah et al (2012) sampled from only two locations at Weija water works and this could have accounted for the low OC concentrations reported. Nyarko et al (2011) however, reported much higher OCs concentrations in *Sardinella aurita* (Spanish sardine or Round sardinella) from the coastal waters of Accra-Tema. Compared to other studies done outside Ghana, levels of OCs reported by Monirinh et al (1999) at Kompong Chhnang in Cambodia and Kalyonu et al (2009) in fish species sampled from Konya market in Turkey compared favourably with the levels reported in this study. Concentrations reported by Rochel et al (2008) in Lake Taabo in Cote d'Ivoire were however, higher compared to the present investigation.

Table 4.15: Comparison of OCs concentrations in the study areas to reported data worldwide

Organochlorines	Present study		Darko et al (2008)	Kuranchie-Mensah et al (2012)	Nyarko et al (2011)	Kalyonu et al (2009)	Monirinh et al (1999)	Rochel et al (2007)
P,P'-DDT				0.04–0.16	nd – 11.00			
P,P'-DDE				1.06–1.67	3.00 – 131.34			
P,P'-DDD					nd – 10.67	43.70		
∑DDTs							1.90 -11.00	124.01
α-HCH					30.38 - 1235			
β-HCH					30.32 – 231.69			
γ-HCH	<0.01 – 2.40	0.012 – 4.41		0.40–0.80	28.59 – 239.67			
	<0.01 - 18.40	0.061 – 8.34						
	<0.01 - 12.46							
	0.04 - 23.71	8.87						
	<0.01 - 10.27							
	<0.01 - 16.85							
	<0.01 - 13.24							
	<0.01 - 12.24							
	<0.01 – 44.96							
	<0.01 - 9.21							
	<0.01 – 12.49	0.42						
	<0.01 - 6.88							
	<0.01 - 5.90							
δ-HCH				0.08–0.23	19.38 – 58.00			
∑HCHs						31.70	0.5-22.20	206.00

endrin			nd – 0.21	6.90		24.60
Dieldrin			0.20–0.47	2.80		
α-endosulfan			0.37–0.81	nd – 41.67		
β-endosulfan				16.00 – 50.37		
endosulfan sulfate	<0.01 - 10.53		0.15–0.44	9.67 – 11.31		
methoxychlor	<0.01 - 5.96		nd – 0.18			
Aldrin	<0.01 - 8.14	0.35	7.60–13.54	3.80		11.30
PCB 28	<0.01 –30.20					
PCB 52	<0.01 –32.40					
PCB 101	<0.01- 13.32					
PCB 138	<0.01 - 8.43					
PCB 153	<0.01				0.16 -0.17	
PCB 180	<0.01- 9.85					
∑PCBs	<0.01 -78.07					

Concentrations in parts per billion.

4.12 Bio-concentration factor of organochlorines

The bio-concentration factors calculated for this study are presented in Table 4.16. They were calculated as ratio of mean concentration of OC in a particular fish species to mean OC concentration in water as shown in eqn 4.1.

$$\text{i.e BCF} = \frac{[\text{fish}]}{[\text{water}]} \quad \text{Eqn 4.1}$$

[fish] = mean OC concentration in a particular fish, [water] = mean OC concentration in water.

Table 4.16 also shows BCFs of OCs reported by Muir et al (1996) in Arctic marine fish. The higher the BCF value the more likely the organochlorine will bound to organic matter in sediment and ultimately migrate to fat tissues of living organisms. BCFs ranged from 0.6 x 10^1 for PCB 52 in *Sarotherodon galileu* to 3.47 x 10^3 for p, p$^{'}$ –DDE in *Clarias gariepinus.* In general, bio-concentration factor deduced in the present study for the PCBs were lower than those for the OCPs. Furthermore, BCFs deduced for the compounds in the present study are far lower than those reported by Muir et al (1996). This could be attributed to the fact that marine fishes being larger in size might have higher lipid content and thus, prone to bioaccumulating more organochlorines.

Table 4.16: Bioaccumulation of organochlorines in the Lakes.

	Bosomtwi			***Weija***				
Organochlorines	*Water to Tilapia busumana*	*Water to Hemischromis faciatus*	*Water to Sarotherodon galileu*	*Water to Tilapia zilli*	*Water to Tilapia galilaea*	*Water to Tilapia nile*	*Water to Clarius gariepinus*	*water to fish (Muir et al., 1996)*
α - HCH β - HCH γ - HCH	2.88 x 10^2	1.17 x10^2	1.55 x 10^2	1.56 x 10^2	5.54 x 10^2	1.21x 10^2	3.95 x 10^2	
δ - HCH	1.71x 10^2	8.1 x 10^1	1.94 x 10^2	1.12 x 10^2	3.31 x 10^2	1.15 x 10^2	1.74 x 10^2	
HCH								3.0 x 10^4
heptachlor	8.1x 10	1.11x 10^2	4.40 x 10			8.70 x 10	1.28 x 10^2	
chlordane								5.3 x 10^7
α-endosulfan β-endosulfan	1.52 x 10^2	1.48 x 10^2		6.60 x 10		6.30 x 10		
endrin					2.50 x 10	4.10 x 10		
p,p-DDT p,p-DDE	4.20 x 10^2	2.35 x 10^2		1.22 x 10^2	1.38 x 10^2	1.06 x 10^2	3.47 x 10^3	
p,p-DDD	8.00 x 10	2.00 x 10	3.00 x 10	1.00 x 10	2.49 x 10^2	1.75 x 10^2	1.99 x 10^2	
DDT								3.0 x 10^4
endosulfan sulfate	2.00 x 10	6.60 x 10	5.60 x 10	3.60 x 10		3.51x 10^2	3.00 x 10^2	
PCB 28				5.62 x 10	1.20 x 10	2.00 x 10	5.60 x 10	
PCB 52	3.71 x 10	1.34x 10^2	0.58 x 10	6.62 x 10		2.90 x 10	1.00 x 10	
PCB 101	3.88 x 10^2	3.13 x 10^2	2.54 x 10^2	8.6 x 10^2	1.62 x 10^2	1.20 x 10^2	3.33 x 10^2	

PCB 138	1.67×10^2	1.82×10	5.33×10	
PCBs				4.8×10^7

4.13 Variation of organochlorine compounds in the sediment samples. 4.13.1 Distribution of DDTs

Figure 4.12 and Figure 4.13 show the distribution of DDT and its metabolites in the sediment compartments. In Ghana, DDT was used extensively in the past for agricultural activities. The use of DDT in Ghana for sometime was limited to malaria programs to fight the insect mosquito; however, its use today had been outlawed by the Environmental Protection Agency of Ghana (Agbeve, 2011). Detected DDTs in the sediments were p, p' –DDT, p,p'-DDE , and p,p'-DDD. In Lake Bosomtwi p, p' –DDT was only dominant at Pipie 2 and Ankaase and it accounted for about 50 % of the total DDT load. Similarly, the compound in Weija Lake was prominent at Amanfro and accounted for nearly 30 % of the total DDT load. p,p'-DDE and p,p'-DDD were the most abundant DDT in the study areas. The ratios DDT / (DDE+DDD) were less than one in almost all the sampling locations. The ratio of DDT/(DDE+DDD) can be used to assess or estimate if there is recent input of DDT in the study area (Kurachie-Mensah et al., 2011; Liu et al., 2010). If the ratio is less than one then there is no recent input of DDT and vice versa. The low concentration of p,p'-DDT compared to the sum of its metabolites (DDE+DDD), is an indication that there might not be fresh input of the DDT in the study area. This therefore, suggests that DDTs concentrations might mainly be due to historical use and environmental persistence.

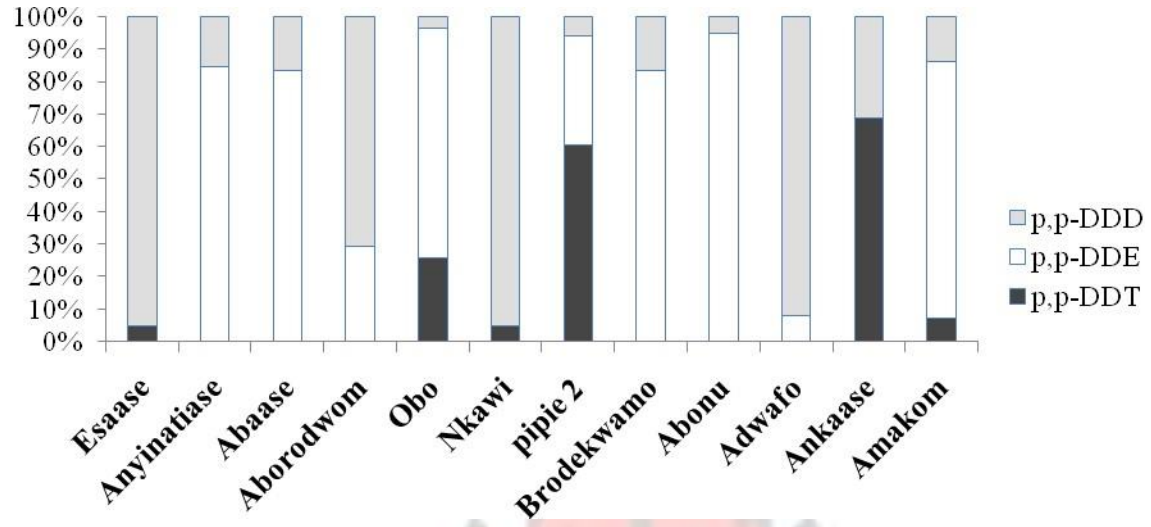


Figure 4.12: Distribution pattern of DDTs in sediments along Lake Bosomtwi

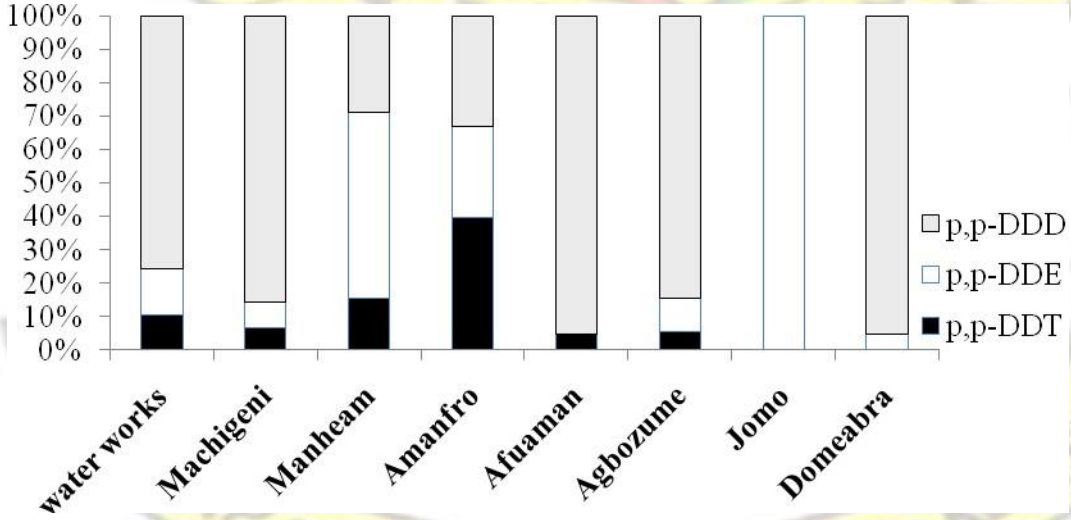


Figure 4.13: Distribution pattern of DDTs in sediments along Weija Lake

4.13.2 Distribution of Hexachlorocyclohexane (HCHs)

1,2,3,4,5,6-hexachlorocyclohexane was used since the beginning of the 20th century, first as technical mixture of isomers (mainly as α, β, γ, δ- HCH isomers) and later in the form of γ- HCH (lindane) in protection of plants and woods against insect attack. It was also used to control parasites and pests in household. Research has shown that only the γ-isomer has insecticidal properties and was sold as insecticide under the trade name lindane (Baird, 1997; Nollet, 2000). In Ghana lindane was historically used in the cocoa industry to control the insects that spread the swollen shoot disease. Figure 4.14 and Figure 4.15 show the percentage distribution of the HCHs in the study areas. The γ- isomer was the most predorminant isomer in sediment samples. It accounted for more than 50 % of total HCHs load in the sampling locations particularly in Lake Bosomtwi. Indeed, it was detected in all the sampling locations. The prevalence of the γ-isomer in the study area was anticipated as it had been used widely as an agrochemical (Bempah et al., 2010). The α and β- isomeric forms were not significant in the sediments from Lake Bosomtwi. On the other hand, the β- isomeric form was quite prevalent in the sediments from Weija Lake and accounted for 50 % of total HCHs at Agbozume and Domeabra. The δ – isomer was also quite prevalent in the sediments from the two Lakes.

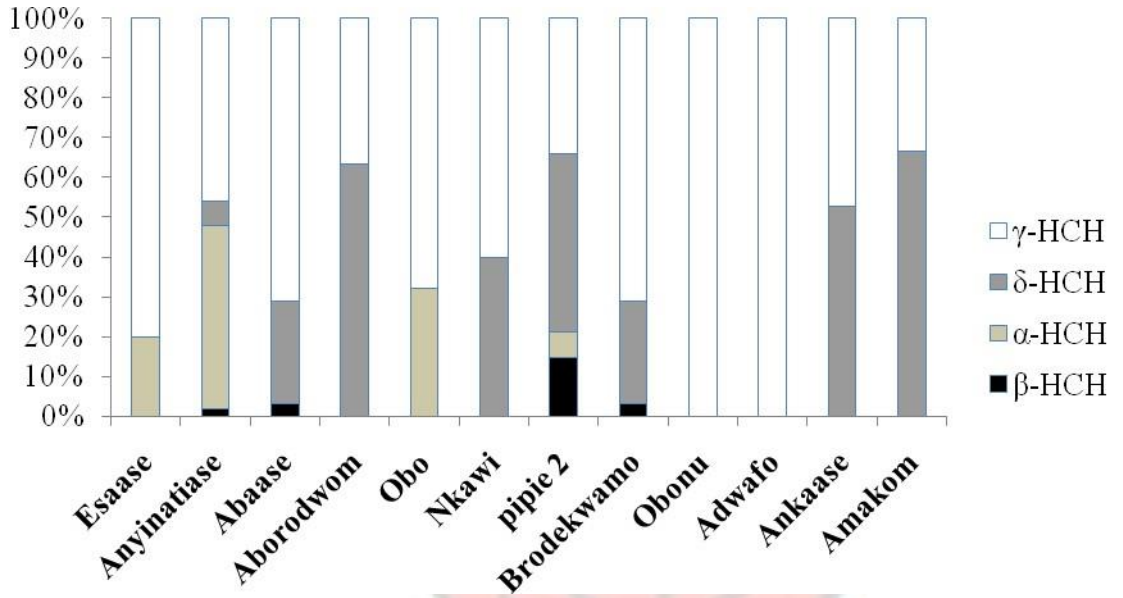


Figure 4.14: Distribution pattern of HCHs in sediments .along Lake Bosomtwi

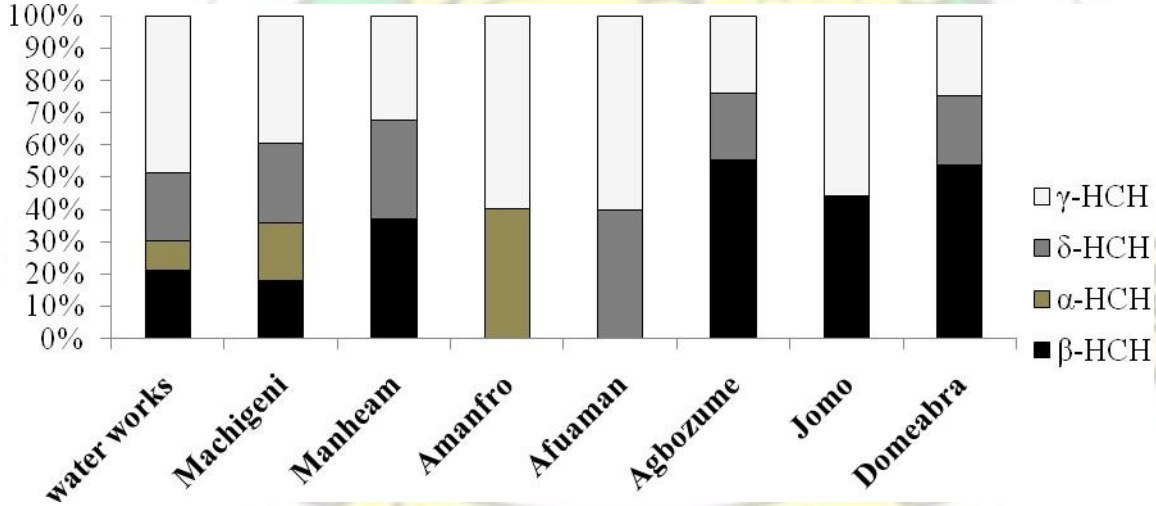


Figure 4.15: Distribution pattern of HCHs in sediments along Weija Lake

.3 Distribution of Endosulfan

Figures 4.16 and 4.17 present the percentage compositions of two isomeric forms of endosulfan as well as the metabolite, endosulfan sulfate. The results show that β is the predominant isomer and accounted for more than 50 % of the total endosulfan load at most of the sampling locations in sediments from Lake Bosomtwi. Indeed, at Abaase, Aborodwom and Adwafo, the isomer accounted for 100 % of the total endosulfan load. The α-isomeric form was less prominent in the sediments from Bosomtwi and accounted for between 5 – 10 % endosulfan load at Nkawi and Pipie 2. Conversely, in the sediments from Weija Lake, both α and β forms were less prominent except at Afuaman where α- form was prominent and accounted for about 80 % of the endosulfan load. Endosulfan breaks down into endosulfan sulfate and endosulfan diol and both have structures similar to the parent compound. The two are therefore of toxicological concern. However, only the endosulfan sulfate was detected and accounted for more than 80 % of the total endosulfans at Esaase and Obo. Indeed, the compound was the most abundant endosulfan in sediments from Weija Lake. The detection of endosulfan sulfate rather than endosulfan diol is an indication that metabolism of the parent occurred through oxidation and not by hydrolysis (Wandiga, 1995).

4.13

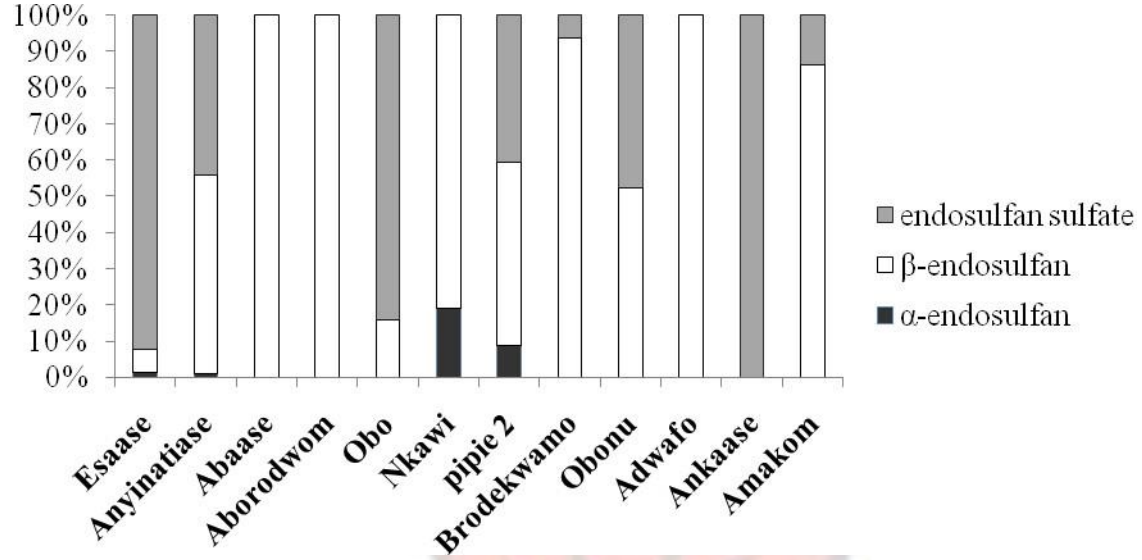


Figure 4.16: Distribution pattern of endosulfans in sediments along Lake Bosomtwi

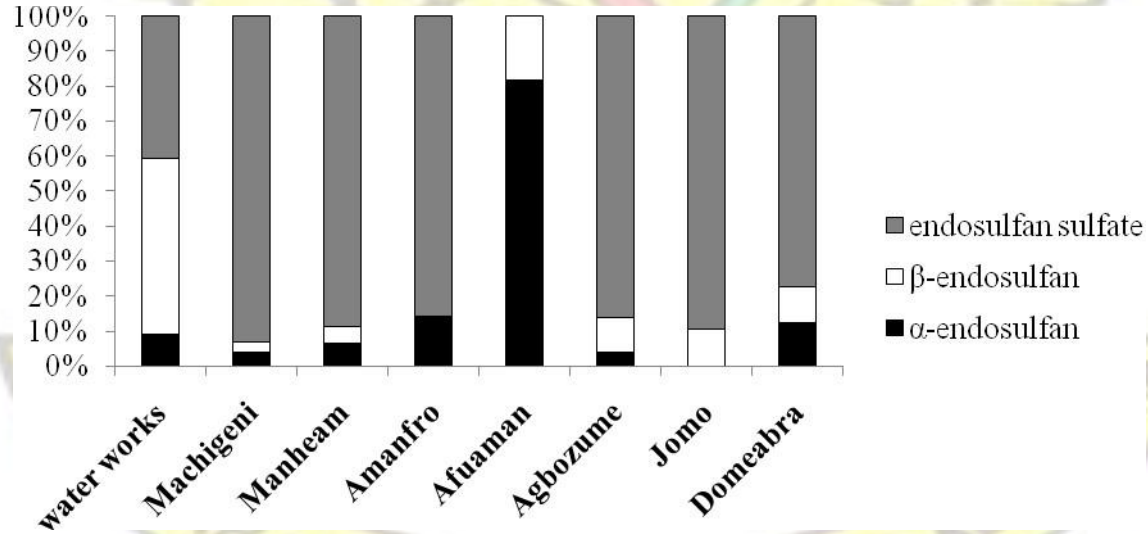


Figure 4.17: Distribution pattern of endosulfan in sediments along Weija Lake

.4 Distribution of Drin

Aldrin and dieldrin are chemicals that were widely used in agricultural throughout the world to control insects in soil. In public health it was used for the control of mosquitoes and tsetseflies, the vectors that cause malaria and sleeping sickness respectively. In Ghana aldrin was used extensively to control pests on cocoa as well as termites under the trade name Aldrex 40. Aldrin breaks down to dieldrin in living systems but dieldrin is known to resist bacterial and chemical breakdown (Oris et al., 2000) The profile of the drins in the sediments from the two Lakes is as shown in Figures 4.18 and 4.19. Dieldrin and endrin were the predominant drins particularly in Lake Bosomtwi. Indeed, the two accounted for 100 % of the total drins load in eight of the sampling locations. Aldrin was the least significant drin, however the chemical was quite significant in the sediments from Weija. It accounted for 50 % of the total drins in sediment from Jomo. The predominance of dieldrin over aldrin came as no surprise since in the environment aldrin is likely to break down to dieldrin (Oris et al., 2000). In the environment endrin breaks down to endrin ketone and endrin aldehyde through photodecomposition and microbial degradation (Bempah et al., 2010). These were however, not detected in the study areas.

4.13

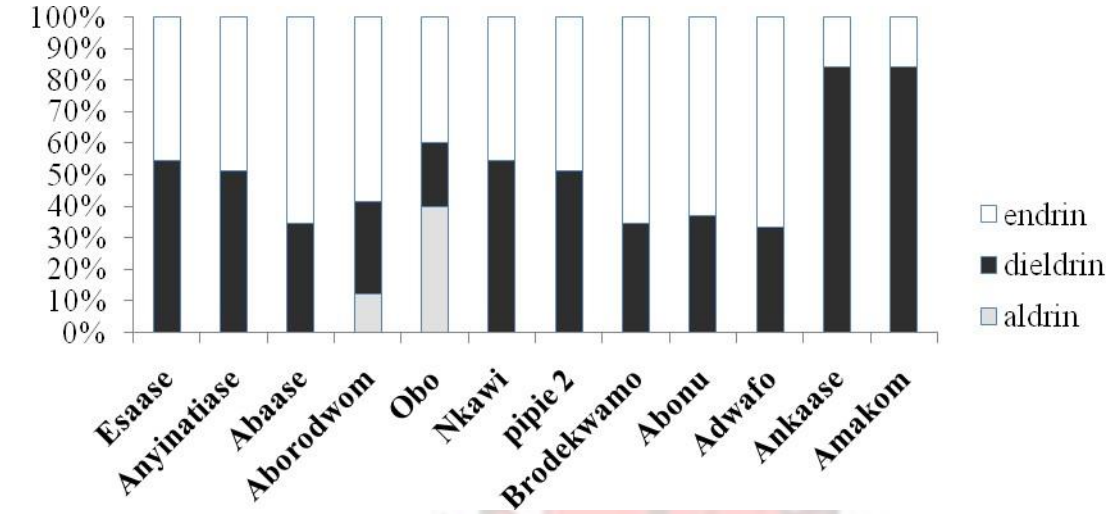


Figure 4.18: Distribution pattern of Drins in sediments along Lake Bosomtwi

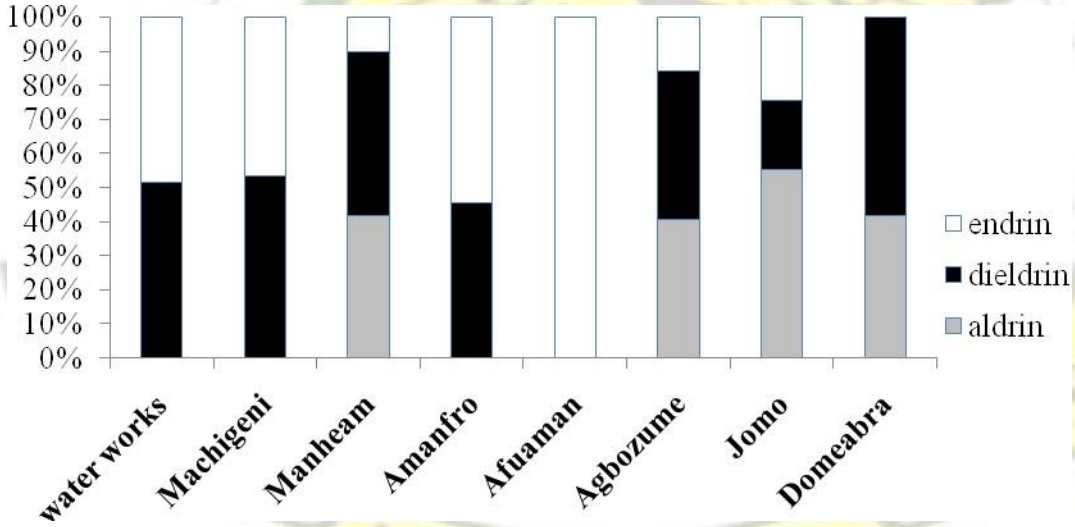


Figure 4.19: Distribution pattern of Drins in sediments along Weija Lake

.5 Distribution of indicator PCBs

Figures 4.20 and 4.21 present the composition of detected indicator polychlorinated biphenyl congeners. PCB 52 was the most ubiquitous and predominant PCB congener in the sediments samples, accounting for more than 50 % composition in sediments from five sampling locations along Lake Bosomtwi. At Adwafo it was the only detected indicator PCB congener. In Weija Lake, it accounted for about 45 – 60 % of the total PCB load at Manheam, Amanfro, Afuaman, Jomo and Domeabra. PCB 28 was also quite abundant in the sediments from Weija Lake compared to its prominence in Lake Bosomtwi. In general, the less chlorinated homologues (# 28, 52 and 101) were more prominent than the most chlorinated homologues (# 138, 153 and 180). The PCB congener 153 was not detected at any of the sampling locations while congener 138 was detected at three and one sampling locations in Bosomtwi and Weija respectively. For the most chlorinated homologues, PCB 180 was quite prominent and accounted for nearly 40% of total PCBs load at Aborodwom, Pipie 2 and Brodekwamo. In the sediment from Weija the congener accounted for about 20 – 35 % of PCB load at Weija water works, Machigeni, Manheam and Jomo.

4.13

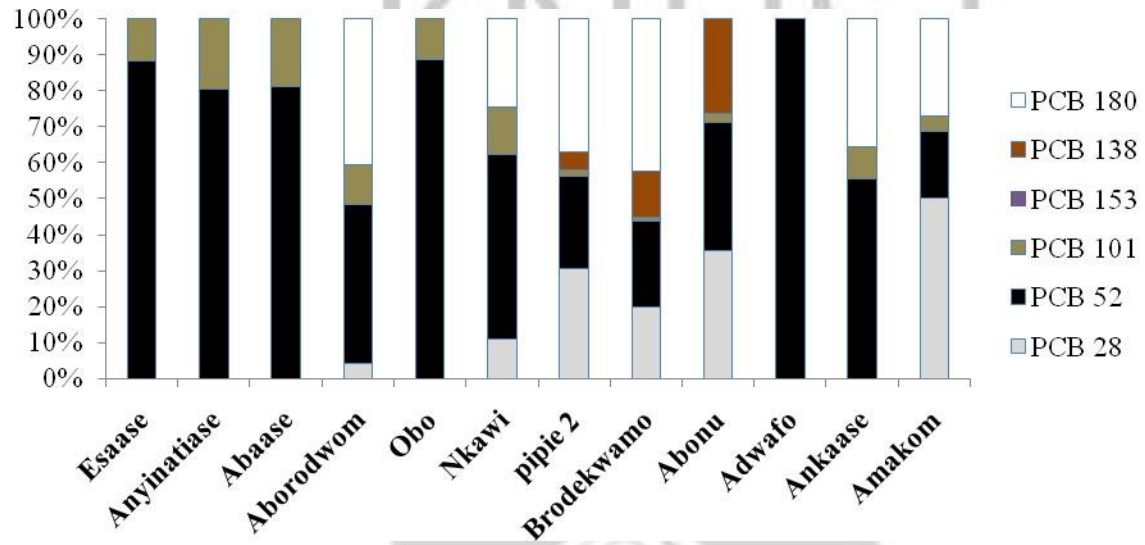


Figure 4.20: Distribution pattern of indicator PCBS in sediments along Lake Bosomtwi

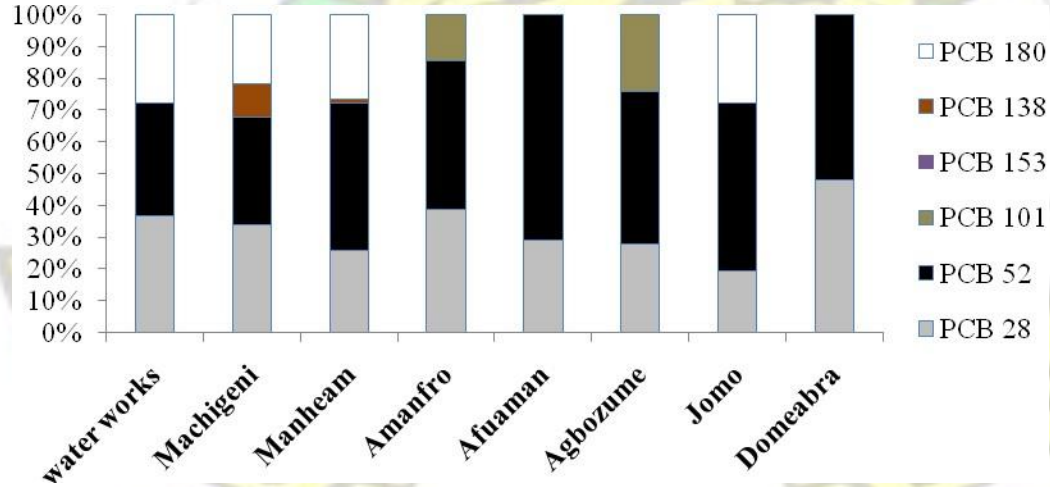


Figure 4.21: Distribution pattern of indicator PCBs in sediments along Weija Lake

4.14 Variation of organochlorine compounds in the fish samples.

4.14.1 Distribution of DDTs

Figures 4.22 and 4.23 show the percentage DDTs in the fishes from the two Lakes. The trend of DDTs distribution in the species from the two Lakes was quite similar. p,p' -DDE and p,p' DDD were the most significant DDT in the fish species. The two accounted for 100 % of total DDT load in *Tilapia busumana* and *Sarotherodon galileu* sampled from Lake Bosomtwi. p,p' – DDD was however, less significant in *Hemiscromis faciatus.* In Weija Lake the two also accounted for 100 % of DDTs in *Tilapia zilli* and *Tilapia galilaea*. The parent compound, p.p – DDT was less prevalent particularly in species from Lake Bosomtwi where it accounted for only 7 % of the total DDT load in *Hemiscromis faciatus*. In *Tilapia nile* from Weija, the specie however, accounted for about 25 % of the DDT concentration and about 10 % of DDT load in *Clarias gariepinus* also from Weija Lake. The trend of DDTs distribution in the fish samples could therefore be a confirmation that DDTs concentrations in the present study were due to historical use or environmental persistence of the compound and not through ongoing applications as the metabolites were more predominant than the parent chemical.

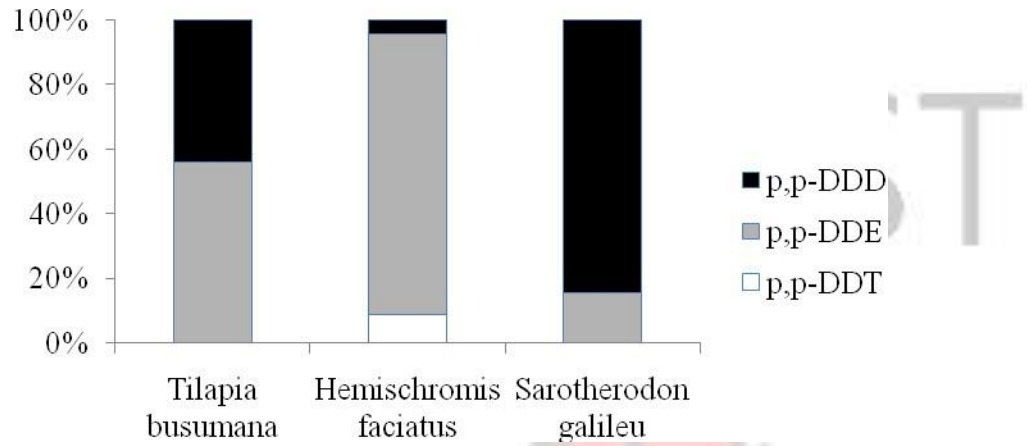


Figure 4.22: Distribution of DDTs in fish samples from Lake Bosomtwi

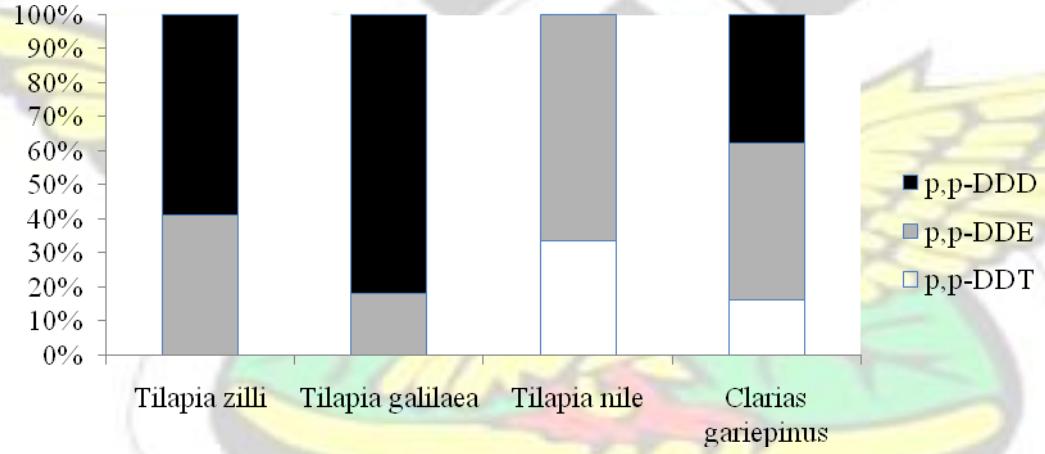


Figure 4.23: DDTs in fish samples from Weija Lake

4.14.2 Distribution of HCHs in fish samples

The profile of HCHs isomers is presented in Figures 4.24 and 4.25. All the four notable isomers were detected in the fish samples. As found in the sediments, the γ isomeric form was the dominant isomer in fish species from Lake Bosomtwi. It constituted about 40 % of HCHs load in all the species from Lake Bosomtwi. The β form was also quite significant in the Bosomtwi species accounting for nearly 30 % of HCHs in *Tilapia busumana* and *Hemiscromis faciatus* and 20 % in *Sarotherodon galileu*. The α and δ forms together constituted about 20 % of HCHs load in *Tilapia busumana* and *Hemiscromis faciatus.* In the Weija Lake γ form again was quite abundant accounting for more than 50 % of HCHs in *Tilapia galilaea*. It was between 20 - 30 % compositions in the other species (*Clarias gariepinus*, *Tilapia nile* and *Tilapia zilli)* .The β and δ forms were also quite significant in the Weija fish species with β accounting for 60 % of HCH load in *Tilapia nile* while the δ form constituted nearly 60 % of HCHs in *Tilapia zilli*. The prominence of the γ isomer could be attributed to the past use of lindane as agrochemical (γ is the main active ingredient in lindane). The α isomeric form was the less significant isomer particularly, in the *Tilapia zilli*, *Tilapia galilaea* and *Tilapia nile* from Weija, However, it was quite prominent in species from Bosomtwi accounting for nearly 20 % of HCHs in both *Tilapia busumana* and *Hemiscromis faciatus.*

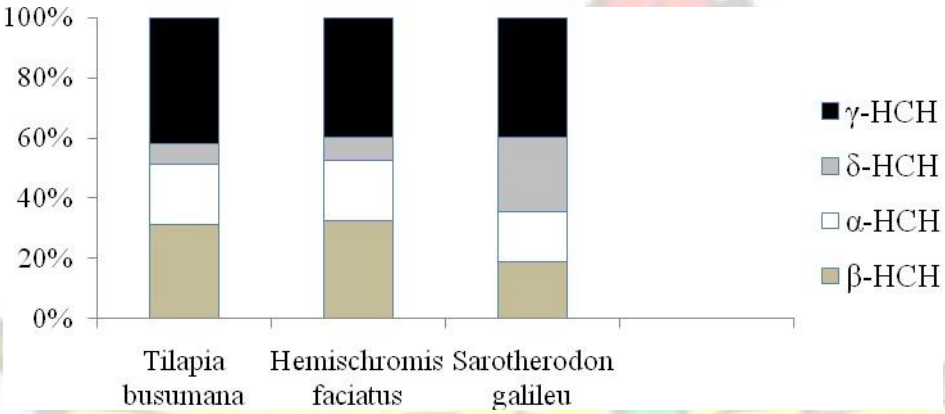


Figure 4.24: HCHs in fish samples from Lake Bosomtwi

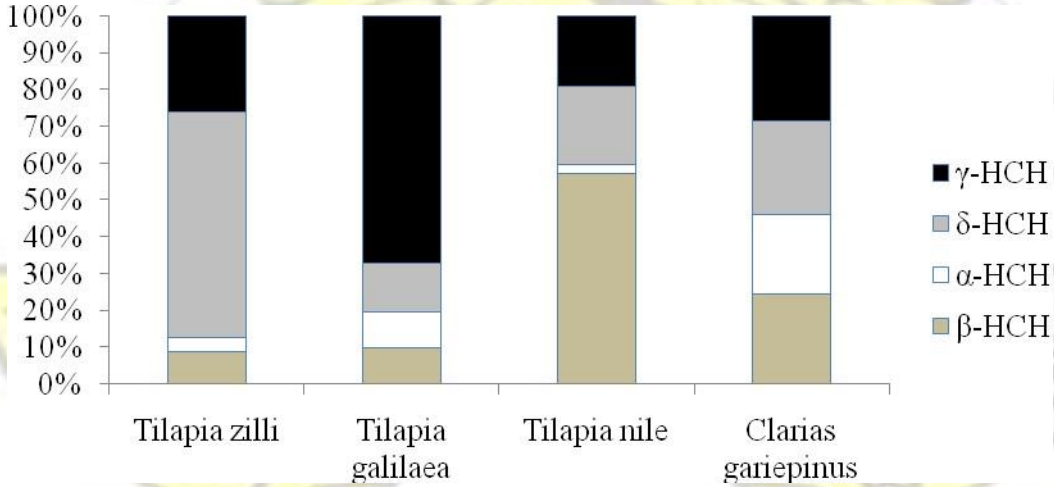


Figure 4.25: HCHs in fish samples from Weija Lake

4.14.3 Distribution of Drins in fish samples

The percentage distribution of drins in the fish samples are presented in Figures 4.26 and 4.27. In the fish species from Lake Bosomtwi, dieldrin was the most abundant drin in the samples. It accounted for more than 50 % of the total drins in all the three fish samples studied. Aldrin was also quite prominent and accounted for more than 30 % of the drins in *Hemischromis faciatus* and *Sarotherodon galileu*. On the other hand, endrin was less significant and was detected only in *Tilapia busumana* with about 10 % of total drins concentration. The distribution pattern of the drins in fish species from Weija Lake was quite different as the three drins were detected in almost all the fish samples. However, as observed in the species from Bosomtwi, dieldrin was the most abundant drin in the Weija species, accounting for more than 50 % of the drins load in *Tilapia zilli*, *Tilapia galilaea* and *Tilapia nile*. On the whole, endrin was the least prevalent drin in the fish samples from the two water bodies.

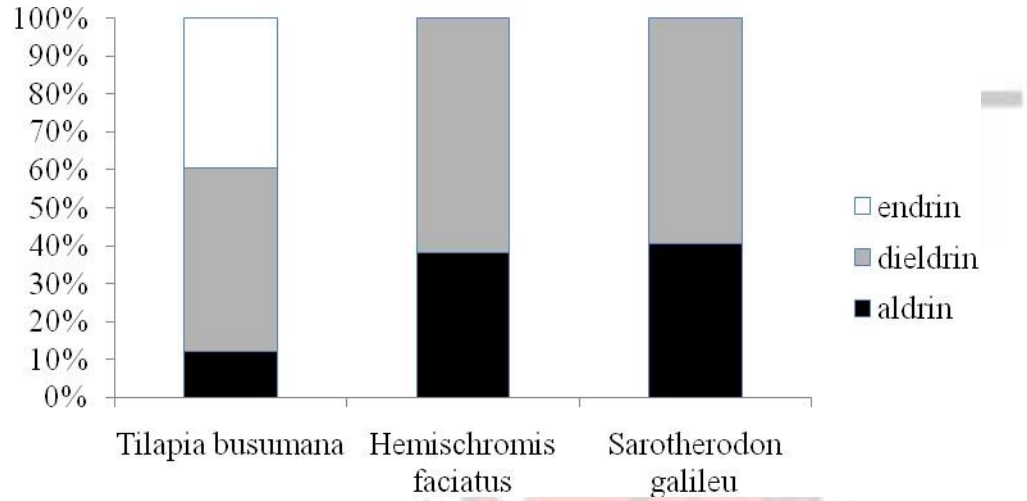


Figure 4.26: Drins in fish samples from Lake Bosomtwi.

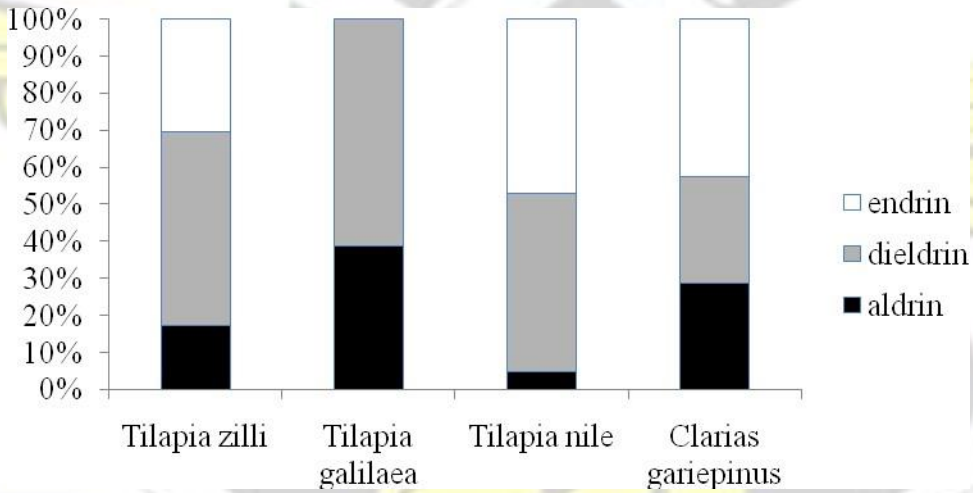


Figure 4.27: Drins in fish samples from Weija Lake.

4.14.4 Distribution of PCBs in fish samples

The profile of indicator PCBs in the fish samples are presented in Figures 4.28 and 4.29. In Lake Bosomtwi PCB congeners, 28, 52 and 101 were the most significant PCBs in the fish species. The three accounted for 100 % of PCB load in *Hemischromis faciatus* and *Sarotherodon galileu*. The congeners, PCB 138 and PCB 180 were only significant in *Talipia busumana* with respective compositions of 40 % and 20 % in the species. PCB 180 was indeed, not detected at all in *Hemiscromis faciatus* and *Sarotherodom galileu.* The trend of PCBs distribution in species from Weija was not different as PCBs 28, 52 and 101 were the most abundant congeners accounting for 100 % of the PCBs load in *Tilapia zilli*, *Tilapia nile* and *Tilapia galilaea*. PCB 138 and 180 were also insignificant congeners in fish species from Weija Lake. They were detected only in *Clarias gariepinus* with a combined percentage composition of about 5 %. Thus, like the sediment samples, the most chlorinated PCBs were also less prevalent in the fish species from the study areas.

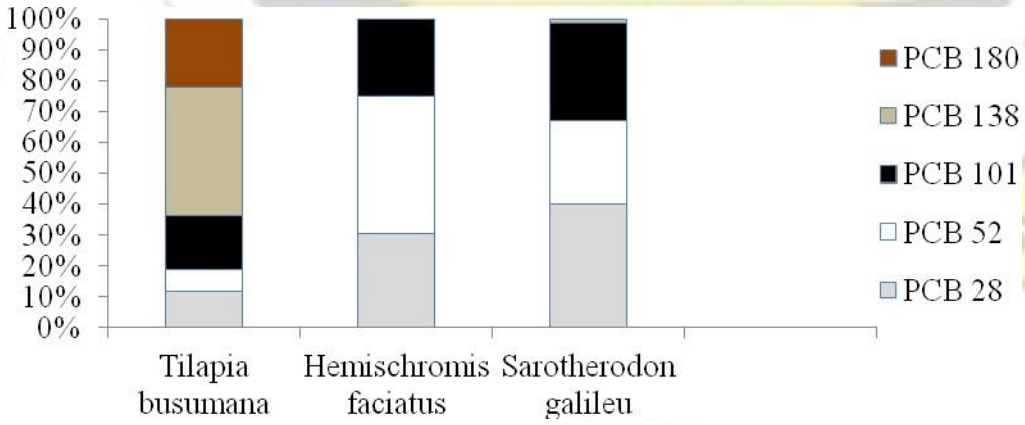


Figure 4.28: PCBs in fish samples from Lake Bosomtwi.

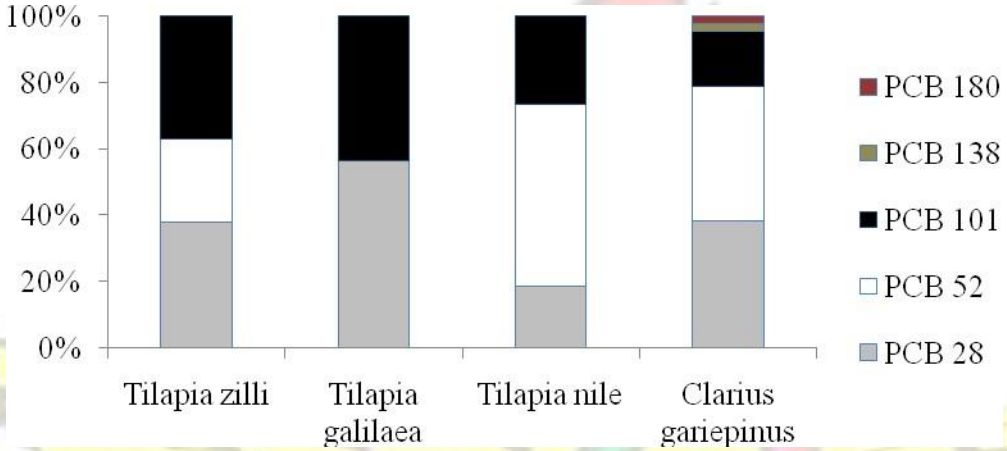


Figure 4.29: PCBs in fish samples from Weija Lake.

4.15 Potential sources of organochlorine pollutants to the study areas

Ghana has officially banned the use of persistent organnchlorines. The sources of organochlorine pesticides in the water bodies could, therefore, be attributed to historical use of these chemicals by farmers and their environmental persistence. The ratio of alpha HCH to gamma HCH ranges from 4 to 15 in technical HCH mixtures and from 0.2 to 1.0 in pesticide lindane (McConnell et al., 1993). In the present study, the ratio ranged from 0.19 to 0.48 in the sediment compartments and

from 0.12 10 0.53 in the fish compartments as presented in Table 4.17. These results therefore, suggest that lindane is the principal sources of HCH in the study areas. The ratio, DDT/(DDE+DDD) is an indication of how recently DDT has been applied to the environment. The ratio of DDT/(DDE+DDD) is therefore used to assess or estimate if there is recent input of DDT in a study area (Liu et al, 2010). If the ratio is greater than one (1) then there is recent or ongoing application of DDT. Analysis of the results showed that in the sediments the ratio ranged from 0.02 to 0.65 while in the fish compartment the ratio was 0.09 to 0.19 (Table 4.17). These values therefore suggest that there might not be fresh input of DDT in the study areas and that the sources of DDT could be attributed to the past use of DDT and environmental persistence of the chemical. The ratios in the water compartment could not be estimated as concentrations of both alpha and DDT were below detection limits in all the water samples.

The presence of indicator PCBs could possibly be linked to release to the environment during various anthropogenic processes such as incineration, combustion, smelting and metal reclamation (Buah-Kwofie et al., 2011; Falandysz, 1998; Ballscmhiter et al., 1987). Even though production of PCBs has been banned globally, significant quantities of these chemicals may still be available, especially in developing countries like Ghana where the importation of old goods of all sorts is still in progress. Old computers, electronics and electrical appliances among other goods are being brought into Ghana on daily basis. Electronic wastes are openly burnt and dumped at uncontrolled locations all over the country and these could contribute to PCBs presence in our environment. Leakages of PCBs from dumped decommissioned transformers and used capacitors into refuse dumps and landfill sites could also have contributed to the sources of PCBs congeners to the Lakes. However, nowadays, when these electrical tranformers are decommissioned, their PCB content is removed and stored to prevent further contamination.

Table 4.17: Ratios of α -HCH to γ -HCH and DDT to sum of its metabolites.

Sediment Compartment	α -HCH / γ -HCH	DDT/(DDE+DDD)
Weija works	0.19	0.12
Machigeni	0.48	0.07
Manheam	-	0.18
Afuaman	-	0.05
Agbozume	-	0.29
Amanfro	-	0.65
Esasse	0.25	0.05
Anyinatiase	1.00	--
Obo	0.48	--
Nkowi	-	0.05
Pipie 2	0.19	0.02
Amakom	-	0.19
Ankaase	-	0.45
Fish Compartment		
Tilapia zilli	0.14	--
Tilapia nile	0.12	0.09
Tilapia galilaea	0.36	--
Clarias gariepinus	0.43	0.19
Tilapia busumana	0.47	--
Sarotherodon galileu	0.51	0.10
Hemischromis faciatus	0.53	--

-α –HCH level was below detection limit; -- DDT level was below detection limit.

4.16 Relationship between sediment carbonaceous materials and organochlorine availability.

The distributions of OCs, including organochlorine pesticides and polychlorinated biphenyls, can be regulated by several factors, including relative concentrations as well as those of their carrier phases during transport (Xing, 1997; Gustafsson et al., 1997; Accardi-Dey and Gschwend, 2002). In sediments organochlorines being organic compounds are most likely to interact with the

carbonaceous materials such as organic carbon, carbohydrates and black carbon in sediments. Against this background, the relationships between organic carbon and black carbon in the sediment with OC concentrations were investigated. Results of plots of OCPs and PCBs concentrations and some carbonaceous materials are presented in Figures 4.30 and 4.31.

As shown in the Figures, OCPs and PCBs concentrations significantly correlated with both total organic carbon (TOC) and black carbon (BC). The correlation coefficient (R^2) ranged from 0.5627 to 0.8288. This suggests that organic carbon and black carbon could be some of the carrier phases of OCs in sediments and therefore may control the distributions of OCPs and PCBs in the sediments. The 60 % correlation between OCPs and PCBs also suggests that OCPs and PCBs might have the same sources before they were transported to the Lakes.

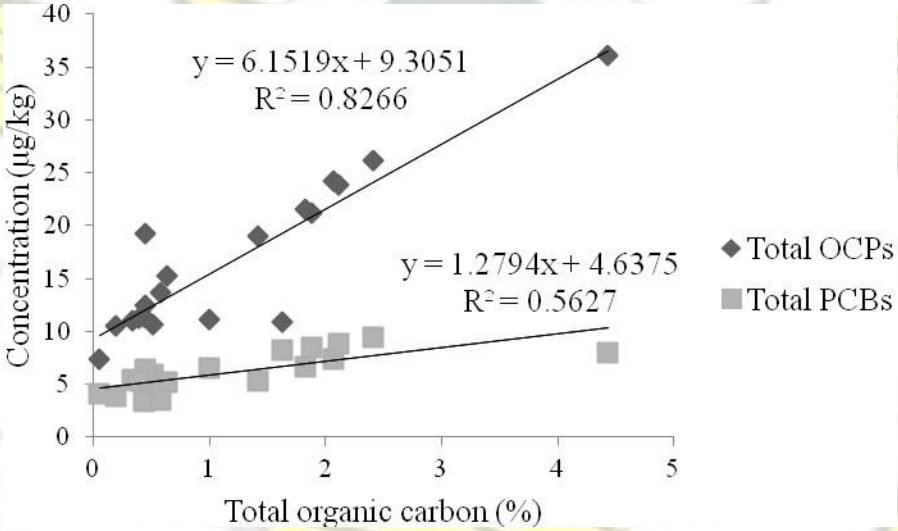


Fig 4.30: Relationship between Total OCs concentration and TOC.

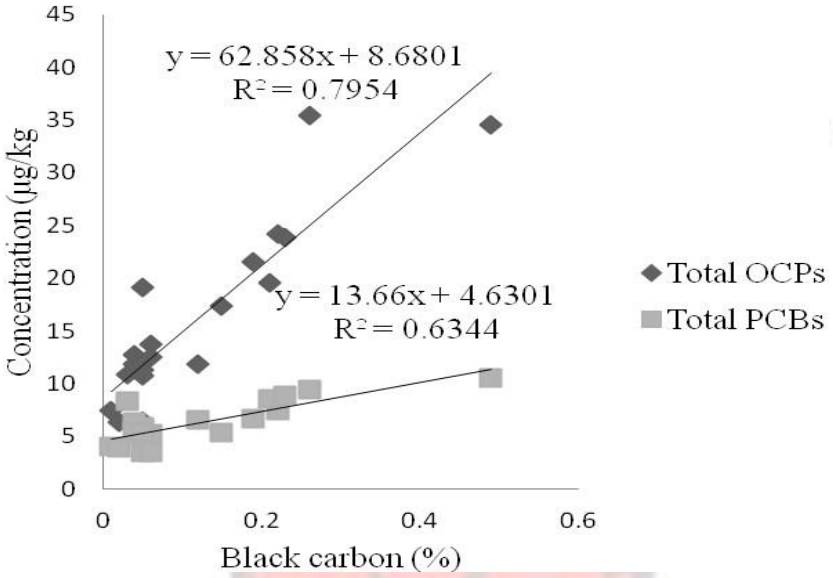


Figure 4.31: Relationship between Total OCs concentration and black carbon.

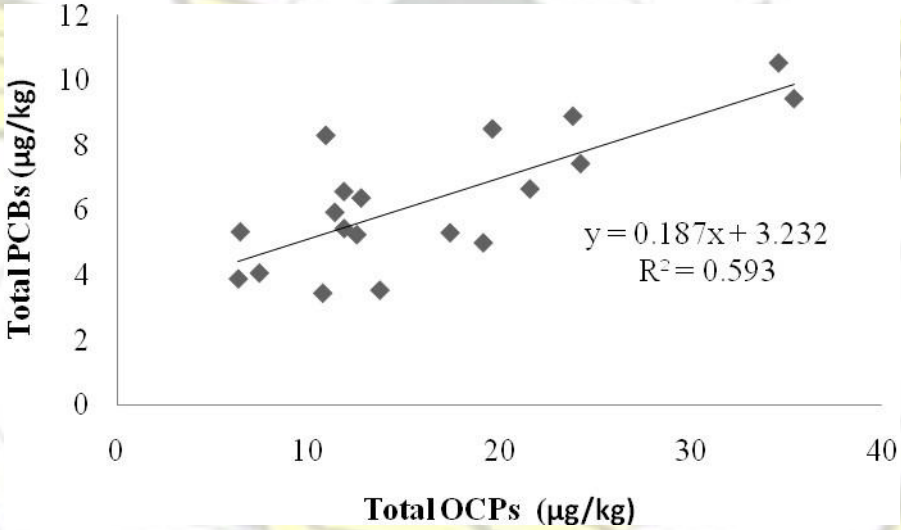


Figure 4.32: Correlation plot between PCBs and OCPs

4.17 Statistical analysis of the OCs

Descriptive statistics showing minimum, maximum, mean concentrations of the organochlorines in the Lakes and data analysis by one way variance (ANOVA) indicating test of significant (Fvalues) as well as the significance (Pvalues) are presented in Tables 4.18, 4.19, and 4.20. Occurrence ratios (x) of the pollutants are also presented in the Tables. The occurrence ratio expresses the ubiquity of the OC. If the ratio is unity (one) then the OC was detected in all the samples analyzed. Zero (0) occurrence ratio is a situation where the OC was not detected.

Descriptive statistics shows that maximum organochlorine concentrations were 4.78 µg/l and 2.55 µg/l in Bosomtwi and Weija water compartments, respectively. The maximum concentration of 4.78 µg/l, was recorded for PCB 52, while 2.55 µg/l was recorded for PCB 28. PCB 52 was therefore the OC with maximum concentration in the water samples analyzed in the two study areas. The analyses also showed that γ-HCH, heptachlor, endosulfan sulfate and PCB 52 were the most ubiquitous OCs in Lake Bosomtwi water with occurrence ratio ranging between 0.50 and 1.00. Similarly, γ-HCH, heptachlor, p,p$^{'}$ – DDD and PCB 52 were the ubiquitous OC in the water samples from Weija with a similar occurrence ratio (0.50 to 1.00). Variance analysis showed that the difference in mean concentrations of the organochlorines in the water samples were statistically significant ($p<0.05$). This could be explained from the fact that the OCs might have reached the study areas through various sources.

Descriptive statistical analysis of the OCs in the sediments (Table 4.23) showed maximum concentrations ranging from 0.55 µg/kg to 7.55 µg/kg and 0.24 µg/kg to 15.21 µg/kg respectively in Bosomtwi and Weija. Indeed, PCB 180 recorded the maximum OC concentration in the sediments from Bosomtwi while endosulfan sulfate similarly registered maximum concentration

in Weija sediments. Occurrence ratios ranged from 0.17 to 1.00 and 0.13 to 1.00 respectively, in Bosomtwi and Weija Lake sediments. Aldrin and PCB 101 were recorded as the least ubiquitous OCs in the Bosomtwi and Weija sediments respectively. γ-HCH, endosulfan sulfate and PCB 52 were the ubiquitous OC in sediments from Lake Bosomtwi, while γ-HCH, dieldrin, endrin and p,p'-DDD were the frequently detected OCs from the Weija sediments. One way analysis of the variance showed that generally, the differences in mean concentrations of the organochlorines in the sediment samples were statistically significant ($p<0.05$), with the exception of α-endosulfan in Bosomtwi sediments and methoxychlor in Weija sediments which had $p>0.05$. Hence, the differences in concentrations of of α-endosulfan in Bosomtwi and methoxychlor in Weija sediments were statistically insignificant.

Descriptive statistical analysis of organochlorine concentrations in the fish samples showed PCB 138 and PCB 52 as OCs 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. For the OCs detected in the fish species, HCHs, heptachlor, aldrin, dieldrin, p,p' –DDE, p,p' –DDD, PCB 28, PCB 52, PCB 101 were the ubiquitous OCs in the fishes from Bosomtwi while HCHs, aldrin, dieldrin, endrin, p,p' –DDE, p,p' –DDD and PCB 28 were the ubiquitous OCs in the fish samples from Weija. Analysis of variance in most cases indicated statistically significance variations in the concentrations of the OCs detected ($P<0.05$). However, the differences in concentrations of β-HCH, aldrin in Bosomtwi species and p,p'-DDD in Weija fishes were statistically insignificant ($p>0.05$).

Table 4.18

: Statistical analysis of organochlorines in the water compartment.

	Bosomtwi						***Weija***					
Organochlorines	min	maxi	mean±SD	x	F value	P value	min	max	mean±SD	x	F value	P value
α - HCH	-	-	-	0			-	-	-	0		
β - HCH	-	-	-	0			-	-	-	0		
γ - HCH	<0.01	0.33	0.06±0.02	0.50	47.39	<0.05	<0.01	0.50	0.16±0.02	0.63	67.31	<0.05
δ - HCH	<0.01	0.45	0.07±0.02	0.42	64.41	<0.05	<0.01	0.14	0.02±.0.01	0.25	24.12	<0.05
heptachlor	<0.01	0.90	0.19±0.03	0.50	185.60	<0.05	<0.01	0.14	0.20±0.02	0.50	254.16	<0.05
aldrin	-	-	-	0			-	-	-	0		
α-endosulfan	-	-	-	0			<0.01	0.20	0.02±0.01	0.25	26.27	<0.05
β-endosulfan	<0.01	0.50	0.04±0.02	0.08	96.55	<0.05	<0.01	0.20	0.03±0.02	0.25	26.27	<0.05
Endosulfan sulfate	<0.01	1.35	0.23±0.05	0.50	264.18	<0.05	0.05	0.20	0.03±0.01	0.25	74.73	<0.05
dieldrin	<0.01	0.10	0.05±0.02	0.08	3.00	>0.05	-	-	-	0		
endrin	-	-	-	0			<0.01	1.30	0.23±0.08	0.25	88.03	<0.05
p,p-DDT	-	-	-	0			-	-	-	0		
p,p-DDE	<0.01	0.30	0.02±0.02	0.17	121.00	<0.05	<0.01	0.25	0.03±0.02	0.13	67.33	<0.05
p,p-DDD	<0.01	4.55	0.86±0.07	0.42	462.45	<0.05	<0.01	0.18	0.04±0.02	0.50	97.44	<0.05
methoxychlor	<0.01	0.14	0.02±0.01	0.08	25.97	<0.05	<0.01	0.08	0.05±0.02	0.13	13.47	<0.05
PCB 28	-	-	-	0			<0.01	2.55	0.63±0.07	0.38	4.10E3	<0.05
PCB 52	0.70	4.78	1.84±0.32	1.00	488.45	<0.05	0.50	2.03	1.35±0.19	1.00	707.80	<0.05
PCB 101	<0.01	0.05	0.02±0.01	0.08	2.57	>0.05	<0.01	0.33	0.04±0.01	0.13	94.08	<0.05
PCB 138	<0.01	1.22	0.11±0.02	0.17	702.50	<0.05	<0.01	1.43	0.18±0.06	0.13	6.81E3	<0.05
PCB 153	-	-	-	0			-	-		0		
PCB 180	<0.01	3.09	0.86±0.07	0.17	7.42E3	<0.05	<0.01	1.14	0.41	0.50	538.10	<0.05

Table 4.19

x= occurrence ratio = sampling points detected/ number of sampling points, - = Not detectable, SD = standard deviation, Number of samples = 24 at Weija and 36 at Bosomtwi, F = test of significance, p = Significance.

: Statistical analysis of organochlorines in the sediment compartments.

	Bosomtwi						***Weija***					
Organochlorines	min	max	mean±SD	x	F value	P value	min	max	mean±SD	x	F value	P value
α - HCH	<0.01	1.20	0.17±0.02	0.33	361.71	<0.05	<0.01	0.24	0.05±0.03	0.25	88.72	<0.05
β - HCH	<0.01	0.55	0.05±0.01	0.33	77.32	<0.05	<0.01	1.05	0.45±0.03	0.63	61.51	<0.05
γ - HCH	<0.01	1.25	0.75±0.06	1.00	137.21	<0.05	0.22	1.28	0.49±0.02	1.00	346.74	<0.05
δ - HCH	<0.01	1.55	0.46±0.09	0.75	555.50	<0.05	<0.01	1.54	0.84±0.09	0.88	3.71E3	<0.05
heptachlor	<0.01	2.47	0.62±0.04	0.83	1.12E3	<0.05	0.40	7.00	2.78±0.33	1.00	3.81E3	<0.05
aldrin	<0.01	1.24	0.12±0.07	0.17	1.02E3	<0.05	<0.01	2.71	1.02±0.07	0.50	2.91E3	<0.05
γ-chlordane	<0.01	0.55	0.15±0.02	0.75	77.28	<0.05	<0.01	2.61	1.42±0.11	1.00	3.00E3	<0.05
α-endosulfan	<0.01	1.00	0.14±0.04	0.42	1.06	>0.05	<0.01	5.68	1.14±0.06	0.88	5.75E3	<0.05
β-endosulfan	0.55	7.50	2.45±0.22	0.92	152.04	<0.05	<0.01	5.64	1.17±0.08	0.88	4.81E3	<0.05
endosulfan sulfate	<0.01	5.44	2..33±0.23	0.67	1.49E3	<0.05	<0.01	15.27	7.92±0.49	1.00	1.80E3	<0.05
dieldrin	0.40	1.13	0.75±0.10	1.00	12.04	<0.05	<0.01	3.78	1.40±0.20	0.88	3.25E3	<0.05
endrin	0.14	1.28	0.87±0.12	1.00	77.27	<0.05	<0.01	0.95	0.63±0.11	0.88	292.80	<0.05
p,p-DDT	<0.01	1.89	0.25±0.04	0.50	374.72	<0.05	0.10	1.30	0.53±0.04	0.63	583.18	<0.05
p,p-DDE	<0.01	4.85	1.26±0.20	0.67	677.54	<0.05	0.5	3.10	1.24±0.09	0.88	2.42E3	<0.05
p,p-DDD	0.20	3.52	1.26±0.12	1.00	122.25	<0.05	<0.01	10.12	2.88±0.16	0.88	7.97E3	<0.05
methoxychlor	0.05	6.34	2.36±0.28	0.92	879.32	<0.05	0.00	2.10	0.71±0.07	0.88	5.58	>0.05
PCB 28	<0.01	6.82	1.62±0.26	0.42	93.47	<0.05	1.35	3.24	2.10±0.13	1.00	612.20	<0.05

Table 4.20

PCB 52	<0.01	6.78	4.55±0.98	0.92	17.49	<0.05	1.56	5.80	3.24±0.31	1.00	319.83	<0.05
PCB 101	<0.01	1.53	0.66±0.13	0.67	31.44	<0.05	<0.01	1.25	0.52±0.06	0.13	2.168E3	<0.05
PCB 138	<0.01	4.92	0.59±0.07	0.25	44.97	<0.05	<0.01	1.04	0.13±0.04	0.25	919.56	<0.05
PCB 153	<0.01	<0.01	-	0.00			<0.01	<0.01	-	0.00		
PCB 180	<0.01	7.55	2.28±0.035	0.42	263.55	<0.05	<0.01	2.37	0.71±0.08	0.50	1.08E3	<0.05

x = occurrence ratio, - = Not detectable, SD = standard deviation, number of samples = 24 at Weija and 36 at Bosomtwi, F = test of significance, p = significance

: Statistical analysis of organochlorines in the fish compartments.

	Bosomtwi						***Weija***					
Compounds	min	max	mean±SD	x	Fvalue	Pvalue	min	max	mean±SD	x	Fvalue	Pvalue
α – HCH	2.20	4.76	3.48±0.56	1.00	50.86	<0.05	0.30	10.27	4.12±0.33	1.00	53.64	<0.05
β – HCH	3.36	5.79	4.74±0.32	1.00	0.954	>0.05	2.21	16.85	9.26±0.48	1.00	28.066	<0.05
γ – HCH	6.17	8.30	7.20±0.55	1.00	13.37	<0.05	7.00	20.80	12.17±0.88	1.00	53.64	<0.05
δ – HCH	0.62	6.66	2.89±0.46	1.00	26.59	<0.05	5.77	12.24	8.61±0.50	1.00	13.38	<0.05
heptachlor	6.55	8.85	7.93±0.48	1.00	12.73	<0.05	<0.01	18.02	7.25±0.20	0.75	126.28	<0.05
aldrin	3.04	6.61	4.96±0.28	1.00	2.251	>0.05	0.84	8.24	5.20±0.46	1.00	148.85	<0.05
γ -chlordane	0.66	17.18	6.27±0.31	1.00	87.72	<0.05	<0.01	5.83	2.36±0.37	0.50	232.38	<0.05
α-endosulfan	<0.01	6.88	3.16±0.25	0.67	164.04	<0.05	<0.01	4.66	1.58±0.04	0.50	173.93	<0.05
β-endosulfan	<0.01	6.63	1.92±0.07	0.33	121.00	<0.05	<0.01	3.55	0.64±0.03	0.25	19.16	<0.05
Dieldrin	4.23	10..70	7.31±0.65	1.00	55.379	<0.05	3.00	12.49	7.30±0.57	1.00	36.48	<0.05
Endosulfan sulfate	<0.01	6.06	6.08±0.51	0.67	44.96	<0.05	<0.01	10.53	6.03±0.44	0.75	169.17	<0.05
Endrin	<0.01	9.90	3.02±0.16	0.33	281.32	<0.05	3.00	6.42	4.74±0.27	1.00	4.81	>0.05
p,p-DDT	<0.01	1.33	0.35±0.03	0.33	39.49	<0.05	<0.01	2.44	0.79±0.08	0.50	22.04	<0.05
p,p-DDE	3.35	10.99	7.55±0.45	1.00	31.069	<0.05	1.65	6.94	3.30±0.63	1.00	19.76	<0.05

Table 4.21

p,p-DDD	0.38	6.02	3.20±0.81	1.00	56.41	<0.05	2.63	12.02	6.13±0.31	1.00	3.36	>0.05
Methoxychlor	<0.01	6.12	1.93±0.16	0.33	1.03E3	<0.05	<0.01	5.62	1.21±0.09	0.25	144.93	<0.05
PCB 28	3.40	7.85	6.34±0.36	1.00	8.50	<0.05	0.00	31.66	11.22±0.88	0.75	347.04	<0.05
PCB 52	2.35	11.28	6.06±0.47	1.00	100.87	<0.05	0.00	32.40	11.08±0.66	0.75	1.01E3	<0.05
PCB 101	5.08	8.25	6.40±0.59	1.00	21.22	<0.05	2.40	13.32	6.76±0.43	1.00	92.46	<0.05
PCB 138	<0.01	18.43	5.88±0.27	0.67	1.86E3	<0.05	<0.01	1.05	0.25±0.05	0.25	303.92	<0.05
PCB 153	<0.01	<0.01	-	0	-	-	<0.01	<0.01	-	0	-	-
PCB 180	<0.01	9.85	2.80±0.29	0.33	90.38	<0.05	<0.01	0.85	0.18±0.03	0.25	121.94	<0.05

x = occurrence ratio, - = Not detectable, SD = standard deviation, F = test of significance, p = significance

4.18 Risk assessment of organochlorine pollution.

Risk assessment of studied organochlorine pollutants was determined by analyzing the ecotoxicology impact of sediments to aquatic species as a result of OC concentration in the sediments as well as impact of organochlorine on humans due to drinking of water and consumption of fishes from the Lakes.

4.18.1 Ecotoxicologyical assessment of sediments

Sediment quality guidelines, ERL and ERM specified by USEPA (1997) and by Canadian Council of Ministers for Environment (CCME, 2002) were used to assess the potential ecotoxicological impacts of the organochlorines measured in the sediments. These benchmarks were used as EPA Ghana does not have its own benchmarks. ERL represents the concentrations at which toxicity may begin to be observed in sensitive aquatic species or ERL indicate concentrations below which adverse effects will not occur whereas, ERM indicate concentrations above which adverse effects will occur in aquatic species. Sediment quality criteria and mean organochlorine concentrations are presented in Table 4.21

Table 4.21: Ecotoxicology impacts of sediments on aquatic species.

Compounds	Bosomtwi sediment(µg/kg)	Weija sediment (µg/kg)	ERL_1	ERM_1

ΣPCB	8.08	6.70	22.70	180.00
p,p'-DDT	0.23	0.53	1.00	7.00
P,P'-DDE	1.26	1.24	2.20	27.00
P,P'-DDD	1.26	2.88	2.00	20.00
ΣDDT	2.75	4.65	5.58	46.10
γ-HCH	0.75	0.49	-	-
Chlordane	0.15	1.42	0.50	6.00

[1]Wurl, 2006.

The ΣPCB, p,p'-DDT, p,p'-DDE, ΣDDT concentrations in both Weija and Bosomtwi sediments were below the ERL values and significantly lower than the ERM values. Toxicity of PCBs, p,p'-DDT, p,p'-DDE and ΣDDT in the sediments to aquatic species can, therefore, be ranked as below ERL. On the other hand, the mean concentrations of p,p'-DDD (2.88 µg/kg) and Chlordane (1.42 µg/kg) in Weija sediments were all above the ERL but below the ERM. Based on these, the toxicity of p,p'-DDD and Chlordane could be ranked as intermediate (Wurl, 2006) in the Weija sediments. However, toxicity of p,p'-DDD (1.26 µg/kg) and Chlordane (0.15 µg/kg) in Bosomtwi sediments were below ERL. The results therefore, suggest that generally, OC pollution in the sediments may not cause adverse effects to aquatic species.

4.18.2 Impact of organochlorine pollution to humans

4.18.2.1 Comparison of organochlorine concentrations to maximum residue limits.

The health effect of organochlorines cannot be underestimated hence, maximum residue limits

(MRLs) have been recommended by different reguratory bodies to regulate human consumption of organochlorines through drinking of water and food consumption. The Weija Lake and Lake Bosomtwi are important water resources in Ghana, it is therefore, important to assess the potential risk of consumption of water drawn from the Lakes and dietary intake of fish from the Lakes by comparing with established maximum residue limits. Levels of organochlorine recorded in the study were compared to standards set by the World Health Organization (WHO), Australian Government (Hamilton et al., 2003), European Union, Food and Agriculture Organization and Italian Government. The results are shown in Tables 4.22 and 4.23. The results showed that mean OCs concentrations reported in this study were generally, below the maximum residue limits of international bodies particularly, concentrations in the water samples. However, levels of endosulfan sulfate and p. p'-DDE in the water samples were closer to Australian guidelines of 0.05 µg/l and 0.06 µg/l respectively. Furthermore, even though levels in the fish samples were lower than levels set by international bodies, the reported levels in the fishes are quite significant. For instance the levels recorded for δ-HCH (12.24 µg/kg) were slightly higher than the European Union MRL (10µg/kg). The results therefore, suggest that though drinking of water and eating of fishes from the two water bodies may not cause health hazard in terms of OCPs pollution, chronic exposure could lead to bioaccumulation. There is therefore, the need to continuously monitor our water bodies for these OCs and related pollutants to ensure the health safety of our people.

Table 4.22: Comparison of mean concentrations of OCs (µg/l) in waters to guidelines of some International bodies

Organochlorines	*Lake Bosomtwi*	*Weija Lake*	*WHO guide*
	-	0.02 [a]	0.05
Endosulfan sulfate	0.03	0.03	[a]
Dieldrin	-	-	0.03
α-HCH	-	-	2.00
β-HCH		0.06	2.00
γ-HCH		0.17	2.00
Endrin	-	0.02	
Aldrin	-	0.02	0.03
p,p-DDT	-	-	2.00
p,p-DDE	0.02	0.03	2.00
Methoxychlor	0.02	0.05	20.00
Chlordane	-	-	0.02
∑DDT	0.88	0.07	[a]
∑PCB	2.83	2.61	[a]

Levels reported represent average concentration of the organochlorine in the Lakes. -not detected'

[a]value not available.

Table 4.23: Comparison of mean concentrations of OCs in fish (μgkg^{-1}) to MRLs of some International bodies

	Bosomtwi			Weija								
OCs	Tilapia busumana	*Sarotherodon galileu*	*Hemischromis faciatus*	*Tilapia zilli*	*Tilapia galilaea*	*Tilapia nile*	*Clarias gariepinus*	US FDA 2001[b]	EU MRL[c]	Australian MRL[d]	Italian MRL	FAO
dieldrin	10.70	4.90	7.36	12.49	5.19	9.59	3.36	300	200	100	200	300
γ-HCH	7.27	7.04	7.36	9.53	13.24	7.28	23.70	300	1000	1000	1000	300
δ- HCH	1.18	1.39	5.83	12.24	6.61	8.03	12.20	[a]	10	[a]	[a]	[a]
aldrin	5.87	3.04	5.03	4.84	8.06	0.93	8.14	[a]	[a]	100	[a]	[a]
endrin	9.21	<0.01	<0.01	6.42	5.08	3.33	4.96	300	50		50	300
p,p'-DDT	<0.02	1.09	<0.01	-	-	0.93	2.44					
p,p'-DDE	18.40	10.99	4.73	2.44	2.75	1.85	6.94					
p,p' -DDD	3.62	0.53	5.62	3.50	12.46	8.77	5.70					
o,p -DDE				11.17	8.50	-	-					
∑endosulfan	3.64	5.90	6.68	6.94	<0.01	2.32	-	[a]	100	[a]	100	[a]
∑DDT	22.02	12.61	11.45	17.11	23.71	11.55	15.08	5000	1000	1000	1000	300
∑PCB	44.56	23.81	27.82	13.99	20.02	22.95	78.07	[a]	200	[a]	[a]	[a]

[b]Sanker et al (2006), [c]Stefanelli et al (2004), [d]APVMA (2012), [a]not available, -not detected, Levels reported are mean organochlorine concentrations.

4.18.2.2 Estimation of daily exposure of organochlorines through dietary eating of fishes from Weija and Bosomtwi.

The daily intake of OCs through dietary consumption of fishes from the study areas are presented in Tables 4.24 and 4.25. The estimated daily exposures were compared to USEPA reference doses which were available. An aggregate daily exposure to organochlorine residue at or below the RfD is generally considered acceptable by the USEPA (Snelder et al., 2008; USEPA, 1996). The values for estimated daily intake ranged 0.002 µg/kg to 0.176 µg/kg and 0.001 µg/kg to 0.0892 µg/kg for children and adults respectively. The maximum exposure daily intake (0.176 µg/kg) was estimated for children on consumption of *Clarias gariepinus* as a result of PCBs contamination. The minimum exposure daily intake (0.002 µg/kg) on the other hand, was also estimated for adults on consumption of *Hemiscromis faciatus* due to PCB 138 contamination. From the results consumption of *Clarias gariepinus* among the fishes happens to provide the highest risk of organochlorine exposure. It is also obvious from the results that the estimated daily exposure for both children and adults through consumption of the studied fishes fell below the USEPA reference doses. The implication is that consumption of the investigated fishes from Lake Bosomtwi and Weija Lake may not pose health risks to humans in terms of OC pollution. Figure 4.33 shows the plot of estimated daily intake of OCs for children against estimated that of adults using three of the studied fishes. The plot reveals that estimated daily exposures of OC to children on

consumption of the fishes are higher than estimated daily exposure to adults. Indeed, the relationship between the two shows that exposure to children is approximately equal to two times those of adults. This trend could be attributed to the small body

weight of children compared to adults. Therefore, children in terms of OC exposure are more vulnerable.

Table 4.24: Estimated daily intake of organochlorines for children (µg/kg body wt) through dietary intake of the fishes.

Organochlorines	*Tilapia zilli*[a]	*Tilapia galilaea*[a]	*Tilapia nile*[a]	*Clarias gariepinus*[a]	*Tilapia busumana*[b]	*Sarotherodon galileu*[b]	*Hemischromis faciatus*[b]		*Reference dose (RfD)*
α-HCH	0.003	0.011	0.002	0.023	0.078	0.008	0.009		
β -HCH	0.007	0.038	0.024	0.027	0.012	0.013	0.010		
δ -HCH	0.028	0.015	0.018	0.028	0.003	0.003	0.013		3.00
γ -HCH	0.022	0.030	0.017	0.054	0.017	0.016	0.017		0.30
Heptachlor	-	0.009	0.043	0.050	0.017	0.018	0.019		0.10
Aldrin	0.011	0.018	0.002	0.019	0.013	0.007	0.011		0.10
γ-chlordane	-	0.009	0.013	-	0.017	0.003	0.002		0.50
α-endosulfan	0.009	-	0.005	-	0.008	-	0.016		0.05
β-endosulfan	0.006	-	-	-	-	0.013	-		
Dieldrin	0.028	0.012	0.022	0.008	0.024	0.011	0.017		0.10
Endrin	0.015	0.011	0.008	0.011	0.021	-	-		0.20
p,p-DDT	-	-	0.002	0.006	-	0.002	-		0.50
p,p-DDE	0.006	0.006	0.004	0.016	0.019	0.025	0.011		0.50
p,p-DDD	0.008	0.024	0.020	0.013	0.008	0.001	0.013		
Endosulfan sulfate	0.019	-	0.024	0.015	0.010	0.012	-		0.05
PCB 28	0.008	0.019	0.008	0.069	0.007	0.017	0.015		
PCB 52	0.005	-	0.023	0.073	0.007	0.026	0.010		
PCB 101	0.008	0.015	0.011	0.030	0.018	0.014	0.012		
PCB 118	0.008	0.012	0.008	-	-	0.006	0.018		
PCB 138	-	-	-	0.002	0.042	-	0.001		
PCB 180	-	-	-	0.002	0.002	-	-		
∑HCHs									
∑DDTs	0.014	0.030	0.026	0.035	0.027	0.028	0.025		
∑PCBs	0.029	0.046	0.050	0.176	0.076	0.063	0.056	0.20	

[a] Fishes from Weija Lake, [b] Fishes from Lake Bosomtwi

Table 4.25: Estimated daily intake of organochlorines for adults (µg/kg body wt) through dietary intake of the fishes.

Organochlorines	*Tilapia zilli*[a]	*Tilapia galilaea* [a]	*Tilapia nile*[a]	*Clarias gariepinus*[a]	*Tilapia busumana*[b]	*Sarotherodon galileu*[b]
α-HCH	0.0013	0.0055	0.0011	0.0117	0.0039	
β -HCH	0.0037	0.0192	0.0122	0.0133	0.0062	
δ -HCH	0.0139	0.0075	0.0092	0.0139	0.0014	
γ -HCH	0.0109	0.0151	0.0083	0.0270	0.0083	
Heptachlor	-	0.0048	0.0217	0.0249	0.0083	
Aldrin	0.0055	0.0092	0.0011	0.0093	0.0067	
γ-chlordane	-	0.0047	0.0067	-	0.0082	
α-endosulfan	0.0049	-	0.0026	-	0.0042	
β-endosulfan	0.0030	-	-	-	-	
Dieldrin	0.0143	0.0059	0.0109	0.0038	0.0122	
Endrin	0.0073	0.0058	0.0005	0.0057	0.0105	
p,p-DDT	-	-	0.0011	0.0028	-	
p,p-DDE	0.0028	0.0031	0.0021	0.0079	0.0096	
p,p-DDD	0.0040	0.0119	0.0100	0.0065	0.0041	
Endosulfan sulfate	0.0095	-	0.0120	0.0076	0.0051	
PCB 28	0.0040	0.0096	0.0038	0.0350	0.0060	

PCB 52	0.0026	-	0.0114	0.0370	0.0036
PCB 101	0.0039	0.0074	0.0055	0.0152	0.0088
PCB 118	0.0041	0.0035	0.0041	-	-
PCB 138	-	-	-	0.0011	0.0210
PCB 180	-	-	-	0.0009	0.0112
∑HCHs	0.0298	0.0472	0.0308	0.0659	0.0198
∑DDTs	0.0068	0.0150	0.0132	0.0172	0.0137
∑PCBs	0.0146	0.0205	0.0248	0.0892	0.0506

	Hemischromis	*Reference dose*
0.0041	0.0044	
0.0066	0.0050	
0.0016	0.0067	3.00
0.0080	0.0083	0.30
0.0092	0.0097	0.10
0.0035	0.0057	0.10
0.0008	0.0011	0.50
-	0.0078	0.05
0.0067	-	
0.0056	0.0084	0.10
-	-	0.20
0.0012	-	0.50
0.0125	0.0054	0.50
0.0006	0.0064	
0.0060	-	0.05
0.0087	0.0074	
0.0129	0.0050	
0.0072	0.0058	
0.0030	0.0088	
-	0.0020	
-	-	
0.0203	0.0244	
0.0143	0.0118	
0.0318	0.0272	0.20

faciatus[b]

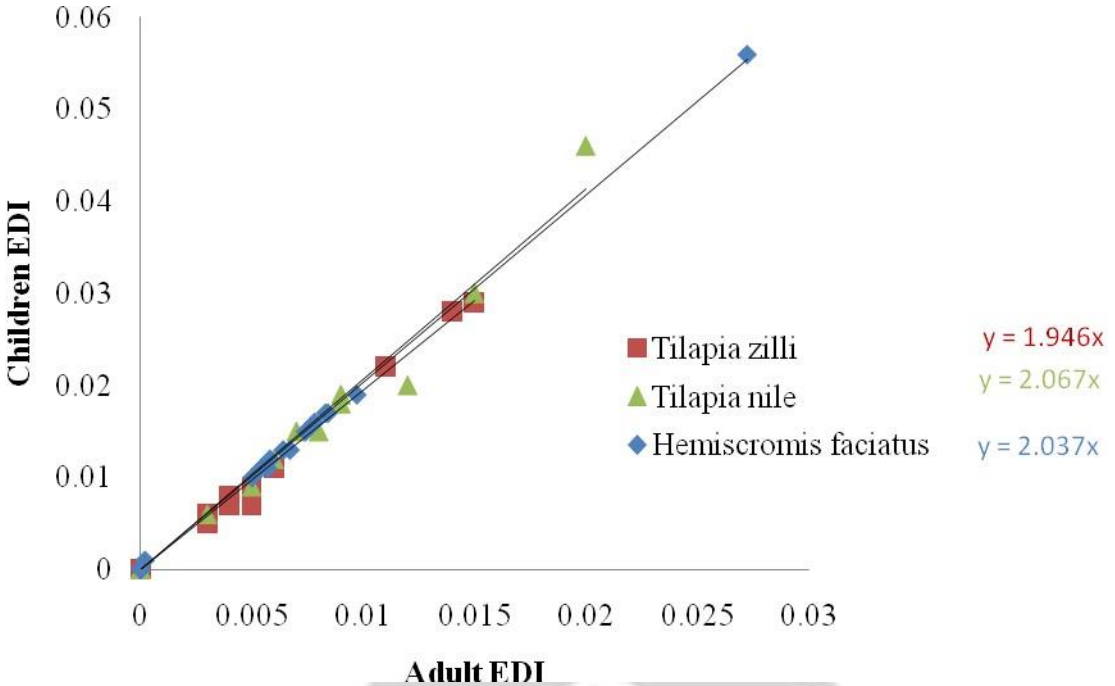


Figure 4.33: Estimated daily intake of children verse estimated intake of adults

4.18.2.3 Estimation of hazard ratio (HR)

The benchmark concentrations for carcinogenic effect were estimated using USEPA cancer slope factors while non - cancer benchmark concentrations for non- cancer effects such as reproductive abnormalities are available USEPA reference doses (RFDs) (USEPA. 1990). Table 4.26 shows the cancer slope factors, available USEPA non-cancer benchmark concentrations and calculated cancer benchmark concentrations for some selected organochlorines. Cancer benchmark concentrations as reported by Dougherty et al (2000) and Jiang et al (2005) are also presented in Table 4.26.

Table 4.26: Cancer slope factors and benchmark concentrations for some organochlorines

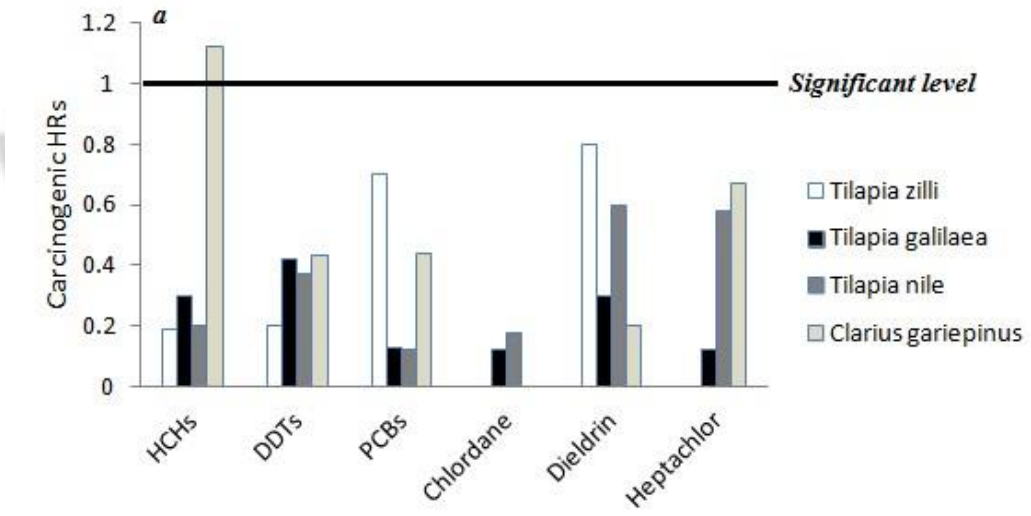
Organochlorine	Cancer slope factor [per (mg/kg/day)]	non-cancer benchmark (µg/kg x day)	cancer benchmark (mg/kg x day)	Dougherty et al, (2000)	Jiang et al (2005)
HCHs	1.50	0.30	0.000153	0.00077	
DDTs	0.34	0.50	0.00035	0.0003	0.00017
Endosulfan		0.60			
Heptachlor	0.36	0.50	0.00018	0.00022	
Chlordane	0.35	0.06	0.000357		0.0016
Dieldrin	16.00	0.05	0.000163		0.00004
PCBs	2.00	0.02	0.000204		0.00029

Comparing the cancer benchmark concentrations deduced for this study with those of Dougherty et al (2000) and Jiang et al (2005), values obtained for this study were comparable to those reported by Jiang et al (2004) but slightly lower than those of Dougherty et al (2000). Hazard ratios (HRs) associated with HCHs listed as (γ-HCH + α –HCH + β- HCH + δ- HCH), DDTs (p,p-DDT + p, p –DDE + p,p –DDD), endosulfan (α-endosulfan + β-endosulfan + endosulfan sulfate), heptachlor, chlordane, dieldrin, and PCBs expressed as simple fractions with significant levels are presented in Figure 4.34 and Figure 4.35 for Weija and Bosomtwi fishes investigated, respectively.

It can be observed that exposure to DDTs, PCBs, chlordane, heptachlor and dieldrin as a result of eating of *Tilapia zilli*, *Tilapia nile* and *Tilapia galilaea* in the Weija Lake present no risk of carcinogenic effect as their HRs values fell below the significance level. However, carcinogenic HRs on exposure to HCHs contamination as a result of eating of *Clarias gariepinus* has HR greater than 1. The toxicological implication is that more than one in one million of the population on

consumption of *Clarias gariepinus* can get cancer. The situation at Bosomtwi is quite different as all the cancer HRs values fell below the significant level. The implication is that eating of the studied fishes from Lake Bosomtwi in terms of OC pollution will not result in carcinogenic effects. Figure 4.35 suggests that there will not be non carcinogenic effects such as reproductive abnormality on consumption of the studied fishes as a result of HCHs, DDTs, chlordane, dieldrin and heptachlor contamination as non carcinogenic HRs for HCHs, DDTs, chlordane, dieldrin and heptachlor OCs were below the significant level. On the other hand consumption of *Tilapia nile, Tilapia galilaea, Clarius gariepinus* from Weija and *Tilapia busumana, Sarotherodon galileu, Hemiscromis faciatus* from Lake Bosomtwi due to PCBs contamination present the toxicological risk of non carcinogenic effect such as reproductive abnormalities (Figure 4.35).

It is imperative to stress that upon ingestion of fish contaminated with OC, bioavailability of the OC may be controlled by chemical properties of the OC. Human variables such as age, sex, diet and state of human health may affect bioavailability. These factors may present some inherent challenges in evaluating the risks to human health due to OC exposure.



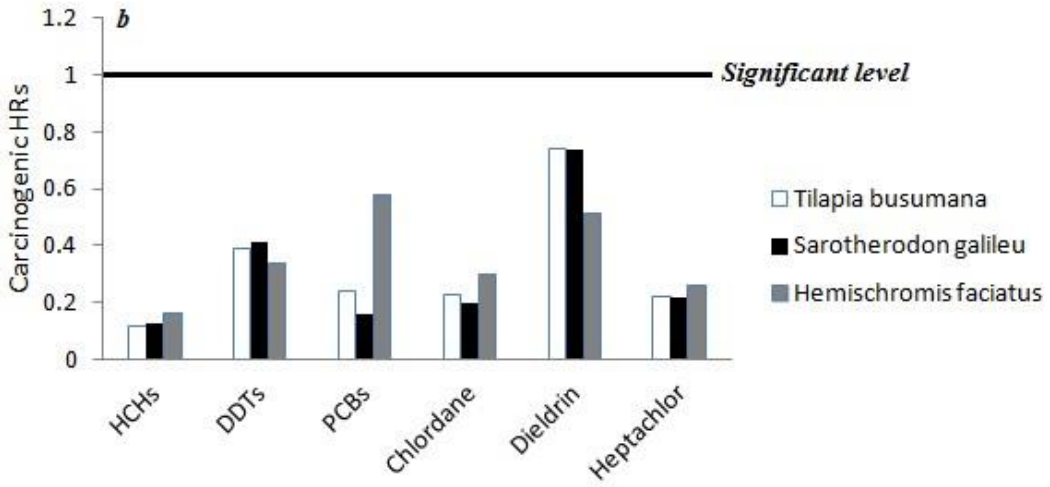
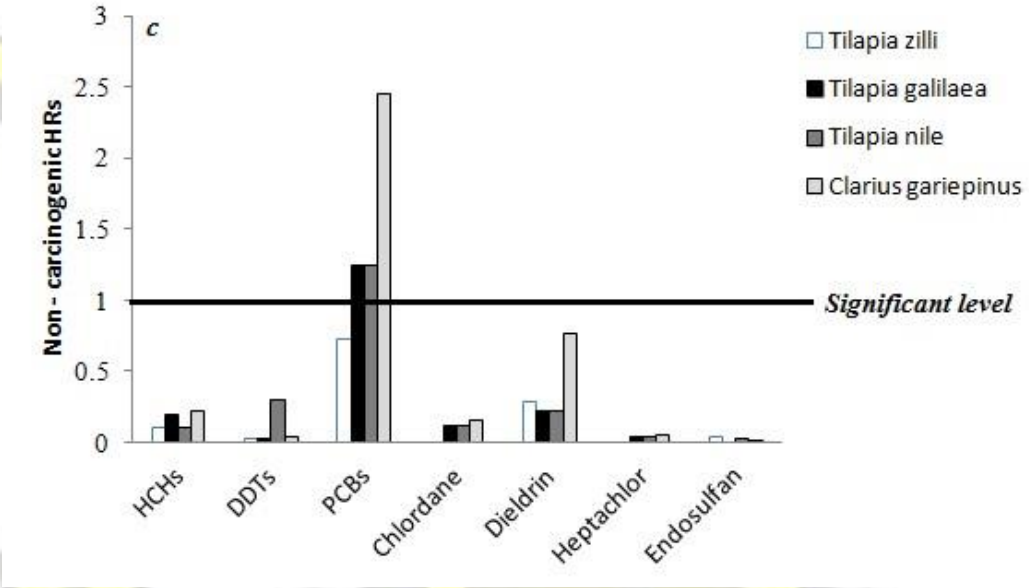


Figure 4.34: Cancer hazard ratios (HRs) on consumption of the studied fishes.



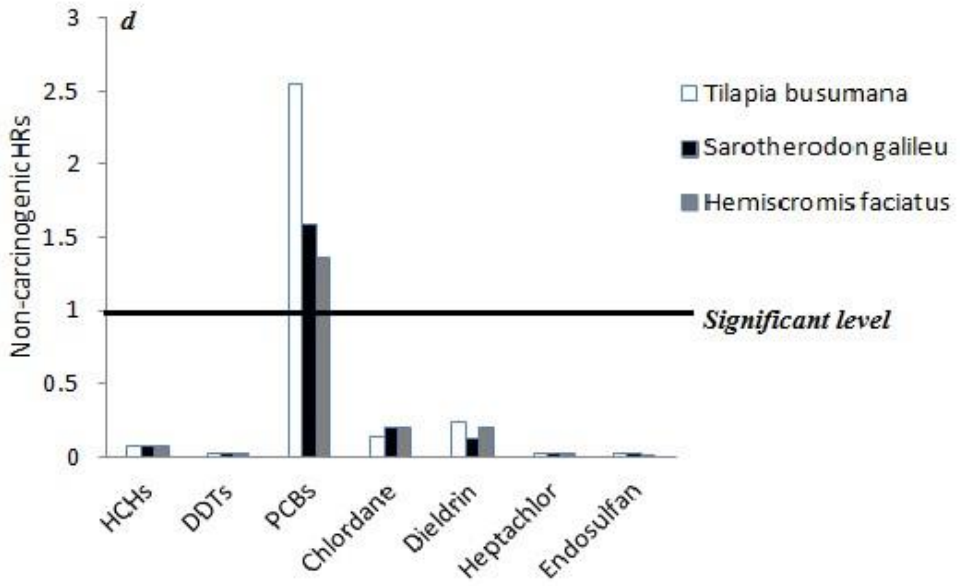


Figure 4.35: Non-cancer hazard ratios (HRs) on consumption of the studied fishes.

CHAPTER FIVE

5.0 Conclusion and recommendation

5.1 Conclusion

From the results presented and discussed, the following conclusions can be drawn.

The presence of persistent organochlorine pesticides (OCPs) and their degradation products as well as indicator polychlorinated biphenyls (PCBs) at varying concentrations were detected in Lake Bosomtwi and Weija Lake. In all, a total of seventeen OCPs and five indicator PCBs were detected at each of the two study areas. Generally, the concentrations of the OCs in the fishes and sediments were significantly higher compared to those in the water compartment. However, the concentrations in the fishes were slightly higher than those reported for the sediment compartment.

The concentrations of organochlorine detected in the study areas were comparable, however; sediments from Weija recorded slightly higher OCPs concentrations than those from Bosomtwi. In Weija Lake PCB 28 was recorded as OC with maximum concentrations in both the water and fish compartments while endosulfan sulfate was the maximum OC in the sediments. Similarly, p,p'-DDD, PCB 180 and PCB 138 were the OC with maximum concentrations in the water, sediments and fish samples respectively from Bosomtwi. Gamma-HCH, heptachlor, endosulfan sulfate, p, p'-DDD, p, p'-DDE, PCB 52 were the most ubiquitous OCs in the Lake Bosomtwi. In Weija Lake the most frequent detected OCs were γ-HCH, heptachlor, endosulfan sulfate, p, p'DDD, p, p'-DDE, dieldrin and PCB 52. In most cases the differences in concentrations of the OCs were found to be statistically significant ($P< 0.05$). The metabolites, p, p'-DDE and p, p'DDD were more significant than the parent DDT in the study areas. The metabolites in most of the samples accounted for more than 80 % of the total DDT load. γ –HCH (lindane) was the dominant isomer among the four isomers of HCHs investigated and accounted for 100 % of HCHs load at some of the sampling locations. The less chlorinated PCBs (# 28, 52 and 101) were more prominent than the most chlorinated homologues (# 138, 153 and 180) with PCB 52 detected in all the sediment and fish samples.

Bioconcentration factor (BCF) studies showed that the fishes had accumulated more OCPs than indicator PCBs. In general, *Clarias gariepinus* from Weija Lake bioaccumulated more OCs than the other species while in Lake Bosomtwi *Tilapia busumana* was found to have bioaccumulated more OCs compared to the other two species.

Analysis of the results indicated that the source of HCHs was potentially, due to past use of the pesticide lindane and not due to the use of technical HCH. The sources of DDTs were found to have resulted from environmental persistence and not from on going application of the chemical.

Anthropogenic processes such as incineration, combustion, smelting and metal reclamation as well as the past practices involving dumping of decommissioned transformers and used capacitors into landfill sites and refuse dumps were attributed as the potential sources of PCB congeners to the study areas.

Carbonaceous materials (organic carbon and black carbon) in the sediments were found to correlate very well with OCPs and PCBs concentrations particularly, the OCPs concentrations. Organic carbon and black carbon could therefore be some of the carrier phases of OCs in sediments and they may therefore, control the distributions of OCs in the sediments.

Ecotoxicology impact of sediments on aquatic species using sediment guidelines suggested that the level of OCs in the sediment may not pose threat to aquatic species. Mean OC concentrations reported in this study generally were below the maximum residue limits of international bodies particularly, concentrations in the water samples. However, levels of endosulfan sulfate and p. p'-DDE in the water samples were closer to Australia guidelines and the levels recorded for δHCH in *Tilapia zilli* sampled from Weia were slightly higher than the MRL set by European Union. Estimated daily intake or exposures to organochlorines through consumption of the studied fishes were far below reference doses stipulated by USEPA. Consumption of *Clarias gariepinus* collected from Weija provided the highest risk of OC exposure while consumption of *Hemiscromis faciatus* from Bosomtwi provided the least risk of OCs exposure. In terms of OC exposure children were found to be more vulnerable compared to adults. Organochlorine exposure analysis showed that for the same quantity of fish consumed children are exposed to more OC than adults and this was attributed to the small body weight of children.

Consumption of *Tilapia zilli*, *Tilapia nile* and *Tilapia galilaea* from the Weija Lake present no risk of carcinogenic effect. However, more than one in one million of the population on consumption of *Clarias gariepinus* can get cancer as a result of HCHs contamination.

Consumption of the studied fishes from the Lake Bosomtwi presented no carcinogenic effect.

5.2 Recommendations

It is recommended that further work should be carried out in subsequent years in other critical water bodies in Ghana, for instance in Volta Lake, Owabi River, Chemu Lagoon, etc to show the extent of OC pollution in them. The study could also be replicated in the Ghanaian marine environment in order to obtain data on ecotoxicology impact of OCs on marine organisms. Assessment of levels of OCs in ground waters could be useful in ascertaining whether these pollutants have entered our ground waters. Conspicuously, absent in Ghana are data on OC pollutants in the air. Hence levels of OC pollutants in air need to be investigated to obtain knowledge on OC pollutants in Ghanaian air compartment. Furthermore, polyaromatic hydrocarbons (PAHs), polybrominated biphenyl ethers (PBDE) could be investigated in future studies.

In estimating the risks of the pollutants to humans actual average body weights of a Ghanaian children and adult should be determined and used for computation instead of adopting the method of United States Environmental Protection Agency. In ecotoxicological evaluation of OCs on humans as a result of consumption of fishes, the effect of cooking on the organochlorine concentrations in the fish compartment has to be investigated since fishes are cooked or fried before eating. This will present the actual or accurate concentrations of OCs that may enter the human body upon eating of fishes. It is time the Environmental Protection Agency of Ghana as matter of urgency develop its own maximum residue level, reference doses, cancer and non cancer

benchmarks and sediments guidelines for OCs and other toxicants. These will serve as Ghana standards so that on assessing toxicity of OCs in Ghanaian environment, Ghana EPA benchmarks would be used.

Policy makers and water resource managers as a matter of urgency should ensure regular monitoring of our water bodies for OCs and related organic pollutants. In view of the immense contributions of the Weija Lake and Lake Bosomtwi to the livelihood of the people within their catchments, management practices should be adopted by both the Government and the Local Authorities to save the Weija and Bosomtwi and other water bodies from pollution. Water Body Management Boards should be set up for Weija and Bosomtwi and these Boards need to be proactive and vibrant in monitoring land use activities within their basins. Community involvement in all the decisions bordering on water management in the basins should be adopted to ensure acceptance and compliance of policies.

Last but not the least there should be sustainable public education on natural resource management In Ghana.

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CHAPTER THREE

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APPENDIX 1

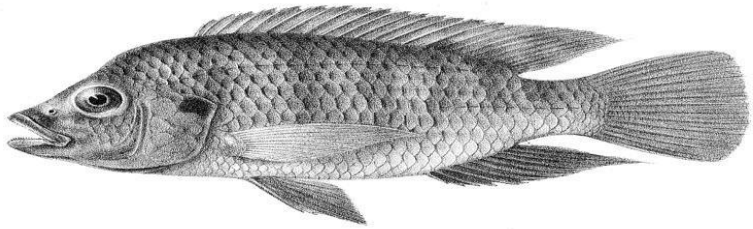
Pictures of some of the studied fishes

Tilapia nile

Tilapia zilli

Tilapia galilaea

Clarias gariepinus

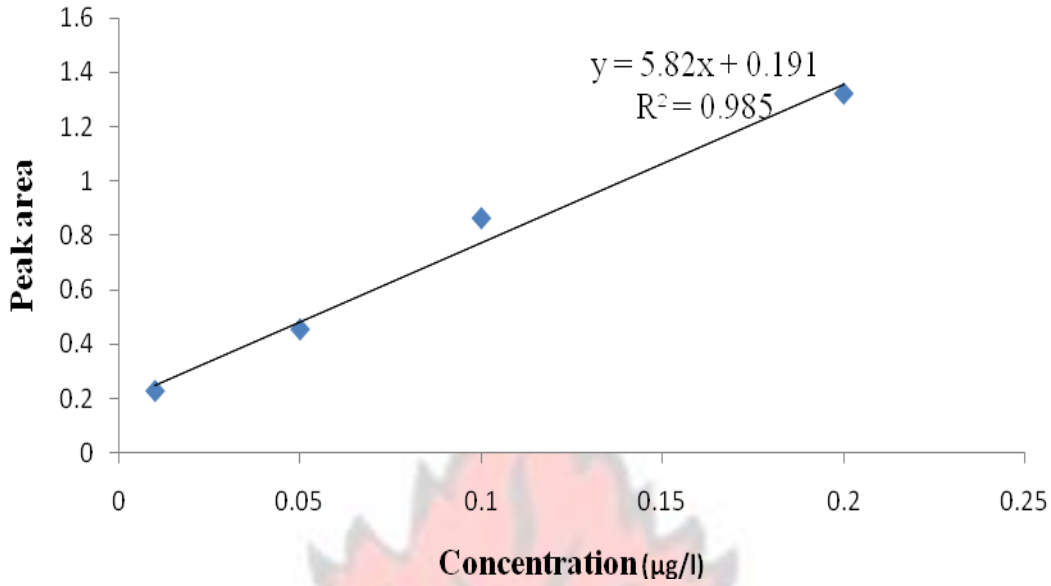


Tilapia busumana

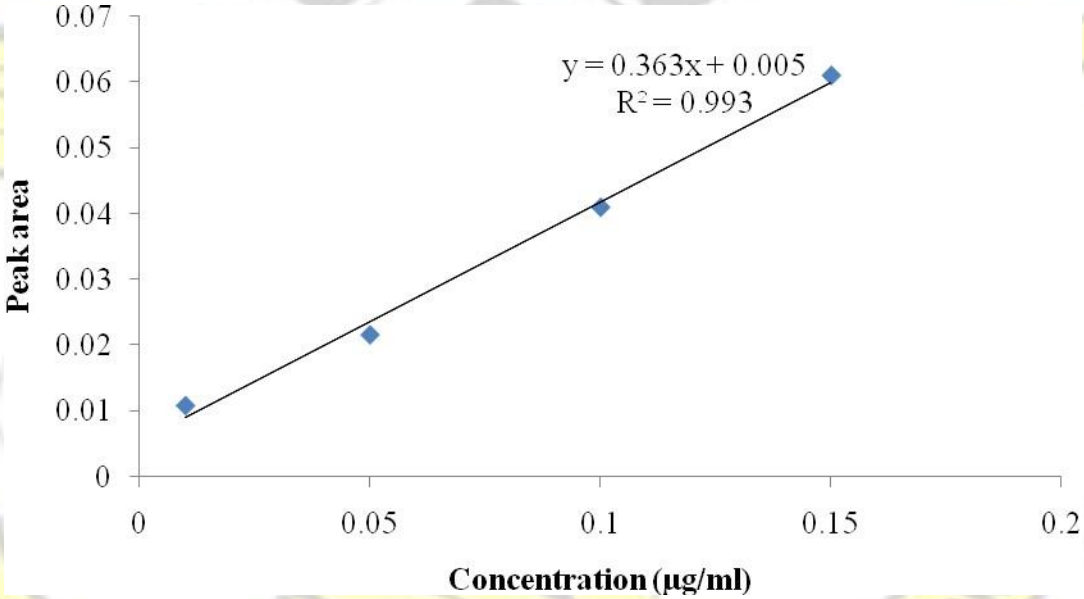
Hemischromis faciatus

APPENDIX 2

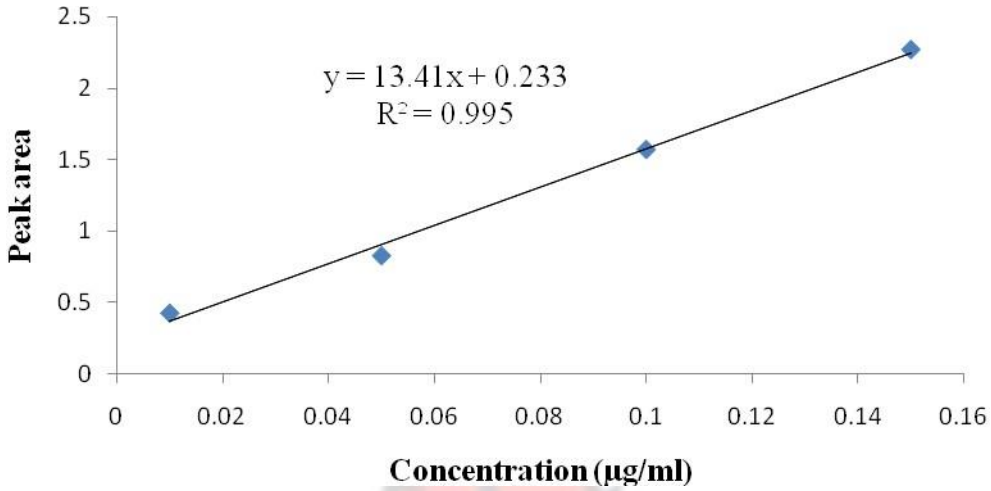
Sample calibration curves



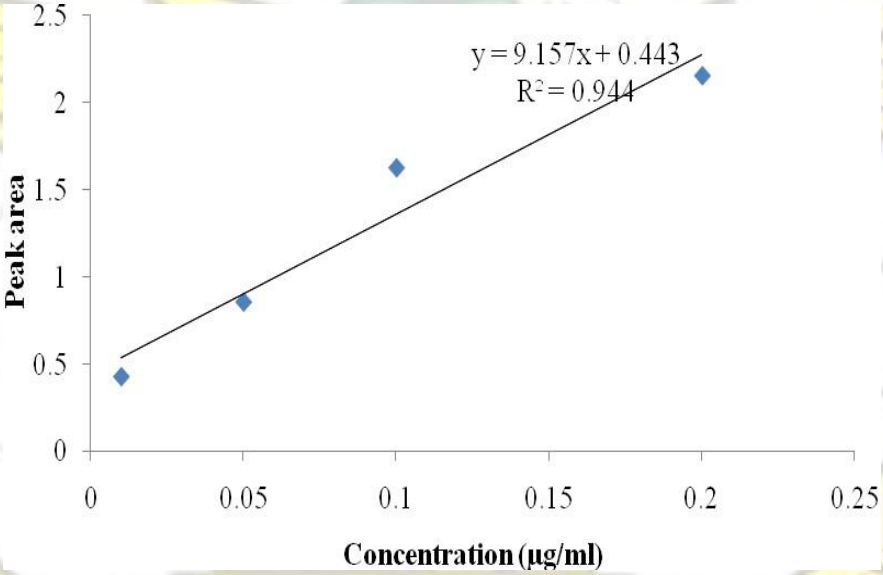
Graph 1: Calibration curve for determination of PCB 52



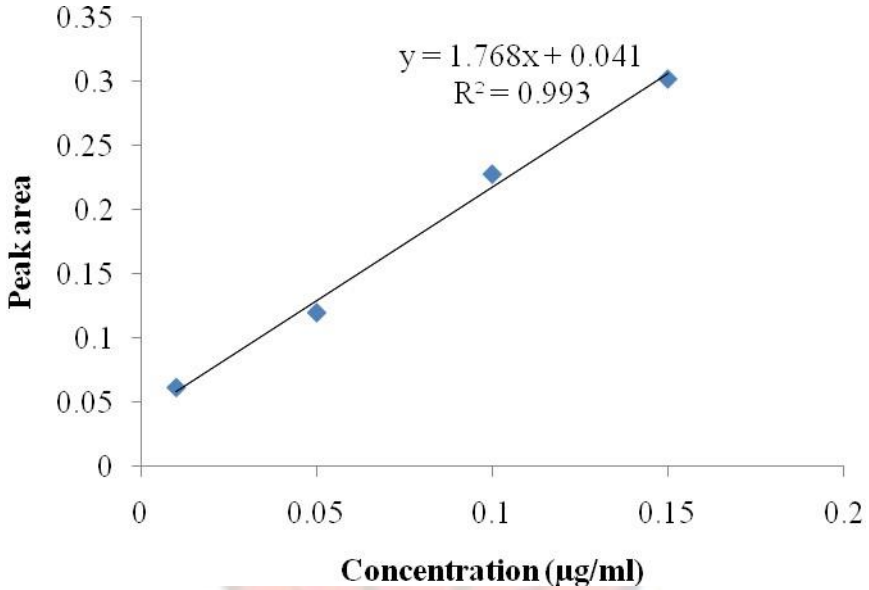
Graph 2 : Calibration curve for determination of β-HCH



Graph 3: Calibration curve for determination of δ-HCH

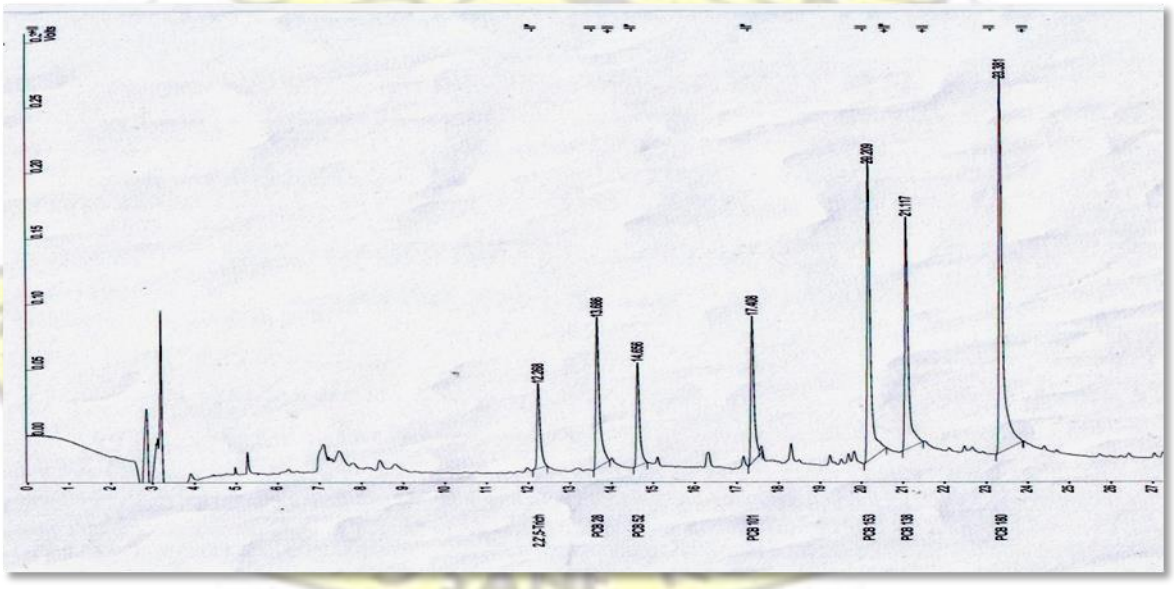


Graph 4 : Calibration curve for determination of p,p'-DDT

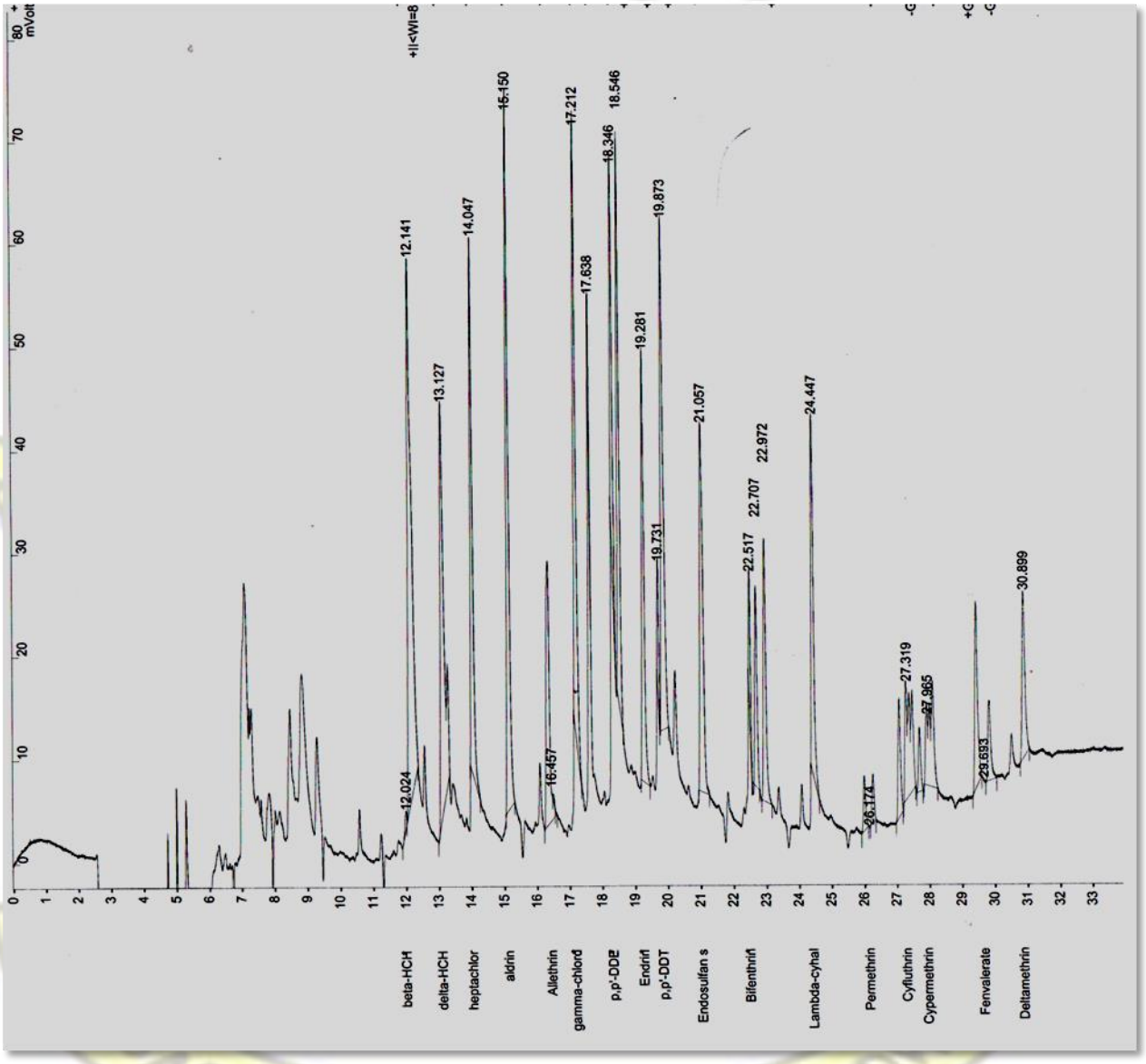


Graph 5: Calibration curve for the determination of β -endosulfa **APPENDIX 3**

Sample chromatograms of the OCs



Chromatogram 1: Chromatogram showing indicator PCBs and internal standard, PCB 18 with retention times in minutes: PCB 18(12.268), PCB 28 (13.686), PCB 52 (14.656), PCB 101 (17.408), PCB 153 (20.209), PCB138 (21.117) and PCB 180 (23.381).



Chromatogram 2: Chromatogram showing organochlorine pesticides and internal standard λcyhalothrin with retention times in minutes: β-HCH(12.347), δ-HCH(13.581), γ-HCH(12.620),

heptachlor(14.047) aldrin(15.403), δ–chlordane(17.584), p,p^1 – DDE(18.348), endrin(19.681), p,p^1 DDT(19.973)

APPENDIX 4

Sample calculations

1. $$\text{Percentage total organic carbon (TOC)} = \frac{(V-v)x\ M\ x\ 0.39}{\text{Weight of sediment}}$$

V = titre volume (ml) of blank, v = titre volume (ml) of sample

M = molarity of ferrous ammonium sulphate.

The factor 0.39 = 3 x 10^{-3} x 100 x 1.3 (3 is the equivalent weight of carbon, 1.3 is the due to 77 % recovery of carbon.)

Corresponding percentage organic matter is computed by multiplying the % TOC by 1.724

i. TOC for sediment sample from Anyinatiase

V = 52.90 ml, v = 29.50 and M = 0.2 M

Therefore TOC = (52.90 – 29.50) x 0.2 x 0.39 / 1

= 1.82 %

Corresponding TOM = 1.82 x 1.724

= 3.14 %

2. Calculation for accuracy and precision for INAA method using NIST-SRM 1566b (Oyster tissue),

i. Accuracy

Measured Cl–38 nuclide

Trial 1 = 0.492 mg/kg

Trial 2 = 0.486 mg/kg

Trial 3 = 0.504mg/kg

Measured average = 0.494±0.007 mg/kg

Reported value = 0.514±0.01mg/kg

$$\textbf{Accuracy} = \frac{\textbf{(reported value} - \textbf{measured value)}}{\textbf{reported value}} \textbf{ x 100}$$

$$= \frac{(0.514 - 0.494) \text{ x } 100}{0.514}$$

= 3.89 %

ii. Precision

Deviations from mean = 0.002, 0.008, 0.01

Sum of deviation = 0.02

Average deviation = 0.02/3 = 0.006667

$$\textbf{Precision} = \frac{\textbf{average deviation}}{\textbf{measured average}} \textbf{ x 100}$$

Precision = Average deviation /measured average x 100

= 0.006667/ 0.494 x 100

= 1.35 %

3. Recovery calculation

$$\text{Recovery} = \frac{\text{concentration of standard recovered}}{\text{level of spiking}} \text{ x } 100$$

Level of spiking sample = 10 µg/kg

Concentration recovered for γ-HCH after extraction and GC analysis = 9.94±0.39 µg/kg Hence recovery = 9.94 / 10 x 100

= 99.4 %

4. Quantification of organochlorines in samples

$$\text{Concentration} = \frac{\text{concentration in final extract x final volume of extract}}{\text{Weight of sample analyzed}}$$

Concentration in final extract is as reported by GC.

i. Sediment sampled from Nkawi,

Concentration of γ –HCH in final extract = 0.0061µg/ml

Final volume of extract = 1 ml

Weight of sample = 10 g

Concentration = $\frac{0.0061 \text{ µg/ml x } 1 \text{ ml}}{10 \text{ g}}$

= 0.00061 µg/g

= 0.61 µg/kg

ii. Water sample from Water works

Concentration of α- endosiulfan in final extract = 0.001 µg/ml

Final volume of extract = 1 ml

Volume of sample = 20 ml

Concentration = $\frac{0.001\ \mu g/ml \times 1\ ml}{20\ ml}$

= 0.00005 µg/ml

= 0.05 µg/l

5. Bio-concentration factor (BCF)

$$\mathbf{BCF} = \frac{\mathbf{[fish]}}{\mathbf{[water]}}$$

[fish] = mean OC concentration in a particular fish, [water] = mean OC concentration in water.

i. p, p'-DDE in *Tilapia busumana* at Bosomtwi.

Mean p, p'–DDE concentration in Bosomtwi water = 0.02 µg/l

Mean p, p'–DDE concentration in *Tilapia busumana* = 8.40 µg/kg

BCF for p, p'–DDE in *Tilapia busumana* = 8.40 / 0.02

= 4.20 x 10^2

ii. PCB 138 in *Clarius gariepinus* at Weija

Mean PCB 138 concentration in Weija water = 0.18 µg/l

Mean PCB 138 concentration in *Clarius gariepinus* = 0.96 µg/kg

BCF of PCB 138 in *Clarius gariepinus* = 0.96 / 0.18

= 0.5 x 10

6. Estimated daily exposure or intake (EDI) of OCs to humans

i. EDI of α-HCH through consumption of *Tilapia zilli*

EDI = mean α − HCH concentration in the fish x rate of fish consumption

Mean α-HCH concentration in the fish (µg/kg) = 1.29

Rate of fish consumption (g/kg body weight/day) = 68.5/70

Hence EDI (µg/kg body wt) = $1.29 \times 10^{-3} \times 68.5/70$

= **0.0013** µg/kg body wt (for adults)

Using average body weight of children of 30 kg

Corresponding EDI for children = $1.29 \times 10^{-3} \times 68.5/30$

= **0.003** µg/kg body wt (for children)

APPENDIX 5

List of publications derived from thesis

Published/Refereed papers.

1. S. Afful, J. A. M Awudza, S. Osae, S.K. Twumasi. Determination of indicator polychlorinated biphenyls (PCBs) by gas chromatography–electron capture detector. Chemosphere 93, 2013, 1556–1560.

2. S. Afful, J.A.M. Awudza, S. Osae, S.K. Twumasi. Persistent Organochlorine compounds in the water and sediment samples from the Lake Bosomtwe in Ghana. American Chemical Science Journal 3(4): 2013, 434-448.

3. S. Afful, J.A.M Awudza, S. Osae, S.K Twumasi. A Validated Gas Chromatography – Electron Capture Detector Method for the determination of persistence organochlorine pesticides. The Journal of Chemical Science. Photon 107, 2013, 223-229.

4. Afful S., Awudza J.A.M., Osae S., Twumasi K. Slyvester., Affum A. Burden of indicator polychlorinated biphenyls and organochlorine pesticides in the Water and Sediments from Weija Lake, Ghana. The Journal of Chemical Science. Photon 109, 2015, 263-273.