QUANTIFICATION OF ORGANOCHLORINE PESTICIDE RESIDUE IN WATER AND SEDIMENTS OF RIVER KIBOS-NYAMASARIA KISUMU, KENYA

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BSC ANALYTICAL CHEMISTRY (KISII UNIVERSITY)

A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY OF THE SCHOOL OF PURE AND APPLIED SCIENCES, DEPARTMENT OF CHEMISTRY, KISII UNIVERSITY

2023

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DEDICATION

This thesis is dedicated to my spouse, Nancy Auma, my daughters, Shaline Magdaline Ochieng, Sheryl Akinyi Ochieng and my son Meshack Ogola Ochieng. My mother, Salina Akinyi Ogola, and my late father, Meshack Ogola Onyach, and my brothers and sisters, for their continued support and encouragement throughout my studies. The work is also dedicated to all people afflicted by pesticide residue toxicity or water pollution worldwide.

ACKNOWLEDGEMENT

I want to acknowledge my supervisors, Dr. Richard Mogwasi and Dr. Kennedy Olale, for their positive criticism, encouragement, and support, enabling me to undertake this research. In addition, I would also like to thank Kisii University administration and KIRDI Management for allowing me to undertake Msc in Analytical Chemistry at Kisii University in the School of Pure and Applied Sciences (SPAS) Department of Chemistry.

ABSTRACT

Due to widespread use and potential for environmental damage, organochlorine pesticides (OCPs) are a prominent class of pesticides that have garnered concern on a global scale for decades. Inadequate regulation has resulted in the contamination of rivers and lakes worldwide. Pesticide residues in water and sediment are becoming more concentrated, posing major health issues for the local population. This study intend to determine the water physicochemical parameters and concentration of restricted or banned organochlorine pesticide residues, including Lindane, Endrine, Endosulfan, Dieldrin, Heptachlor, Hexachlorocyclohexane (HCH), Aldrin, Dichlorodiphenyltrichloroethane (DDT), methoxychlor and their isomers in water and sediments of river Kibos-Nyamasaria from ten sampling points during the wet (April–May) and dry (February–March) seasons. Gas chromatography with a mass spectrophotometer detector was used to determine the organochlorine pesticides residues levels. A muffle furnace was used to determine the soil's organic carbon and organic matter; a hot air oven was used to determine soil moisture; a lab conductivity meter was used to measure soil conductivity; and a pH meter was used to measure water and soil pH. Soil pH ranged from 6.20±0.05 to 7.26±0.06, conductivity ranged from 44.43±0.31 to 233.63±0.25 µs/cm, sediment moisture ranged from 13.14±0.03 to 26.34±0.03%, organic matter ranged from 2.95±0.06 to 9.43±0.11%, organic carbon ranged from 1.71±0.04 to 5.47±0.07%, and pH in water ranged from, 6.93±0.06 to 7.90±0.02 respectively in both seasons. Aldrin pesticide residue had the highest concentration of 8.33±0.58 µg/L during the wet season, while α-HCH had the highest concentration of 8.27±0.06 µg/L during the dry season and in the wet season α-HCH recorded 3.47±0.06 µg/L in river water. In sediments α- HCH had the highest concentration of 3.66±0.02 µg/kg in the wet season and 3.81±0.03µg/kg in the dry season at the entry point to Lake Victoria. Among all the DDTs isomers, p, p'- DDD had the highest concentration of 0.09±0.02 µg/L in the wet season and 0.03±0.02 µg/L in the dry season in water samples and sediments samples, p, p'-DDD had the highest concentration of 3.26±0.03µg/kg in the wet season and 3.28±0.06 µg/kg in the dry season at the entry point to Lake Victoria. o, p'- DDE had the least concentration of 0.32±0.02 µg/kg during the wet season and 0.34±0.08 µg/kg during the dry season in sediment samples. All the DDT isomers detected had a higher concentration in the wet season than the dry season in water samples, with most of them above 0.1 µg/L, which exceeds the maximum residues limits (MRLs) of WHO at the swamps or entry point to Lake Victoria. In the water and sediments from ten sampling points, nineteen pesticide residues were found and their concentrations increased downstream as the river approached Lake Victoria. The correlation between soil pH, conductivity, soil moisture, organic matter, and organic carbon with all 19 organochlorine pesticides studied showing significantly positive correlation at ($P \leq 0.01$). It is necessary to establish measures to reduce the pesticides and find potential sources of the banned pesticides because several pesticides were present at levels beyond the advised limits.

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ABBREVIATIONS

APHA	American Public Health Association
AMDIS	Automated Mass Spectral Deconvolution and Identification System
BHC	Benzene hexachloride
DDT	Dichlorodiphenyltrichloroethane
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
GC-MS	Gas Chromatography- Mass Spectrometer
HPLC	High-Pressure Liquid Chromatography
HCH	Hexachlorocyclohexane
HCB	Hexachlorobenzene
KIRDI	Kenya Industrial Research and Development Institute
KALRO	Kenya Agricultural Research Organization
KEPHIS	Kenya Plant Health Inspectorate Services
KIWASCO	Kisumu Water and Sewerage Company
LVEMP	Lake Victoria Environmental Management Programs
LOD	Limit of Detection
LOQ	Limit of Quantification
MSWS	Mass Spectrophotometer Work Station
MRL	Maximum Residues Limits
NEMA	National Environmental Management Authority
NTU	Nephelometric Turbidity Unit
NIST	National Institute of Standards and Technology
OCPs	Organochlorine pesticides
OC	Organic Carbon

OM	Organic Matter
POPs	Persistent Organic Pollutants
PCA	Principal Component Analysis
PCPB	Pest Control Products Board of Kenya
SD	Standard Deviation
SIM	Selected Ion Monitoring
SPSS	Statistical Packages for Social Sciences
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
UNESCO	United Nations Educational, Scientific and Cultural Organization
USA EPA	United States of America Environmental Protection Agency
WASREB	Water Services Regulatory Board
WHO	World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

Globally, water pollution is one of the most crucial environmental problems due to population increase, rapid industrialization, pollution, soil and sediment contamination by pesticides and other contaminants generated by human activities (Ogola *et al*., 2023; Zhou *et al*., 2020; James & Achieng, 2019; UNESCO, 2015). The concentration and persistence of these contaminants is a serious problems worldwide and are more acute in developing countries that do not have proper waste treatment methods for persistent organic pollutant (POPs) before discharging them into water bodies (Kelle *et al*., 2022; Chowdhury *et al*., 2016; UNESCO, 2015; Abdel-Rasheed, 2011; Yabe *et al*., 2010). According to Paul et al., 2022; Kosgei *et al.*, 2019; Anyanwu et al., 2018; UNESCO, 2015). The main causes of water pollution are industrial discharge, pesticide use, seepage from waste sites, fertilizers, sewage, agricultural waste (pesticides chemicals), decomposing plant, road, rail, and sea accidents involving large oil carriers.

The resulting water pollution is a serious health threat to human life, aquatic and affect the bioecosystem life on Earth (UNESCO, 2015; World Water Council, 2000). As it is needed in their bodies' biochemical processes, water is one of the essential component to sustain life (Kelle *et al*., 2022; Paul et al., 2022; European Parliament, 2021; UNESCO, 2015; UNESCO, 2003). Over 70% of the surface of the world is covered by water, only 3% of which is fresh water, and the remainder is salt water (Ogola *et al*., 2023; FAO, 2017). Only 0.3% of the world's freshwater may be found in lakes and rivers because the majority is frozen to ice in polar regions, lakes, and mountains due to the extreme cold in some regions (FAO, 2017;

UNESCO, 2015; World Water Council, 2000). Sadly, the fresh water available to man for development and life support has been degraded by human activities and rapid industrialization, making the amount of water available to be less than 0.3% (Ogola *et al*., 2023; Kelle *et al*., 2022; James & Achieng, 2019; Igiri et al., 2018; Rehman *et al*., 2018; Ongulu *et al*., 2015; UNESCO, 2015; Abdel-Rasheed, 2011; World Water Council, 2000).

Heavy metals and persistent organochlorine pesticide residues pollution is of particular concern among environmental pollutants due to their toxic effects and bioaccumulation in body tissues, organs, and aquatic ecosystems (Alengebawy *et al.*, 2021; European Parliament, 2021; UNESCO, 2015; WHO, 2009). Pesticides are frequently employed to eliminate or control various agricultural pests in large farms where crops are damaged, and productivity decreases (Kelle *et al.*, 2022; European Parliament, 2021). Insecticides, herbicides, and fungicides are some of the commonly used pesticides (Ogola *et al*., 2023; Alengebawy *et al.*, 2021; European Parliament, 2021; UNESCO, 2015). Some diseases such as Alzheimer's disease, cancer, congenital impairments, and attention-deficit/hyperactivity disorder (ADHD) are related to pesticide use. The pesticide use leads to the nervous system, the respiratory system, the reproductive system, the endocrine system, and the kidneys damage (Ogola et al., 2023; Loha *et al*., 2018; Nicolopoulou-Stamati *et al*., 2016; UNESCO, 2015; Lehtonen, 2009b).

Two million tons of waste, including industrial wastes, chemicals, human waste, and agricultural wastes like fertilizers, pesticides, and pesticide residues, are reportedly dumped into water bodies every day, according to estimates from the United Nations Educational, Scientific, and Cultural Organization (UNESCO, 2015). By reducing the amount of waste and pollutants discharged into the water bodies, water management must be urgently improved at the local, regional, national, and international levels (Ogola *et al*., 2023; Kelle *et al*., 2022; Paul *et al*., 2022; European Parliament, 2021; UNESCO, 2015; Mulei, 2012; Abdel-Rasheed, 2011;Yabe *et al*., 2010).

The primary sources of fresh water for residential use include water streams, rivers, and freshwater lakes (World Water Council, 2000; Alengebawy *et al*., 2021; European Parliament, 2021; FAO, 2017). Major cities and towns worldwide have rivers and streams that pass through them, supplying water to the inhabitants (Kelle *et al*., 2022; Paul *et al*., 2022; European Parliament, 2021). By 2030, 48% of the world's population will reside in cities and towns, necessitating clean and safe water (Kelle *et al*., 2022; FAO, 2017; UNESCO, 2015; Abdel-Rasheed, 2011; UNESCO, 2003; World Water Council, 2000).

Due to industrial and human activities that cause severe pollution downstream, many rivers and streams in Kenya lose water quality after passing through important towns and cities (James & Achieng, 2019). Ogola *et al*., (2023), Rehman *et al*. (2018) reported that, untreated sewage and municipally generated industrial wastes can seriously pollute rivers and cause health issues in towns downstream. Communities that live near rivers and rely on water for household purposes are compelled to hunt for more expensive tap water alternatives, which most people, especially the urban poor, cannot afford (Ogola *et al*., 2023; Abong'o *et al*., 2018; UNESCO, 2015). Toxic chemicals and pathogen concentration in river water pose health risks to people using river water for drinking, irrigation of fruits, vegetables, and crops eaten raw, fishing, bathing, and recreational activities (Kelle *et al.*, 2022; Alengebawy *et al*., 2021; European Parliament, 2021; Rai *et al*., 2019; UNESCO, 2015; Ali *et al*., 2013).

As industrial effluents, agricultural and municipal wastes get their way into the water bodies (rivers and Lakes), chemical and biological contaminants, including pesticides residues, enter into water bodies, particularly surface waters (Ogola *et a*l., 2023; Kelle *et al.*, 2022; Huang *et al*. 2020; Wei *et al*., 2019). Some persistent pesticide residue accumulates in the waters and sediments of rivers, which are exposed to industrial waste and agricultural activities, which is a common problem in most developing countries like Kenya (Ogola et al., 2023; James & Achieng, 2019; Kosgei et al., 2019; Singh et al., 2017; Ongulu et al., 2015; Shanbehzadeh et al., 2014; Abong'o et al., 2014; Okungu & Opango, 2012; Walakira & Okot-Okumu, 2011; Louhi *et al*., 2012; Abongo, 2009).

Organochlorine Pesticides (OCPs) are a significant category of pesticides that have sparked global concern for decades due to their widespread use and potential for environmental toxicity (Ogola *et al*., 2023; Kelle *et al*., 2022; Paul *et al*., 2022; Syed *et al*., 2014). Organochlorine Pesticides (OCPs) are broken down into the toxaphene group, cyclodiene compounds, hexachlorocyclohexanes (HCH), and DDT and its variants (Kelle *et al.*, 2022; Paul *et al*., 2022; Chen, 2005). DDT typically contains a mixture of p, p'-DDT, o, p'-DDT, p, p'-DDE, and other trace impurities with the isomeric compositions of p, p'-DDT 77.1%, o, p'-DDT 14.9%, p, p'-DDD 0.3%, o, p'-DDD 0.1%, p, p'-DDE 4.0%, and o, p'-DDE 0.1% (Syed et al., 2014; Saoke, 2005). The p, p'-DDD has insecticidal properties and is commercially available as an insecticide (Ogola *et al*., 2023; Ssebugere *et al*., 2009; Saoke, 2005).

The Hexachlorocyclohexanes are stereoisomeric compounds such as α, β, γ (lindane), and δ–HCH (Paul *et al.*, 2022; Chen, 2005). Hexachlorocyclohexanes have significant bioaccumulation potential (Kelle *et al*., 2022; Paul *et al*., 2022; Chen *et al*., 2009), while lindane was banned in seed dressing in 1998 but is still used illegally as a pesticide to control cotton insect infestations (Humphreys *et al.*, 2008). Contrarily, cyclodienes are chlorinated hydrocarbons that are part of the bridging cycle and include the following: endrin, chlordane, aldrin, dieldrin, heptachlor, and heptachlor epoxide (Kelle *et al.*, 2022; Paul *et al.*, 2022; Chen, 2005). Only aldrin and dieldrin are restricted for termite control in the building industry because their metabolites are more hazardous and persistent than the original substances, and their use was banned in Kenya in 1986. Dieldrin and heptachlor epoxide are more dangerous and persistent than the original substances (European Union, 2021). Due to their low cost, broad-spectrum, extended residue effect, and low toxicity, these OCPs were widely used in Kenya from the 1940s until the late 1970s (Omwenga *et al*., 2016; Saoke, 2005).

In 1982, the Kenyan government established a pest control products board to regulate pesticide manufacturing, distribution, application and to prohibit, ban or restrict environmentally persistent organochlorine pesticides which are harmful to human and aquatic life (European Union, 2021; Abong'o *et al*., 2018; UNESCO, 2015).

However, despite the ban or restriction, there is evidence from previous studies of their continuous usage in Kenya (Ogola *et al*., 2023; Abong'o *et al*., 2018; Ndunda *et al*., 2018; Saoke, 2005). Farmers have continued to use the OCPs, due to their success in managing diseases such as malaria and typhoid (Abong'o *et al*., 2018; Ndunda *et al*., 2018). As a result, many rivers and streams lose their water quality after passing through large agricultural fields and major towns/cities due to downstream pollution (James & Achieng, 2019). Farmers with banned pesticides dump them into rivers or farms, causing pollution, particularly in surface waters from run-offs (Paul *et al*., 2022; Huang *et al*., 2020; Wei *et al*., 2019).

In the Kibos and Miwani areas of Kisumu, there are large sugarcane plantations and smallholder farms where farmers frequently use pesticides to control pests. The synthetic chemical pesticides which are commonly used in Kisumu County are Boric Acid, Acephate, Deet, glyphosate, Dichlorodiphenyltrichloroethane (DDT), Metaldehyde, Diazinon, Dursban, Malathion. (Ogola *et al*., 2023; Onchieku, 2019; Osoro *et al*., 2016; Abong'o *et al*., 2018; Lehtonen, 2009a). Traces of these chemicals find their way into river Kibos-Nyamasaria through run-offs and eventually drain their constituents into Lake Victoria, the world's largest tropical freshwater lake (FAO, 2017; UNESCO, 2015) . The communities living in Lake Victoria catchment areas who depend on river waters for their domestic use are forced to look for alternative expensive tap water that most cannot afford, especially the urban poor (Ogola *et al*., 2023; Abong'o *et al*., 2018; UNESCO, 2015).

Sediments and wetlands provide habitats for many aquatic organisms like mudfish and catfish and the breeding ground for several organisms (Alengebawy *et al.*, 2021; European Parliament, 2021; UNESCO, 2015). The sediments in river banks and wetlands sometimes act as sources and carriers of pesticide residues in the water bodies posing health risks to both human and aquatic life (Ogola *et al*., 2023; Kelle *et al*., 2022; Paul *et al*., 2022; Alengebawy *et al.*, 2021; European Parliament, 2021; UNESCO, 2015; Singh & Kalamdhad, 2011).

Sediment analyses are important because they may act as reservoirs rather than ultimate sinks, allowing absorbed chemicals to remain in the aquatic biota for extended periods (Kelle *et al*., 2022; Paul *et al*., 2022; Ochoa & Maestroni, 2018). Most of the time, the sediments which are in contact and constant interaction with the river water are not monitored for their safety (Ogola *et al*., 2023; Alengebawy *et al.*, 2021; European Parliament, 2021; Singh *et al.*, 2017; UNESCO, 2015; Singh *et al*., 2011). Therefore, this study reports and determines the concentrations of organochlorine pesticides from sampling point S1 to S10 that have either been banned or restricted for use in water and sediments of River Kibos-Nyamasaria whose source is south Nandi forest and drains into Lake Victoria during two seasons: wet season (April-May) and dry season (February-March).

Levels of persistent pesticide residues in River Kibos-Nyamasaria waters and sediments have not been documented in details in any of the earlier research compared to other nearby rivers like river Nyando. As a result, we suggested determining level of organochlorine pesticide residue present in the river Kibos-Nyamasaria, which runs through Kisumu County's Kisumu City. Previous studies have indicated that persistent pesticides, toxic chemicals and waste discharges from industries are a possible cause of water pollution in rivers draining into Lake Victoria, whereby some have been reported to have contaminant concentrations slightly above the World Health Organization (WHO) acceptable limits and those of the Kenya National Environmental Management Authority (NEMA) (Ogola *et al*., 2023; James & Achieng, 2019; Kosgei *et al*., 2019; Ongulu *et al*., 2015; Okungu & Opango, 2012; Walakira & Okot-Okumu, 2011).

1.2 Statement of the problem

Pesticide residue poisoning is a global health concern, with an estimated 300,000 deaths recorded yearly worldwide (Alengebawy *et al.*, 2021; European Parliament, 2021; UNESCO, 2015; WHO, 2009). Currently, around two million tons of pesticide chemicals are used globally annually. 50 % are constituted by herbicides, 30 % by insecticides, 18 % by fungicides, and 2 % by other pesticides such as rodenticides and nematicides (Ogola *et al*., 2023; European Parliament, 2021). 80% of restricted or banned pesticides and chemicals are used in developing countries (Alengebawy *et al*., 2021; European Parliament, 2021; UNESCO, 2015; WHO, 2009). Studies by Karanja *et al.* (2021), Joubert et al. (2020), Jayaraj *et al.* (2016), and WHO (2008) reported that only 0.3% of applied pesticides reach the target insect, and the remaining 99.7% are released into the environment.

The World Health Organization (WHO) estimated in 2016 that, environmental factors, including chemical, physical, and biological hazards to human health introduced into water bodies, were responsible for approximately 24% of the global disease burden and 23% of all deaths (Wolf *et al*., 2018; Prüss-Ustün *et al*., 2017; Neira & Prüss-Ustün, 2016).

In Kenya, more than 93 % of the farmers wash the used pesticide and chemical bottles in nearby canals, streams, rivers, and lakes. More than 6 % of the users do not wash the bottles but dispose of them directly into the water bodies, contributing to pollution of water system (European Parliament, 2021; UNESCO, 2015). Pesticide residues get into the river through leaching and surface runoff and bioaccumulate in sediments (Ogola *et al*., 2023; Alengebawy *et al*., 2021; Abong'o *et al*., 2018).

In Kisumu County, Kenya, there have been a series of media reports on both local and national televisions and newspapers on complains about the pollution of Lake Victoria through rivers draining into it (Karanja, 2021; County Government of Kisumu, 2019). In 2019 and 2020, there were demonstrations of residents living in Kibos-Nyamasaria area complaining of water pollution by various industrial activities and poor farming methods in the area (Ogola *et al*., 2023; Karanja, 2021; Simiyu *et al*., 2019; Kanoti *et al*., 2019; County Government of Kisumu, 2019; Ministry of Health, 2018).

Further to this, information gathered from nearby health facilities revealed that most residents were diagnosed with several conditions related to abdominal problems, high blood pressure, abnormal heart rhythm, vomiting and nausea, cancer of the skin, bladder, liver, and lungs, itching, skin rashes, and other ailments (Karanja, 2021; Annual, 2020; Kanoti *et al*., 2019;

Alsheimer, 2018; Ministry of Health, 2018). For example, out of 100 patients treated in Jaramogi Oginga Odinga Teaching and Referral Hospital (JOOTRH) from the Kibos-Nyamasaria area, 30% complained of abdominal problems, high blood pressure, abnormal heart rhythm, vomiting, nausea, itching, and skin rashes, while 3% of patients had cancer while in Kibos Prison Dispensary out of 80 patients, 40% had high blood pressure, abdominal problems, abnormal heart rhythm, vomiting, nausea, itching and skin rushes while 4% patients suffered from different types of cancer (Karanja, 2021; Annual, 2020; Ministry of Health, 2018).

This indicated that the residents could be consuming pesticide residues in their diets unknowingly making them to show the symptoms or suffer from the indicated ailments. (Ministry of Health, 2018).This study was carried out to establish the levels of organochlorine pesticide residues from Kibos-Nyamasaria river which supplies the water used by residents to ascertain whether it was the one responsible for the ailments experienced.

1.3 Justification and Significance of the Study

Previous studies have indicated waste discharges from industries and poor farming methods as possible causes of water pollution (Ogola *et al.*, 2023; Kosgei *et al.*, 2019; James & Achieng, 2019; Ongulu *et al.*, 2015; Okungu & Opango, 2012). The river Kibos-Nyamasaria, however, has not been shown to contain organochlorine pesticide residue in any prior research reports despite pesticides being used in the area. Persistent pesticide residues used in agricultural, industrial and human activities get into the river water through leaching and surface runoff and bioaccumulate in sediments then contaminate the river water which the locals normally use for domestic purposes. This investigation identified the levels of organochlorine pesticide residues that would pose a serious health risk to the locals.

The research study aims to raise awareness of the risks associated with using contaminated waters among locals and communities so that they may put protective measures in place to reduce and prevent adverse health consequences from contaminated river waters. The findings of this study will serve as a basis for future similar studies. The results can be used by relevant government agencies concerned with environment and health for policy formulation and control of water pollution. The study confirms the level of pollution of river Kibos-Nyamasaria and suggests possible preventive measures to be adopted among the residents, farmers, and industries to control the pollution.

Figure 1.1: Pictures showing river Kibos-Nyamasaria and human activities along the river

1.4 Objectives of the Study

1.4.1 Main objective

To quantify the levels of organochlorine pesticide residues and to study selected physicochemical parameters in both the water and sediment of River Kibos-Nyamasaria, Kisumu County, Kenya.

1.4.2 Specific objectives

The specific objectives were to:

1. Quantify the concentration of organochlorine pesticide residues present in the water of River Kibos-Nyamasaria.
2. Determine the concentration of organochlorine pesticide residues in the sediment of the River Kibos-Nyamasaria.
3. Determine the levels of selected physico-chemical parameters of water and soil sediments such as pH, conductivity, Total Suspended Solids, Total Dissolved Solids, turbidity, moisture, organic matter, and carbon and soil structure of River Kibos-Nyamasaria.
4. Investigate the relationship between the physicochemical parameters of the water and sediments and the levels of selected organochlorine pesticide residues.

1.5 Research questions

1. Which organochlorine pesticide residues are present in the water and sediments of River Kibos-Nyamasaria?
2. What quantity of organochlorine pesticide residues are present in the water and sediments of River Kibos-Nyamasaria?

3. What are the levels of selected physico-chemical parameters of water and soil sediments such as pH, conductivity, Total Suspended Solids, Total Dissolved Solids, turbidity, moisture, organic matter, and carbon and soil structure of River Kibos-Nyamasaria?
4. What is the relationship between the physicochemical parameters and the quantity of organochlorine pesticide residues?

1.6 Limitations of the study

1. Duration of the study was very short to cover other type of organochorine pesticides.
2. Procurement delay since some of the organochlorine pesticides mixed standards and chemicals used in GC-MS were to be imported through local suppliers.
3. Managing time for research and other normal daily activities was a problem.
4. Collection of samples in a swampy area towards the lake was very difficult because of the fear of dangerous animal like hippopotamus, crocodile, and snakes.

CHAPTER TWO

LITERATURE REVIEW

2.1 Causes of river water pollution

Rapid population growth over the last decade in many African countries, coupled with a steep increase in industrialization, urbanization, and agricultural land use, has increased contaminants in water bodies (Ogola *et al*., 2023; Alengebawy *et al*., 2021; European Parliament, 2021; UNESCO, 2015; Abong'o *et al*., 2018). These contaminants have caused undesirable effects on the lives of human beings, animals, plants, and the aquatic environment (Abong'o *et al*., 2014; Osibanjo *et al*., 2011; Kithiia, 2007).

In Africa, high contaminants in most water bodies have lowered the water quality and increased its toxicity, making it unfit for both domestic use and aquatic environment (Ogola *et al*., 2023; Abong'o *et al*., 2014; Yabe *et al*., 2010; Abongo, 2009). Extreme poverty, poor economy, social under-development, lack of strong policies and reinforcement of law have led to rapid pollution of the freshwater system in Africa as compared to the developed countries (European Parliament, 2021; UNESCO, 2015; Abong'o *et al*., 2014; Yabe *et al*., 2010; WHO, 2009; Abongo, 2009). Rapid industrial expansion in contemporary Africa has not been accompanied by health and environmental safety regulations comparable to those in the US, Canada, or Europe (World Health Organization, 2010; WHO, 2009).

There is little information on the effects on human health, hazardous exposures to trash, air pollution, water contamination, and pesticide residues increase in Africa (Karanja *et al.*, 2021; WHO, 2009). According to data from the European Parliament (2021) and UNESCO (2015), 12.48% of farmers use harmful chemicals and pesticides. Pesticides prohibited in the

European Union may end up in Kenya (European Parliament, 2021; UNESCO, 2015). The proportion of people in Africa aware of the list of banned pesticides is negligible.

Most Kenyans are unaware of the right techniques for using and disposing of pesticides (European Parliament, 2021; Abong'o *et al.*, 2014; Abongo, 2009). More than 93% of Kenyan farmers wash their used pesticide and chemical bottles in nearby canals, streams, rivers, and lakes after applying pesticides and chemicals, while more than 6% do not wash the bottles at all and instead dump them into the water bodies (Ogola *et al*., 2023; European Parliament, 2021; UNESCO, 2015).

Lack of awareness of proper pesticide use and improper industrial waste disposal proved to be one of the key reason behind the common diseases and deaths of the farmers and people in Kenya (Ogola et al., 2023; Alengebawy *et al*., 2021; European Parliament, 2021; UNESCO, 2015). Organochlorine pesticide residue contamination causes environmental harm in Kenya, but government agencies do not regularly analyze the impact (European Parliament, 2021; Ndunda *et al.*, 2018; Abong'o *et al*., 2014; Abongo, 2009).

Previous studies have shown that long-term exposure to pesticide residues leads to cancer and organ system toxicity such as abdominal, skeletal, reproductive, respiratory systems, cardiovascular, urinary, and peripheral nervous systems (Alengebawy *et al*., 2021; Ali *et al*., 2019; Rahimzadeh *et al*., 2017). Organochlorine pesticide residues are of particular concern among environmental pollutants due to their harmful effects on human and aquatic life (Alengebawy *et al*., 2021; European Parliament, 2021; UNESCO, 2015; Kithiia, 2007).

Pesticides such as herbicides, insecticides, and fungicides are applied in large sugarcane plantations in the Kibos area of Kisumu, which get their way into the river Kibos-Nyamasaria through runoff. Most residents of Kisumu, especially in the informal settlements living along the rivers and Lake Victoria, depend directly or indirectly on these water bodies for their domestic use (Ogola *et al*., 2023; Kosgei *et al*., 2019; Ndunda *et al*., 2018; James & Achieng, 2019; Yahaya *et al*., 2017; Ongulu *et al*., 2015; Okungu & Opango, 2012).

Determining the concentrations of specific organochlorine pesticide residue in the Kibos-Nyamasaria area, where the Kibos-Nyamasaria River flows through to Lake Victoria, is therefore advisable. Several industrial and agricultural operations are going on in this area, which could pollute the river and the lake. Studies have reported water pollution in rivers like Nyando draining into Lake Victoria being polluted and might be posing health risks to communities living along the river and aquatic life in the Lake. (Kosgei *et al*., 2019; James & Achieng, 2019; Abong'o *et al*., 2018; Ongulu *et al*., 2015; Okungu & Opango, 2012).

2.2 River sediment pollution

Sediments are tiny soil particles that collect at the bottom of rivers, lakes, and other bodies of water. It can come from the decomposition of plants and animals and soil erosion (Issaka & Ashraf, 2017). Sediment can be moved and deposited in a new location by a stream or river water and consist of tiny minor minerals and rocks as well as the remains of animals and plants, and they can be as large as a boulder or as small as a grain of sand (Huang *et al*., 2020; U.S.EPA, 2019; Chequer *et al*., 2013).

Sediments are typically lifted and deposited on the river banks when the stream or rivers flood a place and are mainly in the form of small fine loose clay, sand, or silt (U.S. EPA, 2019; Chequer *et al*., 2013). Polluted sediment typically lowers the water quality in most urban areas (U.S. EPA, 2019; Issaka & Ashraf, 2017) due to sediment deposited onto the river bed or suspended in the river. Increased turbidity and cloudiness due to residues, limit aquatic plants' photosynthesis by obstructing sunlight and increasing water temperature

(U.S. EPA, 2019; Chequer *et al*., 2013). Over time, the mud builds up on the stream or river bottom through the process of sedimentation, which can reduce habitat for the aquatic community by clogging the spaces between larger boulders, gravel, and cobble, which are mostly the breeding grounds for marine life hence leading to faster reduction of aquatic community population significantly if the sediments are polluted with toxic chemicals from water runoff (Ogola *et al*., 2023; Huang *et al*., 2020; U.S.EPA, 2019; Issaka & Ashraf, 2017; Yahaya *et al*., 2017; Chequer *et al*., 2013).

In most cases, topsoil is lost through erosion when it rains and finds its way into streams, rivers, and lakes (U.S. EPA, 2019; Chequer *et al*., 2013). As the top soil is being washed through runoff into the rivers, contaminated top soil with toxic chemicals such as pesticide residues from agricultural, industrial, and human activities is carried into the streams, rivers, and lakes. This contaminates river water and soil sediment (Ogola *et al*., 2023; Abong'o *et al*., 2014; Yahaya *et al*., 2017; Abongo, 2009).

Sediment poses greater stream and river water quality deterioration and health risks as, in most cases, it carries other water pollutants, such as heavy metals, pesticide residues, organic chemicals, nutrients, and pathogens along with it (Loha *et al*., 2018: Abongo, 2009; Lehtonen, 2009a; Kaigwara *et al*., 2002). Major contributors to sediments contamination are toxic chemicals from agricultural activities, industrial waste dumping, industrial manufacturing activities, municipal and local waste disposal, and excessive fertilizer or pesticide used by farmers (Ogola *et al*., 2023; James & Achieng, 2019; Loha *et al*., 2018; Nthusi, 2017; Osoro *et al*., 2016; UNESCO, 2015; Abong'o *et al*., 2014; Lehtonen, 2009a). Some contaminants or pollutants are dissolved in the water and washed downstream quickly into the rivers and lakes. In contrast, others may remain stuck to sediment on the bottom of the stream, river, or lake bed for many years hence affecting or reducing the aquatic community population (Ndunda *et al*., 2018; Yahaya *et al*., 2017; Nthusi, 2017; UNESCO, 2015; Abong'o *et al*., 2014; Abongo, 2009).

From the previous studies, long-term exposure to toxic chemicals and organochlorine pesticides residues from water, sediments, and fish leads to various types of cancers and organ system toxicity such as stomach, skeletal, reproductive, respiratory systems, and peripheral nervous system (Ogola *et al*., 2023; Alengebawy *et al*., 2021; Huang *et al*., 2020; Ali *et al*., 2019; Loha *et al*., 2018; Adesiyan *et al*., 2018; Nthusi, 2017; Rahimzadeh *et al*., 2017; Osoro *et al*., 2016; UNESCO, 2015; Abong'o *et al*., 2014; Jaishankar *et al*., 2014).

2.3 Pesticide residue in river water and their effect on human health

Insecticides, fungicides, herbicides, rodenticides (vertebrate poisons), and nematicides (nematodes) are some of the chemicals used to manage or kill different pests (Rajmohan *et al*., 2020; Jayaraj *et al*., 2016). Farmers use pesticides to control plant diseases, weeds, and pests, increasing the quality of crop products. They are dangerous and poisonous if not appropriately used as recommended and can cause serious harm to other organisms and the environment (Rajmohan *et al*., 2020; Fosu-Mensah *et al*., 2016; UNESCO, 2015; Atieno Abongo, 2009; Lehtonen, 2009a; Jordan, 2002). Abong'o *et al.* (2014) stated that pesticides are toxic, and their frequent exposure can cause several ill health effects to both human and aquatic life if they get into the river water or lake water through runoff. Pesticides are linked to various diseases, including respiratory problems, cancer, heart and kidney diseases (Ogola *et al*., 2023; Loha *et al*., 2018; Ndunda *et al*., 2018; UNESCO, 2015).

Agriculture is considered important for economic development and growth in most African countries, and in Kenya, it's considered the backbone of the economy (Nthusi, 2017;

UNESCO, 2015; Abong’o *et al*., 2014; Abongo, 2009). Loha *et al*.(2018) and Abong’o *et al*.(2014) reported that agriculture is the basis for economic growth, food security, foreign exchange, and employment creation. Rapid population increase has led to increased use of pesticides and agro-chemicals in Kenya to produce more food to meet the increased demand (Nthusi, 2017; Abong’o *et al*., 2014; Abongo, 2009). Farmers commonly use organochlorine pesticides despite their bioaccumulation in the food chain, environmental toxicity, and aquatic and human beings (Ogola *et al*., 2023; Alengebawy *et al.*, 2021; Jayaraj *et al*., 2016; Nicolopoulou-Stamati *et al*., 2016; Yehia, 2012; Jordan, 2002).

2.4 Organochlorine pesticide residues in River water and sediment

Organochlorine pesticides (OCPs) are chlorinated hydrocarbon derivatives used in agriculture and the chemical industry, according to Jayaraj *et al*. (2016) and Jordan (2002). One of the countries that limits the use and production of numerous organochlorine pesticides is Kenya (Abong'o *et al*., 2014; Abongo, 2009; Nthusi, 2017). However, due to their accessibility, efficiency, lax import controls, and lack of adequate logistics to monitor the use of pesticides in the nation, some farmers continue to use them in significant amounts (Alengebawy *et al*., 2021; Nthusi, 2017; Abong'o *et al*., 2014; Abongo, 2009).

The organochlorine pesticides include Aldrin, dieldrin, endosulfan sulphate, α–endosulfan, methoxychlor, α-HCH, β – endosulfan, Endrin, Heptachlor, Heptachlor- epoxide, Lindane, β-HCH, δ –HCH, o, p'- DDT, p, p’ – DDT, o, p'- DDD, p, p'- DDD, o, p' – DDE and p, p'- DDE. (Ogola et al., 2023; Rajmohan *et al*., 2020; Fosu-Mensah *et al*., 2016; Jayaraj *et al*., 2016).

Persistent organic pollutants (POPs) are one of the pesticides that are harmful to both human and other living things because of their stubbornness in nature to biodegrade (Alengebawy *et al*., 2021; Jayaraj *et al*., 2016; Jordan, 2002). The most extensively used pesticide in agriculture with a high persistence is dichlorodiphenyltrichloroethane (DDT), which is fairly toxic, has a half-life of 2–15 years, and has been outlawed in several countries (Alengebawy *et al*., 2021; Jayaraj *et al*., 2016). The second is endosulfan, a typical agricultural pesticide with a half-life of 50 days and also environmental persistence (Jayaraj *et al*., 2016; Jordan, 2002). DDTs and Endosulfan bio-accumulates in plants, animals, and aquatic populations like fish over an extended period and contaminates human food (Ogola *et al*., 2023; Alengebawy *et al*., 2021; Jayaraj *et al*., 2016). DDTs and Endosulfan has a very high absorption rate in the gastrointestinal tract and can harm a person's central nervous system if consumed excessively (Ogola *et al*., 2023; Jayaraj *et al*., 2016; Jordan, 2002).

Many pesticides, including organochlorines, are applied on farms whereby only a small fraction reaches the target pests while the rest is deposited on soil from where they gets into the river water through runoff (Scheme *et al*., 2019; Jayaraj *et al*., 2016). Most organochlorine pesticides and their byproducts are poisonous. According to numerous studies (Ogola *et al.*, 2023; Alengebawy *et al.*, 2021; Rajmohan *et al.*, 2020; Jayaraj *et al*., 2016; Fosu-Mensah *et al*., 2016; Jordan, 2002), they have a wide range of negative health impacts on men, including cancer, reproductive system malformations, congenital disability, neurological damage, and immune system damage. They also cause the deaths of birds, animals, and aquatic populations, including fish, when they consume plants or utilize contaminated water, according to Rajmohan *et al*. (2020) and Jayaraj *et al.* (2016).

Because pesticides are difficult to degrade in the environment (they withstand chemical, physical, biological, and microbiological processes of degradation), they harm ecosystems (Alengebawy *et al.,* 2021; Fosu-Mensah *et al*., 2016; Jordan, 2002). Organochlorine pesticides can damage the environment, including water bodies like streams, rivers, lakes, seas, and oceans, by dispersing off-site by air-drift and surface runoff (Rajmohan *et al.*, 2020; Jayaraj *et al.*, 2016; Abong'o *et al.*, 2014).

Ogola *et al*., (2023), Nthusi (2017), Osoro *et al*.(2016), Abong'o *et al*.(2014), and Abongo (2009) have reported that poor farming methods in Kenya are the major contributors to rivers in Winam gulf and Lake Victoria pollution. Banned Organochlorine pesticides such as lindane, aldrin, and dieldrin are still commonly used by some farmers around the lake Victoria region from where they are swept by rain and water run-off into the rivers and eventually into Lake Victoria (Osoro *et al*., 2016; UNESCO, 2015; Abong'o *et al*., 2014). Organochlorine pesticide residues have caused ill health effects to several people and aquatic life as some are carcinogenic and toxic to humans and other living organisms (Ogola *et al*., 2023; Osoro *et al*., 2016; UNESCO, 2015; Abong'o *et al*., 2014; Abongo, 2009; Lehtonen, 2009a). Pesticide poisonings are often misdiagnosed and under reported since the related illnesses appear similar or identical to other illnesses (Jayaraj *et al*., 2016; Jordan, 2002). Pesticide residues are the remains of pesticides on food substances after application on farm food crops (Yahaya et *al*., 2017; Firehun and Yohannes , 2015).

Different regulatory bodies in various countries and WHO stipulated maximum allowable limits for organochlorine pesticide residues. Over some time, organochlorine pesticides have caused harmful health effects following frequent or continuous exposure at low concentrations (Alengebawy *et al.*, 2021; Loha *et al*., 2018; UNESCO, 2015; Abong'o *et al*., 2014; Lehtonen, 2009a; Kaigwara *et al*., 2002). Low concentrations of pesticide residues do not always cause immediate health effects but with time, they can cause severe diseases like asthma, cancer (including non-Hodgkin's lymphoma and leukemia), the development of Parkinson's disease, anxiety and depression, attention deficit and hyperactivity disorder

(ADHD) (Alengebawy *et al.*, 2021; Nthusi, 2017; Jayaraj *et al*., 2016; UNESCO, 2015; Abong'o *et al*., 2014; Lehtonen, 2009b).

2.4.1 Structures of organochlorine pesticides (OCPs) studied, uses and health effect

The following table summarizes the structure, uses, and ill health effects associated with some organochlorine pesticides in humans being.

Table 2.1: Biochemical effects, structure, and uses of major organochlorine pesticides

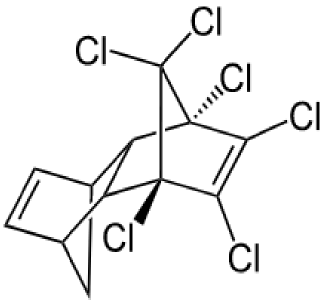
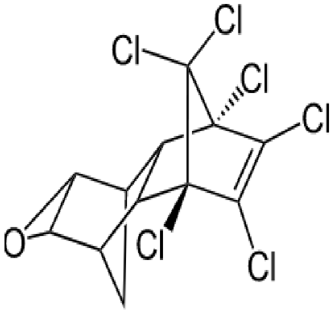
Name of the organochlorine pesticides	**Structure of OCPs**	**Uses**	**Health effects and restricted or banned date**
Aldrin ($C_{12}H_8Cl_6$)		Used as an insecticide for vegetables, sugarcane, bananas, citrus, maize, oil seed rape, turf, ornamentals, and onions	Effects that are neurotoxic, genotoxic, immunotoxic, tumorigenic, cause nausea and vomiting as well as muscle twitching and aplastic anemia. Banned in 1986 by US EPA. Restricted then Banned in Kenya in 2004.
Dieldrin ($C_{12}H_8Cl_6O$)		They are used as insecticides to control termites, locusts, tropical disease vectors, and non-food seed and plant treatment.	A carcinogenic agent. Effects that are neurotoxic, genotoxic, immunotoxic, tumorigenic, cause nausea and vomiting as well as muscle twitching and aplastic anemia. Causes damage to internal organs through prolonged or repeated exposure. Banned in 1986 by EPA US and restricted in Kenya in 1986, then banned in 2004.

Table 2.1: Biochemical effects, structure, and uses of major OCPs continues'

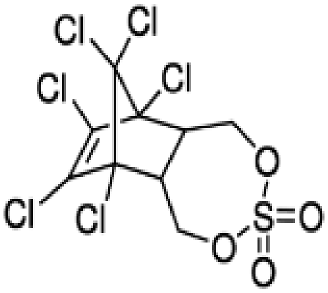
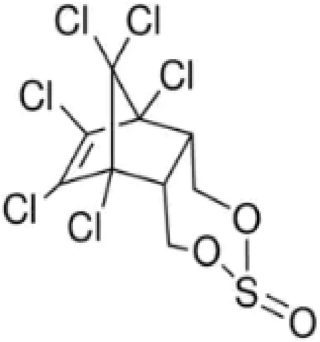
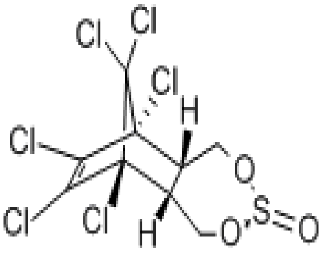
Endosulfan Sulphate ($C_9H_6Cl_6O_4S$)		They are used as insecticides, acaricides, and pesticides against aphids, fruit worms, beetles, leafhoppers, moth larvae, and white flies on various crops.	Hazardous to the aquatic environment, long-term hazard, cause irritation, headache, giddiness, blurred vision, nausea, vomiting, diarrhea, and muscle weakness. Severe poisoning may cause convulsions and coma. Impacts spermatogonial cells, sperm morphology, sperm quality, male sex hormone abnormalities, DNA damage, and mutation. Banned in 1985 by US EPA.
α –endosulfan ($C_9H_6Cl_6O_3S$)		Used as an insecticide on crops, grains, cotton, fruit, vegetables, and sugarcane, tobacco. Used as a wood preservative to protect wood from decay and insect attack.	Highly toxic to mammals and a neurotoxin to the central nervous system Lead to tremors, hyperactivity, or decreased breathing and ability to produce saliva. US EPA has banned it since 1982.
β – endosulfan ($C_9H_6Cl_6O_3S$)		They are used as an insecticide on crops, grains, cotton, fruit, vegetables, and tobacco. Used as a wood preservative to protect wood from decay and insect attack.	Cause acute and chronic toxicity, convulsions (shaking violently), and death. Banned in 1985 by US EPA.

Table 2.1: Biochemical effects, structure, and uses of major OCPs continues'

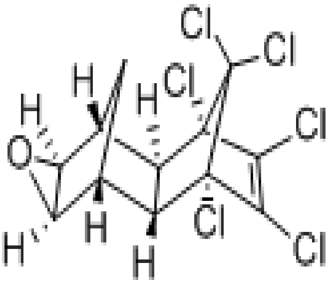
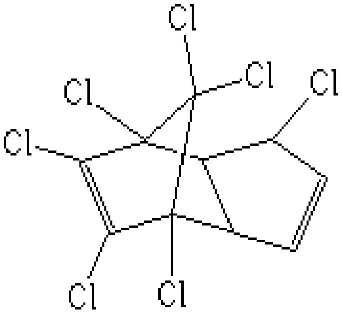
Endrin ($C_{12}H_8Cl_6O$)		Used as a pesticide to control insects, rodents, and birds	Exposure to Endrin can cause nausea, vomiting, diarrhea, loss of appetite, sweating and weakness, headache, lightheadedness, dizziness, and convulsions (fits). Lower exposure can affect concentration, memory, and muscle coordination convulsions, jerking of legs and arms, twitching facial muscles, collapse, or even death. Restricted in 1986. Banned since 1991by US EPA.
Heptachlor ($C_{10}H_5Cl_7$)		Corn, small grains, and sorghum are all protected from pests by the use of an insecticide in soil and seed treatments. Additionally used to manage termites, cutworms, grubs, ants, and other household and agricultural pests.	A carcinogenic agent, it affects the nervous system, Neurological effects, including irritability, salivation, and dizziness. Dust inhalation results in agitation, trembling, and collapse. Ingestion results in gastrointestinal tract discomfort, vomiting, diarrhea, and nausea. Dust exposure causes mild skin discomfort and eye irritation. Banned in Kenya and by US EPA in 1986.

Table 2.1: Biochemical effects, structure, and uses of major OCPs continues'

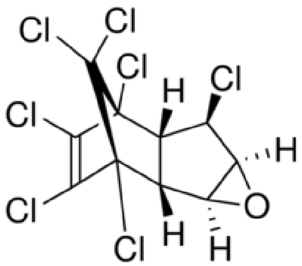
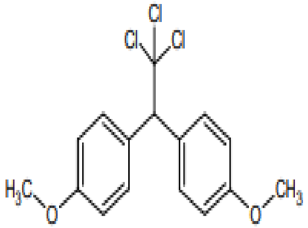
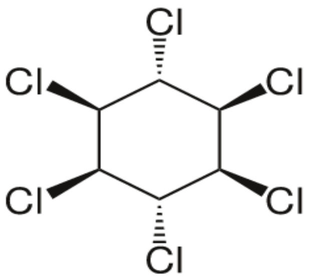
Heptachlor – epoxide ($C_{10}H_5Cl_7O$)		Insecticides	Carcinogenic and Banned in 1986 by US EPA and Kenya.
Methoxychlor ($C_{16}H_{15}Cl_3O_2$)		They are an insecticide against flies, mosquitoes, cockroaches, chiggers, and other insects. It is used on agricultural crops and livestock, animal feed, barns, grain storage bins, home gardens, pets, lakes, and marshes.	Cause reproductive damage, anxiety, dizziness, headache, confusion, weakness, "pins and needles" in arms or legs, muscle twitching, and tremor. Higher levels can cause convulsions and even death. Nervous system effects include tremors, convulsions, short-term memory, and reproductive system effects. Banned in 2000 (US EPA, 2004)
Lindane (γ-HCH) (Gamma-hexachlorocyclohexane) or Gamma benzene hexachloride (γ-BHC) ($C_6H_6Cl_6$)		They are used as acaricides, fungicides, and agricultural insecticides and as a pharmaceutical Treatment for lice, scabies, and killing mites.	Neurotoxicity interferes with GABA neurotransmitters and other biological functions from the brain to the endocrine and cardiovascular systems.Congenital impairments result from damage to the human liver, renal, nervous, and immunological systems; cancer produces neurotoxicity, reproductive toxicity, and hepatotoxicity. Restricted in 2002 and banned in 2009 in Kenya.

Table 2.1: Biochemical effects, structure, and uses of major OCPs continues'

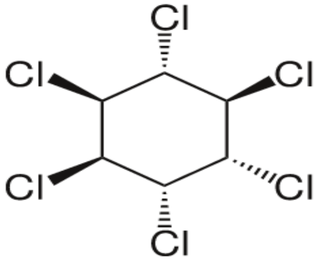
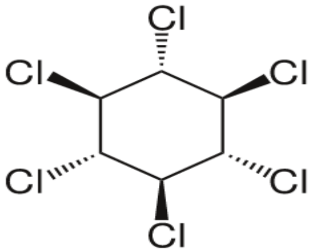
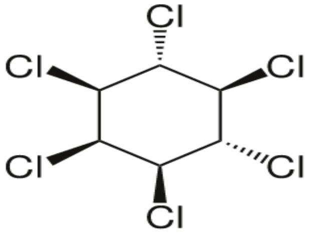
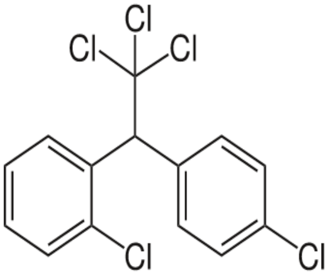
α-HCH (Alpha–hexachlorocyclohexane) ($C_6H_6Cl_6$)		Used as insecticide and fungicides for many crops and vegetables	Carcinogenic effects may lead to blood disorders, dizziness, headaches, and alterations in blood sex hormone levels. Affect the liver and kidney. Banned 2004 in Kenya.
β-HCH (Beta–hexachlorocyclohexane) ($C_6H_6Cl_6$)		Insecticides, fungicides, and pesticides	Cause DNA damage, cancer, neurodegenerative diseases, metabolic disorders Banned in 1985 US EPA
δ –HCH (Sigma– hexachlorocyclohexane) ($C_6H_6Cl_6$)		Insecticides, fungicides, and pesticides.	Carcinogenic agent Cause Cysts in hands, itching, psoriasis, eczema, leucoderma, and skin rashes. Banned in 1985 US EPA.
o, p'- DDT (Ortho, para'-dichlorodiphenyltrichloroethane) or 1-chloro-2-[2,2,2-trichloro-1-(4-chlorophenyl) ethyl] benzene ($C_{14}H_9Cl_5$)		Insecticides and pesticides.	Carcinogenic agent. Causes lacrimation, salivation, anorexia, bradycardia, abdominal pain, hyperactivity, anxiety, depression, and vomiting. Banned in 1985 by US EPA.

Table 2.1: Biochemical effects, structure, and uses of major OCPs continues’

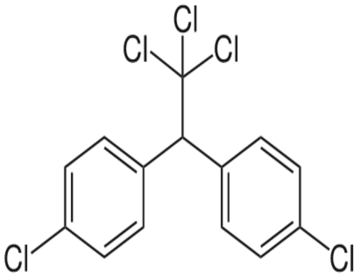
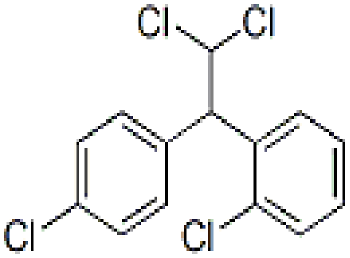
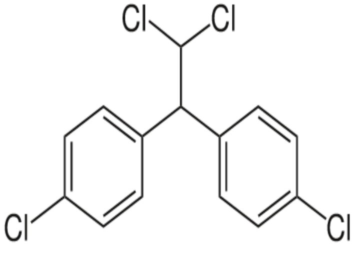
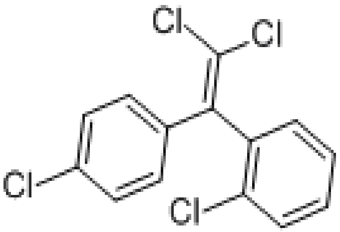
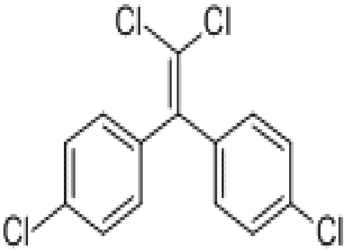
p, p’ – DDT (Para, para’-dichlorodiphenyltrichloroethane) or 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane ($C_{14}H_9Cl_5$)		Insecticides and pesticides.	Carcinogenic agent. Causes lacrimation, salivation, anorexia, bradycardia, abdominal pain, hyperactivity, anxiety, depression, and vomiting. Banned in 1985 by US EPA.
o, p’- DDD (Ortho, para’-dichlorodiphenyldichloroethane) or 1,1 dichloro-2 (o-chlorophenyl) 2-(p-chlorophenyl) ethane ($C_{14}H_{10}Cl_4$)		Insecticides and pesticides.	Carcinogenic agent. Causes lacrimation, salivation, anorexia, bradycardia, abdominal pain, hyperactivity, anxiety, depression, and vomiting. Banned in 1985 by US EPA.
p, p’- DDD (Para, para’-dichlorodiphenyldichloroethane) or 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl) ethyl] benzene ($C_{14}H_{10}Cl_4$)		Insecticides and pesticides.	Carcinogenic agent. Causes lacrimation, salivation, anorexia, bradycardia, abdominal pain, hyperactivity, anxiety, depression, and vomiting Banned in 1985 by US EPA.

Table 2.1: Biochemical effects, structure, and uses of major organochlorine pesticides

o, p' – DDE (Ortho, para'-dichlorodiphenyldichloroethylene) or 1,1 dichloro-2 (o- chlorophenyl) - 2-(p- chlorophenyl) Ethylene) ($C_{14}H_8Cl_4$)		Insecticides and pesticides.	Carcinogenic agent Causes lacrimation, salivation, anorexia, bradycardia, abdominal pain, hyperactivity, anxiety, depression, and vomiting. Banned in 1985 by US EPA.
p, p'- DDE (Para, para'-dichlorodiphenyldichloroethylene) or 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl) ethyl] benzene ($C_{14}H_8Cl_4$)		Insecticides and pesticides.	Carcinogenic agent. Causes lacrimation, salivation, anorexia, bradycardia, abdominal pain, hyperactivity, anxiety, depression, and vomiting. Banned in 1985 by US EPA.

(Adopted from; Alengebawy *et al*., 2021; Nthusi, 2017; Fosu-Mensah *et al*., 2016; Jayaraj *et al*., 2016; Abongo, 2009; Jordan, 2002).

2.4.2 Mechanism of Organochlorine Pesticide residues Toxicity

According to Alengebawy *et al*. (2017), Naqvi *et al*., (2016), Jayaraj *et al.* (2016), and Jordan (2002), organochlorine pesticide poisoning stimulation central nervous system which affect the brain functions. Jayaraj *et al*. (2016) reported, cyclodienes like gamma-aminobutyric acid (GABA) are antagonists to endosulfan and lindane, preventing the calcium ion influx and Ca^{2+} and Mg-ATPase, which releases neurotransmitters. Organochlorine pesticides exhibit diverse impacts on the central nervous system, affecting sodium and calcium channels, as well as interfering with γ-aminobutyric acid (GABA) neurotransmission by blocking specific GABA receptors, which contributes to their neurotoxic effects (Naqvi *et al*., 2016; Jayaraj *et al*., 2016). According to Naqvi *et al*. (2016) pyrethrins and pyrethroids, which fall under sodium channel modulators, bind to sodium channels, causing them to remain in an open state. This, in turn, leads to tremors and, ultimately, fatality or death. Regarding chloride channel regulation, three mechanisms are involved: activation of chloride channels (avermectins), inhibition of gamma-aminobutyric acid (GABA) receptors (organochlorine pesticides), and the activation of the GABA-gated chloride channel (bifenazate) (Alengebawy *et al.*, 2021; Rajmohan *et al*., 2020; Naqvi *et al*., 2016;Jayaraj *et al*., 2016; Fosu-Mensah *et al.*, 2016).

By interfering with the operation of the endocrine system and molecular circuits, organochlorines primarily serve as endocrine-disrupting chemicals (EDCs) (Jayaraj *et al*., 2016; Jordan, 2002). Numerous organochlorine compounds are carcinogenic and neurotoxic. Whether indirect or direct, pesticide exposure stimulates steroid metabolism and neuromuscular problems (Jayaraj *et al*., 2016). According to numerous studies (Alengebawy *et al.*, 2021; Rajmohan *et al*., 2020; Jayaraj *et al*., 2016; Naqvi & Campus, 2016; Fosu-Mensah *et al.*, 2016; Jordan, 2002), organochlorine pesticides are primarily to blame for human hypertension, cancer, cardiovascular disorders, and other linked ill-health issues (Table 2.1).

2.4.3 Effects of Organochlorine pesticide residues toxicity in human health

According to Rajmohan *et al*. (2020) and Jayaraj *et al*. (2016), short-term exposure of humans to organochlorine pesticides can result in symptoms such as diarrhea, headache, dizziness, nausea, vomiting, tremors, convulsions, confusion, muscle weakness, stinging or painful eyes, blisters, blindness, slurred speech, rashes, salivation, and sweating. Long-term exposure may cause severe damage to the liver, kidney, central nervous system, bladder, and thyroid damage and may even cause death (Fosu-Mensah *et al*., 2016; Jayaraj *et al*., 2016; Jordan, 2002). Jayaraj *et al*. (2016)**,** Fosu-Mensah *et al*. (2016), and Jordan (2002) have linked liver and kidney cancer and other human diseases to pesticide toxicity (Table 1).

2.5 Analytical techniques (GC-MS) used for the analysis of organochlorine pesticide residue.

The following methods can be used for the analysis organachlorine pesticides in water and sediment samples. GC-MS method preferred in this study because of its availability and ability to separate and quantify the volatile and thermally stable molecules effectively in river water and sediment samples.

2.5.1 Gas chromatography (GC) equipped with electron capture detector (ECD) or FID

Chromatography is an analytical method employed to separate chemical substances based on their differential partitioning between a stationary phase and a flowing mobile phase, effectively isolating components within a sample mixture (Atieno Abongo, 2009; Olivieri, 1990). Gas Chromatography with an Electron Capture Detector (GC-ECD) is predominantly utilized in environmental testing for the detection of organochlorine pesticides, herbicides, Polychlorinated biphenyls (PCBs), and various halogenated hydrocarbon compounds, boasting advantages like high sensitivity, simplicity, and efficient separation of mixture components (Nthusi, 2017; Abongo, 2009).

Moreover, GC with an electron capture detector typically employs a beta emitter like 63Ni or radioactive tritium to ionize the carrier gas (Kenkel, 2013; Patnaik, 2011). Fast, beta particles from the radioactive source collide with the molecules of the carrier gas, leading to impact ionization in GC, generating a consistent and measurable current (Kenkel, 2013; Patnaik, 2011; Abongo, 2009). During analysis, electrons are captured and the current is reduced when

GC eluates contain organic molecules with electronegative functional groups such as nitro groups, halogens, or phosphorous. The reduction in electron flow is proportionate to the amount of electrophilic sample components, compared to a signal without sample compounds (Kenkel, 2013; Patnaik, 2011; Abongo, 2009).

In an ECD, electrons from the sample are captured as certain molecules pass through the detector, leading to a reduction in the measured current, which is recorded as a positive peak in the chromatogram (Linde Group, 2020; Abongo, 2009). ECDs in GC are typically a thousand times more sensitive than GC- Flame Ionization Detectors, enabling the detection of compounds at significantly lower concentrations that is why it is a preferred choice for environmental analysis. On the other hand, Flame Ionization Detector (FID) is the most sensitive gas chromatographic detector for hydrocarbons like butane or hexane (Linde Group, 2020; Nthusi, 2017; Kenkel, 2013; Abongo, 2009).

2.5.2 Liquid chromatography-Mass Spectrophotometer (LC-MS)

Liquid chromatography-Mass Spectrophotometer (LC-MS) separates sample components before introducing them to the mass spectrometer (MS), which generates and detects charged ions. LC-MS provides valuable data about molecular weight, structure, identity, and quantity of specific sample components, with the advantage of identifying and quantifying a broader range of compounds with minimal sample preparation (Linde Group, 2020; Kenkel, 2013; Patnaik, 2011). One of the primary advantages of GC-MS in comparison to LC-MS is the high reproducibility of mass spectra generated using electron impact (EI). The electron impact ionization process in GC-MS is a hard ionization method, resulting in highly reproducible mass spectra across different instruments (Linde Group, 2020; Nthusi, 2017; Kenkel, 2013; Patnaik, 2011; Abongo, 2009).

2.5.3 Gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry combines gas chromatography's and mass spectrometry's separation properties to identify distinct substances inside a test sample (Ogola *et al*., 2023; Alpha *et al.*, 2013; Abongo, 2009). GC alone is typically employed for separating stable, volatile molecules in a sample. In contrast, GC-MS identifies analytes by fragmenting them based on their mass-to-charge ratio. (Nyaundi *et al*., 2021; Osoro *et al*., 2016; Nthusi, 2017; Koigi, 2015; Abongo, 2009).

The major components of GC-MS (Figure 2.1)

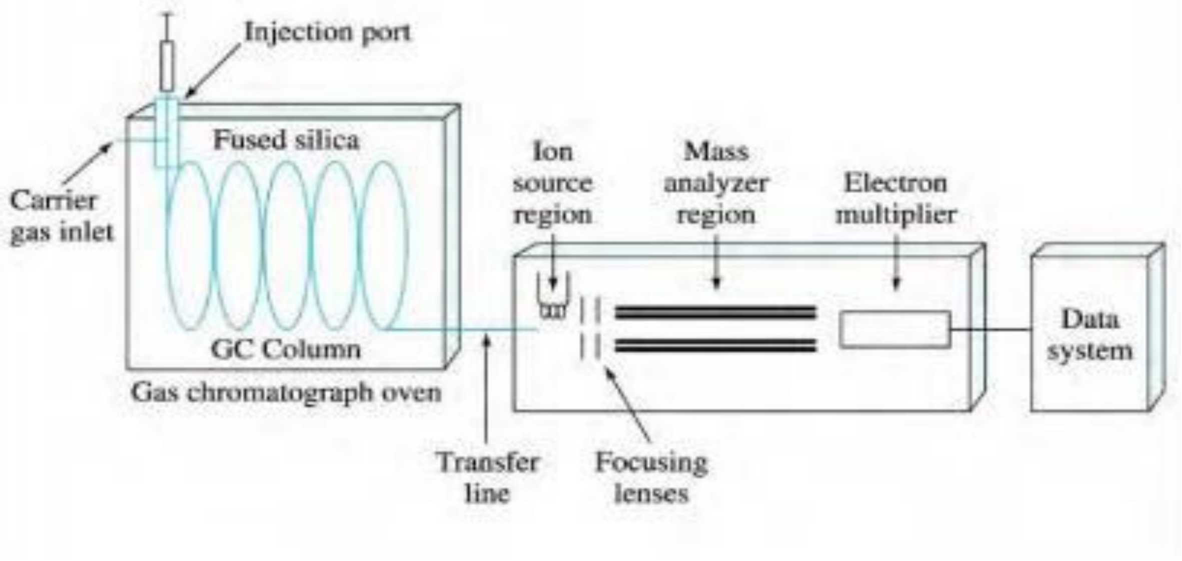


Figure 2.1: Diagram of a GC-MS instrument used (Source: Koigi, 2015; Abongo, 2009)

In the GC-MS analytical method, a particle's mass is expressed as the ratio of its mass (Da) to the number of electrostatic charges (e) it carries in the sample. This technique commonly employs electron impact (EI) and chemical ionization (CI) procedures, measuring mass-to-charge (m/z) in Da/e (Lisouza et al., 2019; Epa US, 2016; Abongo, 2009; US EPA, 2007). GC-MS offers notable advantages, including speed, high sensitivity, simplicity, and effectiveness in separating components within mixtures. Furthermore, it provides improved confidence in sample identification, expanded molecular ion capabilities, a wider range for analyzing thermally labile and low volatility samples, increased sensitivity for complex compounds, and widespread accessibility, setting it apart from other methods. (Nyaundi *et al*., 2021; Nthusi, 2017; Osoro *et al*., 2016; Koigi, 2015; Abongo, 2009; APHA, 2002). Therefore, the GC-MS is widely used for monitoring and tracking organic pollutants, pesticides, herbicides, Polyaromatic hydrocarbons (PAH), dioxins, chlorophenols, dibenzofurans, and gasoline (Nyaundi *et al*., 2021; Nthusi 2017; Osoro *et al*., 2016; Koigi, 2015; Abongo, 2009; APHA, 2002).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The river Kibos-Nyamasaria area of Kisumu East District, Kisumu County, served as the study's location. Kisumu is between a Latitude of 0° 05' 60.00" N and a longitude of 34° 44' 59.99" E (Kisumu County, 2020). The land area of Kisumu County totals 2085.9 km^{2,} and it has a population of 1,155,574 (Statistics, 2020; KNBS, 2019). Kisumu East district altitude ranges between 1100 to 1160 meters above sea level and between longitude 34.767956° or (34° 46′ 4.6416″ E) and latitude -0.091702 or (0° 5′ 30.1272″ S). Kibos area where the river passes has geographical coordinates of 0° 40' 0" South, 34° 49' 0" East. (Ogola *et al*., 2023; Masimbe, 2018; Onyango *et al*., 2014).

River Kibos-Nyamasaria passes through Kisumu City before draining into Lake Victoria. Vihiga County, Nandi County, and Kericho County, all counties with significant agricultural activity, are Kisumu County's neighbors. The county is located along the northern, western, and portion of the southern borders of the Winam Gulf, where the Kibos-Nyamasaria River empties its waters into Lake Victoria (Ogola *et al*., 2023; Nthusi, 2017; Odada *et al*., 2006).

The sources of river Kibos-Nyamasaria are the Nandi escarpment and South Nandi Forest. The river flows through several kilometers (about 25 km) before draining into Lake Victoria. Kibos-Nyamasaria river flows within the Lake Victoria drainage basin from the high plateau of South Nandi Forest to the downstream end at Nyanza gulf or Winam gulf (Ogola *et al*., 2023). The river section drainage starts from the dam site up to the existing water supply diversion, which is dominated by rapid and followed by the gently undulating plateau to a point where Awach and Kibos confluence or merge or flow together. A few kilometers off this junction, the canalized section of the river starts, and the river finally drains into Lake Victoria through Nyalenda and Dunga swamps in Winam Gulf (Ogola *et al*., 2023).

The river Kibos-Nyamasaria traverses through Kisumu City, which has a population of about 721,082 (Kenya National Census, 2019), and flows along Kasule and Nyalunya sub-locations in Central Kolwa location (Kisumu East sub-county), agricultural farms, an industrial area in Kibos and several informal settlements such as Wathorego, Obuolo, Kibos slums, Mbeme area, Oland Ouko, Nyamasaria, Nyalenda, and Kisumu Dunga area before emptying its waters into Lake Victoria.

Water from the river Kibos-Nyamasaria is mainly used by people living in the informal settlements along the river for domestic use, cooking, drinking, bathing, fishing, and irrigation (Ogola et al., 2023; Masimbe, 2018). The samples for the study were collected along the river Kibos-Nyamasaria from 10 sampling points, as shown in the map of the study sites (Figures 2 and Table 2). The sampling started where the River Awach and Kibos confluence or merged to form river Kibos-Nyamasaria, sampling point S1 and ended where it drains into Lake Victoria, sampling point S10 (Figure 2).

3.2 Description, classifications, and human activities at the sampling points along River Kibos-Nyamasaria

Samples of river water and sediments were collected from ten sampling sites purposely selected along the river Kibos-Nyamasaria during the dry season (February - March) and the wet or rainy season (April – May). The first sampling point (S1) was from where the river Kibos and Awach merged to form River Kibos-Nyamasaria, while the rest were distributed along the river, as shown on the map of the sampling sites (Figure 2). The final sampling point

(S10) was where the river enters or drains into Lake Victoria. Table 2 describes the human activities around the sampling points along the river Kibos-Nyamasaria and various abbreviations used during the sampling and analysis.

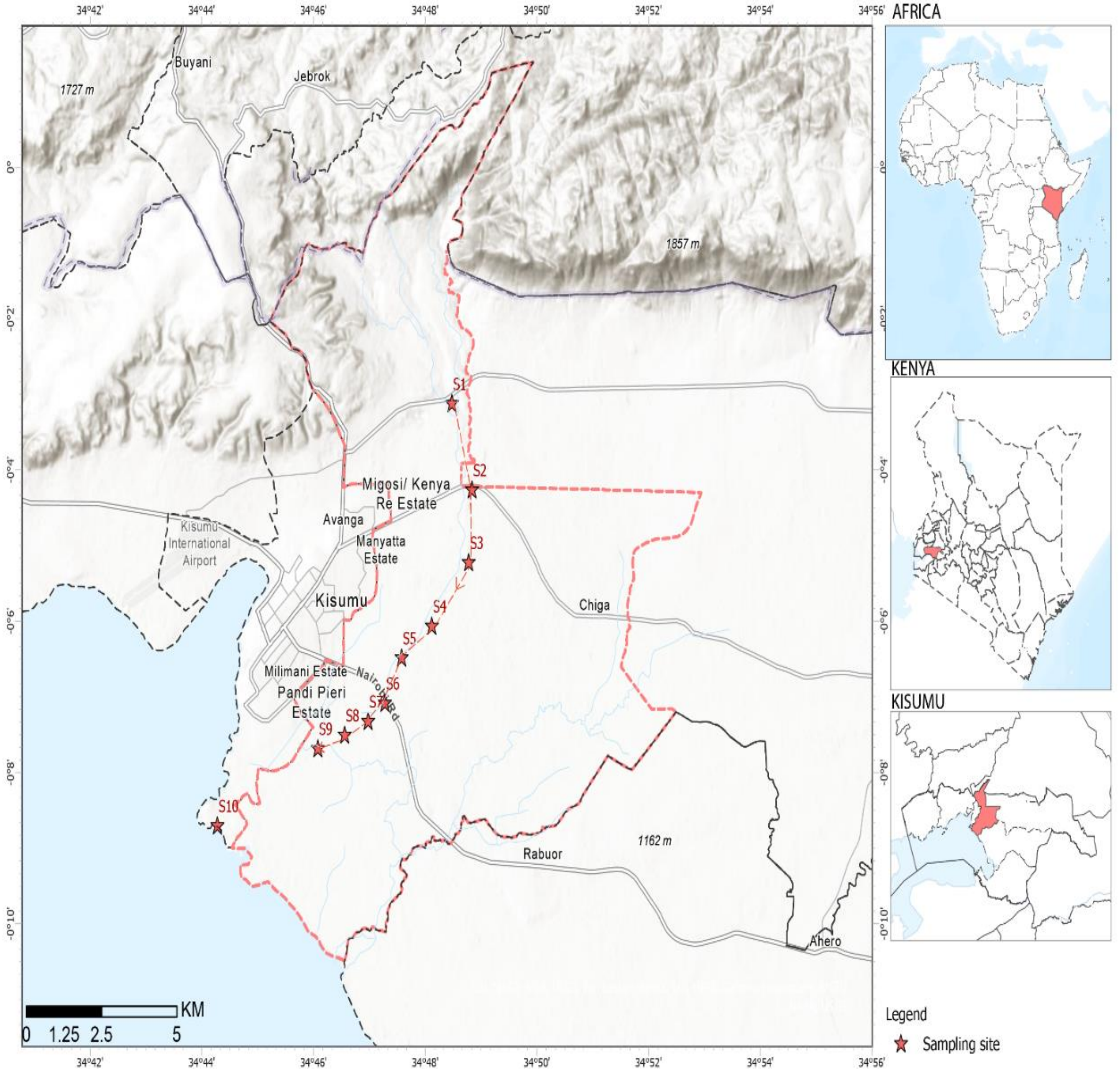


Figure 3.1: Map of Kisumu City showing rivers and sampling points along river Kibos-Nyamasaria

Table 3.1: Water and sediment at different sampling points in river Kibos-Nyamasaria

Sampling Site	Site intervals (approx.Kms)	Sampling Site descriptions	GIS Position N (+) /S (-) E		Human activities around the sampling points
			N (+) /S(-)	E	
S1	S1 =0	At the convergent of River Kibos & Awach near Guba Bridge Kibos	-0.052^0	34.808^0	Large-scale sugarcane farming, Bushes, Human settlement, maize, tomatoes, cassava farms on river banks, effluent discharge from factories, KALRO farms, cattle, and human watering points
S2	(S1-S2) = 3	Kibos Bridge near Kibos market	-0.071^0	34.814^0	Human settlement, maize, tomatoes, cassava farms on river banks, effluent discharge from Kibos market, cattle watering, and human watering points.
S3	(S2-S3) =2.5	Foot bridge near Kunya Market or Adasa school	-0.087^0	34.813^0	Human settlement, maize, tomatoes, cassava farms on river banks, domestic effluent discharge from the market, cattle watering, Human watering, and bathing point.
S4	(S3-S4) =2	Olad Ouko bridge	-0.101^0	34.802^0	Human settlement, tomato, maize, and cassava crops along rivers, watering places for domestic animals and cattle, human bathing areas, and river sand gathering are all common.
S5	(S4-S5) =1.5	Foot Bridge near Jamilo Academy	-0.108^0	34.793^0	Human settlement, fields of maize, tomatoes, and cassava along rivers, watering places for domestic animals and cattle, human bathing areas, and river sand harvesting.
S6	(S5-S6) =2	Nyamasaria bridge	-0.118^0	34.788^0	Human habitation, farms growing maize, tomatoes, and cassava along rivers, watering places for household animals and livestock, sand harvesting, a location for selling and treating wood, and the disposal of domestic waste from the estates and market at Nyamasaria.
S7	(S6-S7) =2	Behind Nyamasaria Estate	-0.122^0	34.783^0	Human settlement, tomato, maize, and cassava crops along rivers, drinking holes for domestic animals and livestock, public restrooms, and river sand gathering.
S8	(S7-S8) =2	Near KIWASCO Nyalenda wastewater treatment plant	-0.125^0	34.776^0	Human habitation, riverbank crops of maize, tomatoes, and cassava, domestic animals, and cattle watering well, Human watering point, KIWASCO waste dumping point, and swimming area
S9	(S8-S9) =2	Nyalenda farms	-0.128^0	34.768^0	Human settlement, maize, tomatoes, cassava, etc. farms on river banks, human, domestic animals, and cattle watering points, part of Nyalenda swamp
S10	(S9-10) =4	Point of entry to Lake Victoria	-0.145^0	34.738^0	Nyalenda swamp, Dunga wetland, fishing activities, Human settlement at Nyalenda, Nanga, and Dunga Estates

S – Samples and the numbers - sampling points, e.g., S1 is the first, and S10 is the last sampling point.

3.2.1 Sample size

The sample size was determined using Ahlbom 2017 formula given by;

$$n = \frac{Z^2 P(1-P)}{e^2}$$

Where;

n = is the sample size,

z = is the z-score associated with a level of confidence,

p = is the sample proportion, expressed as a decimal,

e = is the margin of error, expressed as a decimal, which gave a sample size total of 120. Thirty water samples and 30 sediment samples were collected during the rainy (April - May 2022) season, and the other sets were collected during the dry (February- March 2022) season by collecting three samples at each sampling site.

3.3 Sampling and Sample Collection Procedure

Water and sediment samples from the river were collected from 10 sampling points identified, as shown in Figure 3.1. Water samples were collected using sterile 2.5 L amber screw cap glass bottles for analysis of selected organochlorine pesticide residues according to Nyaundi *et al.*(2021), Ndunda *et al.*(2018), and Abongo (2009) methods. The screw cap amber glass bottles for collecting samples were thoroughly cleaned with soap and distilled water and rinsed with acetone before sample collection at the sampling points using a grab sampling method. The river water was sampled by dipping the sample bottle at 20 cm below the water surface, in turbulent midstream positions, projecting the mouth of the container against the flow direction of the river water. Water samples collected were treated to avoid degradation of the pesticides in the water samples by microorganisms by adding 1.0 g mercuric chloride followed by thorough mixing for 5 minutes.

Using a soil auger to scoop sediments in triplicate within a length of 50 m from the left river bank, midstream, and right river bank, 200g of representative soil sample was taken from the composite sample at each research location. Then, these sediments were thoroughly mixed over a fresh sheet of aluminum foil (Ogola *et al*., 2023; Nyaundi *et al*., 2021; Nyaundi *et al*., 2020; Alex *et al*., 2019; Abong'o *et al*. The samples were placed into a labeled self-sealing zip-lock polythene bag after being wrapped in labeled aluminum foil and a black plastic bag. Before being taken to the lab for additional storage, processing, and analysis, the samples were first briefly stored in polyurethane cooler boxes (Ogola *et al*., 2023; Abongo, 2009). After each usage, the glassware used for sample collection, preparation, and analysis was thoroughly cleaned with double-distilled de-ionized water before being dried overnight in an oven at 105^0 C.

Abong'o *et al*. (2018) and APHA, 2002 methods were used to treat river water and sediment samples before laboratory analysis. Water samples were stored at 4^0 C while sediments were stored in aluminum containers at -20^0 C in the laboratory deep-freezer before further sample preparation, extraction, clean-up, and analysis within seven days. Gas chromatography (GC) determined organochlorine pesticide residues, which were equipped with a mass spectrophotometer (MS) as a detector.

3.4 Chemicals and Reagents

Fisher Scientific (USA), Aldrich Chemical Company, and BDH (UK) delivered the analytical and HPLC-grade chemicals used in the inquiry through their local suppliers. By injecting 1 µL standards into a Scion 456-GC gas chromatography system fitted with an 8400-auto sampler and MS detector, purchased certified organochlorine pesticide reference standard mixture of over 99% pure isodrin was used as an internal standard for identifying and quantifying pesticide residues in the samples (Ogola *et al*., 2023; Abong'o *et al*., 2018; Nthusi, 2017; Ndunda *et al*., 2018; Osoro *et al*., 2016). Other standards used in the study were EPA CLP organochlorine pesticide mix SS, 1×1, Tol: Hex (50-50), 2000µg/ml (standard), Decachlorobiphenyl (internal standard), Accustandard Pentachloronitrobenzene, 1.0 mg/ml (internal standard) and Standard reference materials SRM 2261 and SRM 2275 (Nyaundi *et al*., 2021; Nyaundi *et al.*, 2020; Alex *et al*., 2019; Abong'o *et al.*, 2018; Fang *et al.*, 2017; Nthusi, 2017; Osoro *et al*., 2016; Abong'o *et al*., 2015; US EPA, 2007).

Hexane, acetone, dichloromethane, and isooctane were the solvents from local merchants in Kenya by Kobian Ltd. or Fisher Scientific (USA). Analytical grade anhydrous sodium sulphate, sodium chloride, aluminum oxide, sodium hydroxide, hydrochloric acid, nitric acid, mercury chloride, methanol, and other chemicals required for analysis were supplied by Fisher Scientific (USA) to local suppliers in Kenya (Ogola *et al*., 2023; Abong'o *et al*., 2018; Nthusi, 2017; Osoro *et al*., 2016; Abong'o *et al*., 2015).

Acetone and n-hexane, multipurpose solvents, required triple distillation before usage. A few solvents, such as diethyl ether and HPLC-grade hexane, were bought at 99% purity and didn't need to be distilled. Concentrating the solvent and passing it through a GC-MS to look for any peaks other than the solvent's own allowed researchers to determine the purity of the HPLC-grade hexane (Abong'o *et al*., 2018; Nthusi, 2017; Abong'o *et al*., 2015). After being dried at 120 ^{0}C for at least two hours or overnight in a hot air oven, sodium chloride and activated charcoal were chilled in desiccators before use (Ogola *et al*., 2023; Abong'o *et al*., 2018; Nthusi, 2017; Abong'o *et al*., 2015).

Before being used to clean up sample extracts, anhydrous sodium sulfate and Florisil (magnesium silicate) was activated at 200^0 C and 350^0 C, respectively, in a hot air oven

(Abong'o *et al*., 2018; Nthusi, 2017; Osoro *et al*., 2016; Abong'o *et al*., 2015). Local suppliers provided the cleaning detergents that were utilized. After spending two hours soaking in 5% nitric or chromic acid, glassware were cleaned with tap water, rinsed with distilled water, and then completed with triply distilled methanol. After that, the apparatus was dried for four or more hours at a temperature of 105^0 C in a hot air oven before use (Ogola *et al*., 2023; Abong'o *et al*., 2018; Nthusi, 2017; Osoro *et al*., 2016; Abong'o *et al*., 2015).

3.5 Analytical Methods

The physicochemical examination of water and soil samples and sample preparation, extraction, cleanup, and analysis of organochlorine pesticide (OCP) residues from river water and sediment samples used the analytical methodologies and techniques listed below.

3.5.1 Physicochemical analytical methods of river water and soil samples

A 930-precision pH meter (Biobase) measured water and soil samples' pH. Conductivity, TSS, and TDS were measured using the WTW in-lab 720 conductivity meter, while turbidity of the waters was measured using Hanna LP 2000 Turbidity meter. Moisture tests of soil were done using the Memmert hot air oven method set at 105^0C overnight. Soil organic matter (OM) and soil organic carbon (OC) in the soil were determined using a muffle furnace. In contrast, the soil structure test was determined using the Mason Jar test method (Jeffers, 2019; Abdel-Rasheed, 2011; APHA 2002; APHA 1998).

3.5.2 pH determination method for water and soil samples

A 930-precision pH meter (Biobase) measured water and soil pH. The meter was calibrated using buffer solutions with 4, 7, and 10 pH values. The pH of a water sample was measured by dipping the electrode into a 50 ml solution of water sample in a 100 ml beaker, spinning, and waiting a minute to get a steady reading. For soil samples, 20 g of soil was weighed using an analytical balance, then transferred into a 50 ml beaker, and 40 ml distilled water was added in a ratio of 1:2. The suspension was stirred for 30 minutes, and then pH readings were recorded. The same suspensions prepared and used for pH readings were kept and used for measuring soil conductivity (Abdel-Rasheed, 2011; APHA, 2002; APHA, 1998).

3.5.3 Conductivity determination

Conductivity measurements in water samples were carried out using a calibrated WTW in-lab 720 conductivity meter using solutions and water samples, which were used to measure pH. To calibrate the instrument, standards with conductivities of 84, 1413, and 12880 µS were employed before assessing the samples' conductivity. The procedure involved immersing the electrode in the sample solution, gently swirling it, and allowing up to a minute for the reading to stabilize before recording the measurements. Before switching the samples, the electrodes were thoroughly cleaned with tissue and distilled water (Abdel-Rasheed, 2011; APHA, 2002; APHA, 1998).

3.5.4 Total Dissolved Solids (TDS)

By placing the filter paper in the filtration assembly and filtering three separate 20 ml volumes of distilled water, the filter paper used for TDS measurement was cleaned. The suction eventually eliminated all traces of water. Dishes were dried at 105^0C in an oven, cooled in desiccators, and weighed right before use. With a wide bore pipette, measured volumes of the water samples were pipetted onto the filters as they were agitated with a magnetic stirrer. The sample volume (about 50 ml) was chosen to give between 10 and 200 mg of dried residue, after which it was rinsed three times with 10 mL of distilled water. After the filtrations were finished, the suctions lasted for another three minutes. Total filtrates were placed on weighed evaporation plates with washings, where they were then evaporated to dryness in an oven at 105^0 C. After evaporation, the consecutive portions were applied to the same dishes to produce between 10 and 200 mg of dried residue. The oven temperature was initially set at 20^0 C to prevent splattering and then increased to 105^0 C after one hour of evaporation. The leftovers were chilled in a desiccator before being weighed and recorded for calculations (Abdel-Rasheed, 2011; APHA, 2002; APHA, 1998).

Calculation

$$\text{Total Dissolved Solids / L (mg)} = \frac{(A - B)\,1000}{\text{Sample (mL)}}$$

Where:

A = weight of residue, dried + dish, mg
B = weight of the dish, mg.

3.5.5 Total Suspended Solid (TSS)

The filter papers were cleaned in this procedure by placing the filter papers on the filtration assembly and filtering three separate 20 mL volumes of distilled water. The filters were put on metal dishes and dried for one hour in an oven set to 105°C. Dry filter and crucible combined if a Gooch crucible was utilized. The leftovers were weighed after being chilled in a desiccator to maintain an even temperature. The cleaned, dried, and weighed filter paper was used to assemble the filtration system. To fix it, filter sheets were moistened with a small amount of distilled water. A measured amount of water was pipetted using a large bore pipette onto the filter after thoroughly stirring the samples with a magnetic stirrer. The sample volume (about 50 ml) was chosen to produce between 10 and 200 mg of dry solids, depending on the sample type. Three separate 10 mL amounts of distilled water were used for washing. After the filtrations were finished, the suction ran for roughly three minutes. Next, the filters were carefully removed and put on the aluminum weighing dishes. As mentioned, the drying, cooling, and weighing processes were carried out until a steady weight was attained and recorded for computations (Abdel-Rasheed, 2011; APHA, 2002; APHA, 1998).

Calculation

$$\text{mg Total Suspended Solids / L} = \frac{(A - B)\,1000}{\text{mL sample}}$$

Where:

A = weight of filter + dried residue, mg, and
B = weight of the filter, mg

3.5.6 Turbidity Determination in water samples

After calibrating the instrument per the manufacturer's operating instructions with the standards that were run on the instrument range to be utilized, the water samples' turbidity was measured using a Hanna LP 2000 Turbidity meter. When the air bubbles were gone after shaking the sample, the samples were gently stirred before being poured into a sample cell or cuvette (10 mls) for measurement. Before taking measurements, the sample cells or cuvettes were meticulously rinsed with distilled water and gently wiped using a tissue to ensure cleanliness. The instrument display was used to obtain the Nephelometric Turbidity Units (NTU) turbidity measurements (Abdel-Rasheed, 2011; APHA, 2002; APHA, 1998).

3.5.7 Moisture Content Determination

Soil moisture tests were conducted by placing 10 g of soil samples in triplicates in moisture dishes, which were then heated in a Memmert oven at 105°C overnight for 24 hours. The weight of each moisture dish was recorded when empty, after placing the soil, and after the heating process. The variation in weight between the dry soil sample and its original weight before drying was utilized to determine the soil samples' moisture content. The moisture content % was then calculated by multiplying the result by 100 after dividing the weight difference by the sample's original weight (Ministry of Agriculture, Government of India, 2011).

Calculation:

$$\text{Moisture content (\%)} = \frac{(A - B)}{A} \times 100$$

Where: A = weight sample + dish before drying, g
B = weight of dryed sample + dish, g

3.5.8 Total organic matter and total organic carbon determination

Total organic matter and total organic carbon were done using a muffle furnace, a thermo gravimetric analytical method. 10 g of sieved soil (2 mm) was placed into crucibles, weighed, recorded weight, and then put in an MRC muffled furnace set at 105^0 C for 4 hours to remove the moisture from the soil samples. The crucibles with the dried samples were removed, cooled, weighed to the nearest 0.01 g, and recorded as the initial sample weight (W_1).

The dried soil samples were placed into the muffle furnace at 400^0 C for 4 hours, cooled in a desiccator, and weighed to the nearest 0.01 g (W_2). The percentage of organic matter (OM) was calculated by subtracting weight (W_2) from (W_1) and dividing the loss in weight by initial weight (W_1), and multiplying by 100 to get the % organic matter (OM) in the soil samples. The Percent Organic Carbon (OC) was calculated by multiplying the percentage of organic matter (OM) by a factor of 0.58 (Ministry of Agriculture, Government of India, 2011).

3.5.9 Soil structure test

Soil structure tests were done using Jeffers, (2019) Mason Jar Test method. Finely sifted soil samples were used to fill the Manson Jar to 1/3 complete, and added one tablespoon of granular dishwashing detergent. The water was then poured into the glass jar almost to the top, allowing space for a good shake. After vigorously shaking the mixes until homogeneous and slimy, the glass jars' lids were snugly fastened. The glass jars were then placed on a flat surface to rest. The glass jars' sides were marked with a marker pen to indicate the sand component after the mixes had settled for one minute (Jeffers, 2019). Two hours after settling, the glass jars' sides were marked with a marker pen to mimic the silt layer. The final clay layer was identified after letting the mixture sit for a few days until the top water layer became clear. As the soil/water mixtures settled for 48–72 hours, sand, silt, and clay broke into horizons, and their proportions were then clearly displayed. The percentages or proportions of sand, silt, and clay were calculated for the exact height of each layer and assessed using a ruler then computation done (Jeffers, 2019).

% Sand = (height of sand) / (total height of mixture) × 100

% Silt = [(height of silt) – (height of sand)] / (total height of mixture) ×100

% Clay = 100 – % Sand – % Silt

3.6.0 Analytical Methods for Analysis of Organochlorine Pesticides

The subsequent techniques were employed for the preparation of samples, extraction, purification, calibration, validation of the method, and the analysis of organochlorine pesticides in samples of water and soil sediment.

3.6.1 Samples preparations before analysis of OCP using GC-MS

Modified solvent-phase extraction (SPE) techniques from Ogola *et al*. (2023), Osoro *et al*. (2016), Pinto *et al*. (2010) and APHA (2002) were used to extract OCPs from water samples. The glasswares were well cleaned with detergents, soaked in 5% nitric acid, thoroughly rinsed with double-distilled de-ionized water after each use, and then dried for a whole night in a hot air oven at 105^0 C. After being transferred to a 2.5-liter separating funnel, and mixed with 50 ml of 0.2 M dipotassium hydrogen phosphate buffer, a 2.0-liter sample of water was neutralized by adding a few drops of 0.1 N sodium hydroxide and 0.1 M HCl solutions to increase the pH to 7.0. 100 g of sodium chloride was added to the sample to extract organochlorine pesticides from the aqueous phase. The solution was mixed with 60 ml of triple-distilled dichloromethane (DCM) and shaken vigorously for two minutes to release pressure. The phases were adequately separated after 30 minutes of settling correctly. The organic layer was collected in a 250 ml Erlenmeyer flask, and dichloromethane extraction was done twice in 60 ml quantities. The extracts were mixed and cleaned by running them over an Al_2O_3 chromatographic column covered in anhydrous sodium sulfate after being kept in a refrigerator at 4° C. 175 ml of n-hexane was used to elute pesticide residues repeatedly. The resulting elutes were concentrated to 1 ml in a rotary evaporator operated at 40^0 C and then reconstituted in 0.5 ml of HPLC-grade isooctane for GC analysis.

3.6.2 Extraction method of organochlorine pesticide residues from river water samples

Organochlorine pesticide residues were removed from river water using modified Nyaundi *et al*. (2021), Abong'o *et al*. (2018), and Ndunda *et al*. (2018) techniques. With a few drops of either 0.1 N sodium hydroxide (NaOH) or 0.1 N hydrochloric acid (HC1), the pH of a two-liter water sample was increased to 7 in a three-liter beaker. To separate pesticide residues from the aqueous phase into the organic phase, the resulting neutral solution was poured through a 2.5-liter separating funnel. 50 g of oven-dried NaCl was added to the separating funnel and vigorously stirred until the NaCl dissolved. The organochlorine pesticide residues were extracted from the aqueous phase three times using 60 ml of triply distilled dichloromethane before the organic phase was collected in a 250 ml Erlenmeyer flask.

3.6.3 Extraction method of organochlorine pesticide residues from sediments samples

The following methods were used for sediment samples preparation and organochlorine pesticides extractions;

3.6.3.1 Sediment sample preparation before extraction

Environmental Protection Agency (EPA) method 3540 and Soxhlet extraction procedures (Nyaundi *et al.*, 2021; Nthusi, 2017) was used to extract the sediment samples. Samples of wet soil sediment were removed from the deep freezer (-20^0 C), defrosted overnight, and air dry. Pebbles, stones, and plant components from the air-dried samples were removed, crushed, homogenized, and then sieved through a 250 µm mesh sieve size.

Three duplicates of 30g portions of soil sediments were thoroughly mixed with equivalent amounts of anhydrous sodium sulphate before the sample was transferred to a pre-extracted Whatman (9.0 cm) filter paper for extraction with 200 ml of hexane to acetone (3:1v/v) in a 250 ml round-bottomed flask for a minimum of 16 hours. As an alternative, the components were extracted for 24 hours in 200 ml of a 1:3 combination of triply distilled acetone and hexane using a Soxhlet-extractor device. Using a rotary evaporator, each extract was concentrated to a volume of 10 ml. After being maintained in a refrigerator at 4° C, the extracts were combined and meticulously cleaned by passing them over an Al_2O_3 chromatographic column coated in anhydrous sodium sulphate. The elutes reduced to 0.5 ml in HPLC grade isooctane for GC-MS analysis after being reduced to 1 ml in a rotary evaporator at 40° C. The final samples were examined using a premium Scion 456-GC-MS from Scion Instruments following the necessary guidelines (Ogola *et al*., 2023; Nyaundi *et al*., 2021; Nyaundi *et al*., 2020; Alex *et al*., 2019; Abong'o *et al*., 2018).

3.6.4 Clean-up procedure for samples extracts before injection into GC-MS

The following analytical procedures were used to remove impurities from river water and soil sediment extracts before they were analyzed by GC-MS.

.3.6.4.1 Clean-up procedure for river water samples extracts

Before analysis, the river water extract was cleaned using the modified method described by Ndunda *et al*. (2018). 10 ml of water extract was processed through the organic phase using a glass column fixed with a tap and filled with 15g of activated florisil (magnesium silicate, 60–100 mesh size), 4g of activated anhydrous sodium sulphate as a drying agent, and 1.5g of activated charcoal as a decolorizer.

The pesticide residues were then removed from the column using 200 ml sections of 6%, 15%, and 50% diethyl ether in triple-distilled hexane, in that order, at a flow rate of 5 ml/min. In a 500 ml round-bottom flask, the eluents were collected and nearly dried using rotary evaporation. After being reconstituted with 0.5 ml HPLC grade hexane, the eluents were injected into the Gas Chromatography-Mass Spectrophotometer (GC-MS) using the settings defined for detecting organochlorine pesticides.

3.6.4.2 Clean-up procedure for soil sediment samples extracts

According to the modified technique developed by Fang *et al*. (2017), the soil sediments were cleaned. 15 g of activated florisil (magnesium silicate with a mesh size of 60–100), 4 g of activated anhydrous sodium sulphate (drying agent), and 1.5 g of activated charcoal, which served as a decolorizer, were added to a glass column that was 60 cm long and 2 cm in diameter and fixed with a tap to clean the 10 ml of extract. Before being utilized for clean-up, florisil was activated at 350^0 C and anhydrous sodium sulphate at 200^0 C. The extracts were then eluted in hexane using 200 ml of 6%, 15%, and 50% diethyl ether HPLC grades at a 5 ml/min flow rate. Before being transferred to graduated tubes, the three eluents were combined and concentrated in a rotary evaporator at 40^0 C until they were almost dry. The first step was to collect the three eluents in 500 ml round bottom flasks to be fixed in a rotary evaporator. The samples underwent GC-MS analysis after being reconstituted to 0.5 ml in HPLC grade n-hexane.

3.6.5 Standard preparation

100 µg/ml stock solution of organochlorine pesticide mixed standard (EPA CLP organochlorine pesticide mix S.S., 1×1, Tol: Hex (50-50), 2000µg/ml) was prepared in n-hexane and stored in dark flasks at -20 °C in the refrigerator until use. 2.5 µg/ml, five µg/ml, ten µg/ml, twenty µg/ml, and fifty µg/ml working standard solutions were prepared in n-hexane from the stock solution for instrument calibration daily (Kelle *et al*., 2022).

3.6.6 Instrumentation methods

Scion 456-GC Gas chromatography equipped with 8400 autosamplers and M.S. detector (Made by Scion Instruments premium, Netherlands), Rotary Evaporator manufactured by Bibby Sterilin Ltd U.K. and of model RE 300 Stone Staffordshire (Serial No. R000101238), Soxhlet extractor apparatus fixed on heating mantles of model WHM12293 manufactured by Daihan Scientific Co. Ltd Wisd 23 from Korea and Analytical balance of model Citizen Scale C.Y. 204-Serial No. 252157/09 manufactured by Citizen Scale CY 204 in Poland were used in this study.

The certified organochlorine pesticides reference standards were obtained from recommended suppliers stated above and then used in the analysis. Working reference standard solutions were prepared, and each standard solution of 1.0 µL was injected into the Scion 456-GC equipped with an M.S. detector under the following conditions: Scion-5MS High-performance G.C. capillary column or high-resolution Gas chromatography Scion-5MS column of length 30m and 0.25 mm internal diameter (narrow bore) having a temperature range of -60^0 C to 325^0 C and 0.25µm film: sample size: 1.0 µL split ratio 1:20; detector: M.S. Detector at 300^0 C; column temperature was set at 150^0 C held for 1 minute then programmed to 200^0 C at 4^0 C/min and finally to 300^0 C at 4.5^0 C/min; helium flow pressure inlet was set at 20 Psi (138Kpa) minimum 150 Psi (1035Kpa) maximum, and injector temperature was held at 250^0 C. The mass spectra with a known standard with NIST 17 software library installed in GC-MS were used to compare and identify the constituents of the mixed organochlorine pesticides in the reference standard (NIST, 2017).

Data processing was done using MS Work Station 8.2 software and NIST 17 MS library installed in Scion 456 GC-MS (Bramston-cook, 2020; NIST, 2017; Nthusi, 2017; Abongo, 2009; APHA, 2002; APHA, 1998). The peak region for quantification and the individual pesticide retention time were noted and documented. The procedure was repeated for the mixed standard solutions, and the GC-MS was calibrated using the peak regions and acquired retention times. The calibration curves were created using stock solutions with mixed standards for organochlorine pesticides. To guarantee the correctness of the results, the sample eluates were then examined in triplicate using a GC-MS outfitted with 8400 auto samplers.

3.6.7 Instrument calibration and verification of analytical methods

The calibration curve for each analyte under study was constructed to quantify organochlorine pesticides in the water and sediment samples. The calibration curve plotted for the organochlorine pesticides gave straight lines with correlation coefficient (r^2) values of OCPs above 0.995 which shows a high correlation between instrument response and analyte response which were within the acceptable range of $r^2 \geq 0.990$ (appendices 1-19).

The calibration curves' intercepts were very close to zero, indicating that the lines passed close to the origin and that there was minimal matrix interference during the analysis (appendix 1) (Yahaya *et al*., 2017). The regression for the calibration curves were then computed. The points were on straight lines, and correlation coefficient for the calibration were near 0.999 (appendix 1). Organochlorine pesticide standard solutions were created, their concentrations were determined, and the results were compared to the values of the pesticide concentration specified for the standards.

The results of organochlorine pesticides mixed standard shown linearity within the quantities employed (Yahaya *et al*., 2017; Koigi, 2015). The co-efficiency of variances of the certified reference standard determined varied between 0.143 to 0.418%, indicating high reproducibility for each organochlorine pesticide (Appendix 2). The average recoveries obtained with the standards were within the acceptable limits of 70% to 120% (Appendix 2). This demonstrates the study's analytical method had high accuracy and precision. The limit of detection (LOD) of GC-MS was 0.02 µg/ml, which showed that most pesticide residues in the water and sediments could be detected.

3.6.8 Calculation formulas used for quantifications in this research study

This study used the following formulae to calculate the concentration of the organochlorine pesticides detected by GC-MS. EPA CLP organochlorine pesticide mix SS, 1×1, Tol: Hex (50-50), 2000µg/ml (standard) were used for calibration.

External standard calibration procedure,

The amount of material injected from the peak response was calculated using the calibration factor.

$$\text{Calibration factor (CF)} = \frac{\text{Peak Area (or Height) of the compound in the standard}}{\text{Mass of the compound injected (in nanogram, ng)}}$$

The concentration in the sample was calculated using the following equation in case there was no dilution.

$$\text{Concentration } (\mu g/L) = \frac{(A)\,(V_t)}{(V_i)\,(V_s)}$$

Where;

A = Amount of material injected (ng).

V_i = Volume of extract injected (µL).

V_t = Volume of total extract (µL).

V_s = Volume of water extracted (mL).

Formulas used for quantifications of OCPs in this research study

For the water sample, in case where there was dilution, equation **(i)** below was used for the calculation of the concentrations of organochlorine pesticides, while equation **(ii)** was employed to determine the organochlorine pesticide amounts in sediment samples. The samples used in this study's analysis of organochlorine pesticides were not diluted. Hence D in the formulas (i) and (ii) below was set to 1. By choosing a suitable baseline from which the peak area or height was calculated and used for quantitation, the quantity of each component peak in the sample chromatogram that corresponded to the compounds used for calibration was established (Lisouza *et al*., 2019; Epa & Office, 2016; US EPA, 2007).

For Water Samples, the following equation was used**;**

$$\text{Concentration } (\mu g/L) = \frac{(A_x)\ (V_t)\ (D)}{(\underline{CF})(V_i)\ (V_s)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ \text{(i)}$$

Where;

$\mathbf{A_x}$ = Area (or height) of the peak for the analyte in the sample.

$\mathbf{V_t}$ = Total volume of the concentrated extract (µL).

D = Dilution factor if the sample or extract was diluted before analysis.

If no dilution was made, D = 1. The dilution factor is always dimensionless.

$\mathbf{\underline{CF}}$ = Mean calibration factor from the initial calibration (area/ng).

$\mathbf{V_i}$ = Volume of the extract injected (µL). The injection volume for samples and calibration standards were the same.

$\mathbf{V_s}$ = Volume of the aqueous sample extracted was in mL.

The units used in the above formula resulted in a concentration unit of ng/mL, which is equivalent to µg/L (Lisouza *et al*., 2019; Epa & Office, 2016; US EPA, 2007)

For non-aqueous samples (Sediment samples), the following equation was used:

$$\text{Concentration } (\mu g/kg) = \frac{(A_x)\ (V_t)\ (D)}{(CF)(V_i)\ (W_s)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ \text{(ii)}$$

Where A_x, V_t, D, CF, and V_i were the same as for aqueous samples, and

W_s = Weight of sample extracted (g). The wet weight was used in our investigation.

The extracts were to be diluted and reanalyzed in situations where the responses were outside the calibration range of the instrument. When overlapping peaks resulted in integration issues, peak height measurements were advised to be used over peak area integration. US EPA, 2007; Lisouza *et al*., 2019; Yahaya *et al*., 2017; Epa & Office, 2016).

3.6.9 Method Validation

The method validation in this study was done by measuring or weighing 10g of the sediment samples and 10 ml of water samples and then dividing the 10g or 10 ml into two equal portions. One portion was spiked with five µg/ml of organochlorine mixed pesticide reference standard, then thoroughly mixed, and the other portion was left un-spiked. The spiked and un-spiked samples were subjected to the same clean-up and extraction methods, and GC-MS analysis of concentrated extracts (eluates) was done as described earlier. The analytical parameters validated in this investigation included linearity, range, precision, accuracy, sensitivity, and detection and quantification limits. For each organochlorine pesticide under study, analytical curve plots were used to evaluate the limits of detection and quantification, linearity, sensitivity, and range. The limits of detection (LOD) and quantification (LOQ) were determined using the Paul *et al.* (2022) method, and equations 1 and 2 of the Kelle *et al*., (2022) method, which had few differences from the approach used, were then used to corroborate the results.

LOD = 3.3 x $Sy\ /b$ ……………………………………………….……. Equations (1)

Where Sy is the residual standard deviation of the analytical curve, and b is the slope of the analytical curve.

LOQ = 3 x LOD………………………………………………………. Equations (2)

This study evaluated the method's selectivity by separating the analytes. In contrast, the method's accuracy was determined as the average of three replicates, and the method's precision by recovery study. The % recovery was calculated from Equation 3.

$$\% \text{ Recovery} = \frac{X_1 - X_2}{Y} \text{ ………………………………………………... Equations (3)}$$

Where X_1 is the concentration of the spiked sample, X_2 is the concentration of the un-spiked sample, and Y is the concentration of the organochlorine pesticide mixed reference standard added to the spiked sample (Kelle *et al*., 2022).

3.6.10 GC-MS analysis procedure

Using Scion 456-GC gas chromatography outfitted with an 8400 autosampler and MS detector, organochlorine pesticide residue was examined in initially generated water samples and soil sediment extracts. The injector and detector were kept at 250 ^{0}C and 300 ^{0}C. As a carrier gas, helium was employed at a constant flow rate of 2 ml/min. Samples were injected using a pulsed splitless injection mode with a 1µL injection volume. The injection temperature programs used were as follows: 90°C (3 min), 90°C to 200°C (at 30°C/min and hold 15 min), and 200°C to 275°C at 30°C/min and hold time of 5 min (APHA, 1998; Nthusi, 2017; Abongo, 2009).

Scion-5MS High-performance GC capillary column or high-resolution gas chromatography Scion-5MS column of length 30m and 0.25 mm internal diameter (narrow bore) having a temperature range of -60^0 C to 325^0 C and 0.25µm film was used for organochlorine pesticide residues analysis. The mass spectra with a known standard with NIST 17 upgrade MS software library installed in GC-MS were used to compare spectra of the analytes. They identified Constituents of the mixed organochlorine pesticide reference standard (NIST, 2017).

Data were processed using Scion MS Workstation 8.2 software and NIST 17 MS library installed in Scion 456 GC-MS. (Bramston-cook, 2020; NIST, 2017). The concentrations were calculated by exactly weighing all stock solution additions and isooctane. Internal standards calibration using authentic reference standards was used to normalize peak areas of the analytes in the sample extracts (Nthusi, 2017; Abongo, 2009; APHA, 1998). Recovery was carried out by spiking some samples with pesticide standards and extracted as described in 3.6.9 and 3.6.10 above.

Test injections and concentration or dilution factors were determined (Ndunda *et al*., 2018; Nthusi, 2017; Abongo, 2009; APHA, 1998). The chosen standards were then added to the sample extract, and the top layer was quantitatively transferred into the sample vials. Isooctane was injected once into the GC-MS with the normal temperature program for organochlorine pesticide analysis (Nyaundi *et al*., 2021; Nyaundi *et al*., 2020; Alex *et al*., 2019; Abong'o *et al*., 2018; Fang *et al*., 2017; Abongo, 2009) .

3.6.11 Data processing of Chromatograms using installed GC-MS software

Data processing of the chromatograms (Figure 3 and Table 4-5) were done using Scion MS Workstation 8.2 software and NIST 17 upgrade MS library installed in Scion 456 GC-MS (Bramston-cook, 2020; NIST, 2017). Scion MS Workstation 8.2 software created a response factor for each analyte component from the calibration curves of standards. The instrument's software was used to quantify analytes in the sample extract, and analytes were recognized by comparing their retention durations to their standards.

The difficult process of extracting data from GC/MS data files was automated using the NIST 17 update Automated Mass Spectral Deconvolution and Identification System (AMDIS) (NIST, 2017). AMDIS found all the ions that rise and fall simultaneously and assigned them to a single component. It compares the component it found to a collection of spectra and retention indices to recognize and quantify the analytes. When selected ions were recognized in the Selected Ions Monitoring (SIM) mode, qualifier ions were set up with ion ratios to the base peak to check and confirm the identity of a substance. The final report included an "ID" for a match. Selected Ions Monitoring (SIM) data from diverse ions were obtained to provide positive matching to the reference spectrum using a variety of distinctions for substances.

MS Workstation calculates the peak's retention time by computing the zero crossovers of the peak's first derivative. Linear interpolating points determined the precise time before and after the zero crossing when values did not match a data point that was acquired. The start and end points for peak integration are always included in the chromatogram tracing and interconversion of the detector response and concentration per calibration curve. The calculator in the software is used to estimate the peak size or area for a specific peak or region (Bramston-Cook, 2020; NIST, 2017).

3.7 Data Analysis

Statistical Programs for Social Scientists (SPSS), version 23.0 (IBM-SPSS Inc., Chicago, IL, USA), was used to evaluate the data gathered. To establish a significant association in group means between pesticide levels in the water and soil sediment during both seasons, a t-test was performed to compare pesticide levels in water and soil sediment between seasons. The Shapiro-Wilk test was employed to check the normality of the data. The link between organochlorine pesticide residues in water and sediment and particular soil physicochemical properties was investigated using Pearson correlation analysis. Principal component analysis (PCA) was used to analyze the correlate matrix for organochlorine pesticide concentrations in the water and sediments using Varimax rotation and Kaiser Normalization to determine the distribution pattern of pesticides. Extracts for the principal components were created from eigenvalues greater than one by Varimax rotation.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter presents the study results of the concentrations of selected organochlorine pesticides and physicochemical parameters in water and sediments from river Kibos-Nyamasaria. The first section deals with the presentation of the concentration of the organochlorine pesticide, followed by the results presentation of physicochemical parameters of the water and sediments. The last section deals with the relationships between the physicochemical characteristics and the pesticide residual levels and that of the levels in the water and the sediments. The results are presented in tables, and graphs. The figures are statistically analyzed and then discussed.

4.2 Mean percentage recoveries

Appendix 2 displays the typical results of % recoveries, limit of detection (LOD), and limit of Quantification (LOQ) for water and sediment samples. Because the average recoveries obtained were within the acceptable limits of 70 to 120%, the data from the percentage recoveries were not corrected for use. This demonstrates the study's analytical methods' have high accuracy and precision, as recommended (Ogola *et al*., 2023; Paul *et al*., 2022; Abong'o *et al*., 2018; Osoro *et al*., 2016; Abong'o *et al*., 2015; Hellar- Kihampa, 2011; European Commission, 2000; EPA, 2007). Paul *et al*. (2022) calculation method of LOD and LOQ was adopted in this study and confirmed by Kelle *et al*. (2022) method, in which there was not much difference.

In this study, the lower limit of detection (LOD) was determined by three water and sediment samples from the control site, fortified at a lower concentration of 0.02 μg/ml of the mixture of the standard of OCPs, then analyzed in triplicate. LOD was calculated as 3.29 times the standard deviation, while the limit of Quantification (LOQ) was calculated as ten times the standard deviation (Paul *et al*., 2022).

4.3 Identification of the Organochlorine Pesticides residues in the water and sediment samples

The organochlorine pesticide residues in the water and sediment samples were identified by running a mixture of standards of pesticides and the water and sediments using GC-MS and comparing the spectra obtained to identify the organochlorine pesticide residues in the samples. The results are presented in Figures 4.1 and appendices 3 – 6.

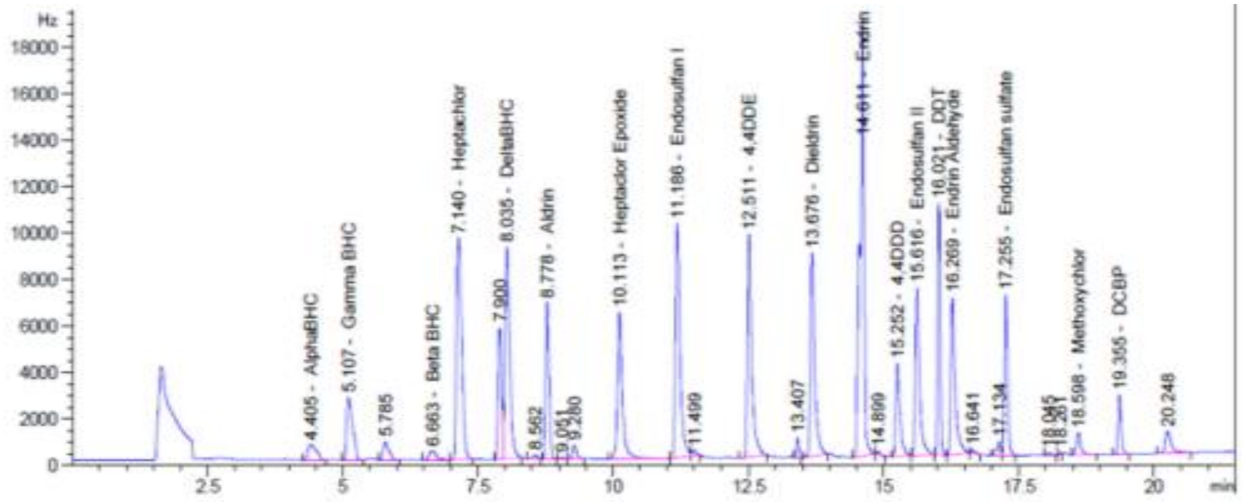


Figure 4.1: Chromatogram of Organochlorine Pesticides mix standards

The spectra show that there were 19 pesticide residues in the water samples (Appendix 3-6) and were identified as Aldrin, dieldrin, endosulfan sulphate, α–endosulfan, methoxychlor, α-HCH, β – endosulfan, Endrin, Heptachlor, Heptachlor- epoxide, Lindane, β-HCH, δ –HCH, o, p'- DDT, p, p’ – DDT, o, p'- DDD, p, p'- DDD, o, p' – DDE and p, p'- DDE. The organochlorine pesticide residues (OCPs) in the sediments samples (Appendix 24) detected were dieldrin, endosulfan sulphate, α–endosulfan, α-HCH, β – endosulfan, Endrin, Heptachlor, Heptachlor –epoxide, Lindane, β-HCH, o, p’- DDT, p, p’ – DDT, o, p'- DDD, p, p'- DDD, o, p' – DDE and p, p'- DDE. Data processing of the chromatograms (Figure 4.1 and appendices 3 - 6) were done using Scion MS Workstation 8.2 software and NIST 17 upgrade MS library installed in Scion 456 GC-MS (Bramston-cook, 2020; NIST, 2017).

4.4 Quantification of organochlorine pesticides in water and sediment samples

The standard calibration curves were used to quantify the concentration of organochlorine pesticide in water and sediment samples. Chromatograms for the identified organochlorine pesticides in samples were obtained for the individual analytes, and the peak areas obtained were used for quantifications.

4.4.1 Quantification of organochlorine pesticides in water samples

The concentration of organochlorine pesticide residues in the water samples was determined, and the results are presented in Table 4.1.

Table 4.1: Seasonal variations of Organochlorine Pesticide residues in River water during the wet and dry seasons at various sampling points

	Water Samples																			
	Wet season - Concentration in (µg/L)										**Dry season - Concentration in (µg/L)**									
OCPs (µg/L)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
Aldrin	8.33±0.58^{a}	3.37±0.06^{f}	5.17±0.07^{de}	4.87±0.06^{e}	5.27±0.06^{de}	5.40±0.04^{cde}	5.73±.06^{cd}	5.87±0.05^{c}	6.67±0.06^{b}	7.20±0.03^{b}	bdl	bdl	bdl	bdl	bdl	Bdl	bdl	bdl	bdl	bdl
Dieldrin	0.00±0.04^{c}	4.67±0.58^{b}	0.16±0.04^{c}	8.67±0.58^{a}	0.10±0.03^{c}	0.11±0.04^{c}	0.11±0.02^{c}	0.12±0.03^{c}	0.13±0.04^{c}	0.21±0.03^{c}	0.00±0.03^{a}	0.00±0.02^{a}	0.10±0.04^{a}	5.46±4.66^{a}	6.03±5.14^{a}	0.11±0.02^{a}	0.10±0.03^{a}	0.12±0.04^{a}	0.13±0.02^{a}	0.12±0.01^{a}
Endosulfan Sulphate	0.00±0.01^{j}	0.02±0.03^{i}	0.03±0.02^{h}	0.09±0.04^{g}	0.11±0.03^{f}	0.17±0.01^{c}	0.16±0.02^{e}	0.16±0.04^{d}	0.17±0.01^{b}	0.23±0.03^{a}	0.00±0.01^{i}	0.01±0.03^{h}	0.02±0.02^{g}	0.04±0.01^{f}	0.04±0.02^{f}	0.04±0.01^{e}	0.05±0.01^{d}	0.06±0.02^{c}	0.06±0.04^{b}	0.06±0.03^{a}
α – endosulfan	0.00±0.00^{j}	0.02±0.01^{h}	0.02±0.02^{i}	0.03±0.01^{g}	0.04±0.03^{f}	0.07±0.02^{e}	0.08±0.01^{d}	0.08±0.04^{c}	0.09±0.10^{b}	0.19±0.09^{a}	0.00±0.01^{e}	0.02±0.03^{d}	0.00±0.00^{e}	0.00±0.00^{e}	0.00±0.01^{e}	0.02±0.03^{d}	0.03±0.02^{c}	0.07±0.10^{b}	0.07±0.01^{b}	0.09±0.10^{a}
β – endosulfan	0.01±0.02^{j}	0.01±0.03^{h}	0.01±0.01^{i}	0.02±0.02^{g}	0.01±0.01^{f}	0.05±0.01^{e}	0.04±0.05^{d}	0.06±0.10^{c}	0.07±0.08^{b}	0.15±0.06^{a}	0.01±0.03^{e}	0.01±0.05^{d}	0.00±0.00^{e}	0.01±0.02^{e}	0.00±0.00^{e}	0.02±0.01^{d}	0.04±0.02^{c}	0.06±0.08^{b}	0.08±0.03^{b}	0.09±0.13^{a}
Endrin	0.01±0.01^{j}	0.02±0.03^{i}	0.03±0.10^{h}	0.04±0.02^{f}	0.04±0.01^{g}	0.05±0.03^{e}	0.06±0.11^{d}	0.07±0.02^{c}	0.09±0.03^{b}	0.10±0.01^{a}	0.00±0.02^{f}	0.02±0.01^{e}	0.03±0.03^{d}	0.03±0.10^{d}	0.02±0.02^{e}	0.09±0.10^{ab}	0.06±0.01^{c}	0.09±0.02^{ab}	0.09±0.01^{b}	0.09±0.10^{a}
Heptachlor	0.01±0.01^{g}	0.01±0.01^{g}	0.02±0.10^{f}	0.02±0.03^{e}	0.04±0.10^{d}	0.04±0.01^{c}	0.04±0.02^{c}	0.04±0.01^{c}	0.05±0.03^{b}	0.05±0.10^{a}	0.01±0.02^{i}	0.01±0.01^{i}	0.01±0.10^{h}	0.01±0.03^{g}	0.02±0.10^{f}	0.02±0.01^{e}	0.03±0.02^{d}	0.04±0.11c	0.04±0.03^{b}	0.04±0.02^{a}
Heptachlor – epoxide	0.00±0.01^{j}	0.02±0.01^{i}	0.02±0.10^{h}	0.06±0.02^{g}	0.06±0.01^{f}	0.07±0.10^{e}	0.07±0.01^{d}	0.08±0.01^{c}	0.08±0.10^{b}	0.09±0.02^{a}	0.00±0.01^{i}	0.01±0.01^{fg}	0.01±0.10^{ef}	0.02±0.02^{de}	0.02±0.10^{cd}	0.01±0.01^{fg}	0.01±0.01^{g}	0.02±0.10^{c}	0.02±0.02^{b}	0.03±0.01^{a}
Methoxychlor	0.03±0.10^{c}	3.23±0.06^{ab}	4.57±0.03^{a}	0.11±0.01^{c}	0.12±0.01^{c}	0.13±0.10^{c}	0.14±0.02^{c}	0.14±0.01^{c}	0.15±0.03^{c}	2.41±1.80^{b}	1.41±1.20^{a}	0.75±1.26^{a}	2.57±0.06^{a}	1.91±1.63^{a}	0.85±1.43^{a}	1.81±1.55^{a}	1.09±1.83^{a}	1.29±2.17^{a}	3.23±0.06^{a}	3.43±0.06^{a}

Table 4.1: Seasonal variations of OCPs in River water during the wet and dry seasons at various sampling points, continues'

OCPs (µg/L)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
Lindane	0.01±0.02^{i}	0.03±0.01^{h}	0.05±0.11^{e}	0.04±0.03^{g}	0.04±0.02^{f}	0.04±0.12^{g}	0.06±0.01^{d}	0.06±0.03^{c}	0.07±0.10^{b}	0.08±0.02^{a}	0.00±0.01^{i}	0.02±0.12^{h}	0.05±0.10^{d}	0.03±0.03^{g}	0.04±0.01^{f}	0.04±0.11^{e}	0.05±0.02^{c}	0.06±0.10^{b}	0.06±0.02^{b}	0.07±0.01^{a}
α-HCH	0.00±0.01^{b}	0.00±0.01^{b}	0.74±0.63^{ab}	2.17±0.06^{ab}	0.88±1.49^{ab}	0.95±1.60^{ab}	2.87±0.06^{ab}	0.88±1.49^{ab}	3.47±0.06^{a}	1.29±2.17^{ab}	0.00±0.00^{c}	0.00±0.00^{c}	0.00±0.00^{c}	0.00±0.00^{c}	0.00±0.00^{c}	5.33±0.58^{ab}	3.33±0.56^{bc}	5.67±0.58^{ab}	5.43±4.63^{ab}	8.27±0.06^{a}
β-HCH	0.00±0.00^{i}	0.00±0.00^{i}	0.02±0.02^{h}	0.08±0.01^{g}	0.08±0.02^{f}	0.09±0.10^{e}	0.09±0.03^{d}	0.09±0.04^{c}	0.10±0.01^{b}	0.10±0.01^{a}	0.00±0.00^{g}	0.00±0.00^{fg}	0.00±0.00^{de}	0.00±0.00^{ef}	0.00±0.00^{fg}	0.00±0.00^{d}	0.00±0.00^{d}	0.01±0.03^{c}	0.01±0.01^{b}	0.01±0.02^{a}
δ – HCH	0.00±0.00^{g}	0.00±0.00^{g}	0.00±0.00^{g}	0.00±0.00^{f}	0.01±0.01^{ef}	0.01±0.10^{de}	0.01± 0.02^{d}	0.02±0.01^{c}	0.02±0.03^{b}	0.02±0.01^{a}	0.00±0.00^{f}	0.00±0.00^{ef}	0.00±0.00^{f}	0.00±0.00^{ef}	0.00±0.00^{ef}	0.00±0.00^{de}	0.00±0.00^{d}	0.02±0.01^{c}	0.02±0.02^{b}	0.02±0.01^{a}
o, p'- DDT	0.00±0.00^{g}	0.00±0.00^{g}	0.00±0.00^{f}	0.00±0.00^{e}	0.01±0.02^{de}	0.01±0.03^{d}	0.01±0.02^{c}	0.02±0.01^{b}	0.02±0.01^{a}	0.02±0.02^{a}	0.00±0.00^{ef}	0.00±0.00^{f}	0.00±0.00^{d}	0.00±0.00^{c}	0.00±0.00^{de}	0.00±0.00^{c}	0.00±0.00^{d}	0.02±0.01^{b}	0.02±0.01^{b}	0.02±0.03^{a}
p, p – DDT	0.00±0.00^{i}	0.04±0.03^{e}	0.02±0.01^{h}	0.02±0.02^{g}	0.03±0.01^{f}	0.04±0.01^{e}	0.05±0.01^{d}	0.06±0.10^{c}	0.07±0.02^{b}	0.07±0.01^{a}	0.00±0.00^{f}	0.03±0.01^{a}	0.00±0.00^{ef}	0.00±0.00^{ef}	0.00±0.00^{e}	0.00±0.00^{ef}	0.00±0.00^{ef}	0.01±0.01^{d}	0.02±0.01^{c}	0.02±0.03^{b}
o, p'- DDD	0.00±0.00^{g}	0.00±0.00^{h}	0.01±0.01^{f}	0.01±0.01^{e}	0.01±0.02^{d}	0.01±0.01^{c}	0.02±0.01^{b}	0.02±0.03^{c}	0.02±0.01^{b}	0.03±0.02^{a}	0.00±0.00^{d}	0.00±0.00^{d}	0.00±0.00^{d}	0.00±0.00^{d}	0.00±0.00^{d}	0.00±0.00^{d}	0.00±0.00^{d}	0.01±0.01^{c}	0.01±0.01^{b}	0.02±0.01^{a}
p .p'- DDD	0.00±0.00^{h}	0.00±0.00^{h}	0.03±0.01^{g}	0.04±0.03^{f}	0.05±0.01^{e}	0.06±0.02^{c}	0.06±0.01^{d}	0.06±0.01^{c}	0.08±0.03^{b}	0.09±0.02^{a}	0.00±0.00^{h}	0.00±0.00^{h}	0.02±0.01^{cd}	0.03±0.02^{c}	0.02±0.01^{d}	0.03±0.01^{a}	0.03±0.02^{b}	0.01±0.01^{g}	0.01±0.01^{f}	0.02±0.01^{e}
o, p' – DDE	0.00±0.00^{h}	0.03±0.02^{f}	0.02±0.01^{g}	0.03±0.01^{f}	0.04±0.02^{e}	0.04±0.03^{e}	0.05±0.01^{d}	0.05±0.02^{c}	0.06±0.02^{b}	0.06±0.01^{a}	0.00±0.00^{g}	0.00±0.00^{g}	0.01±0.01^{f}	0.01±0.01^{e}	0.01±0.02^{d}	0.02±0.01^{c}	0.02±0.01^{c}	0.02±0.02^{c}	0.02±0.01^{b}	0.03±0.02^{a}
p, p'- DDE	0.00±0.00^{f}	0.00±0.00^{f}	0.00±0.00^{f}	0.01±0.00^{e}	0.01±0.00^{d}	0.01±0.00^{d}	0.02±0.00^{c}	0.02±0.00^{c}	0.02±0.01^{b}	0.02±0.01^{a}	0.00±0.00^{f}	0.00±0.00^{ef}	0.00±0.00^{f}	0.00±0.00^{ef}	0.00±0.00^{e}	0.02±0.01^{c}	0.02±0.01^{d}	0.02±0.02^{bc}	0.02±0.01^{b}	0.02±0.02^{a}

Means within a row followed by different letters (a, b, c, d, e, f, g) are significantly different ($p < 0.05$) with respect to the sampling site and OCPs. **S=**Sampling Site; **bdl**=below detectable limit, results are in **µg/L** and S1- S10 are sampling points.

Graphical presentation of total mean concentration of OCPs in water samples (wet and dry season)

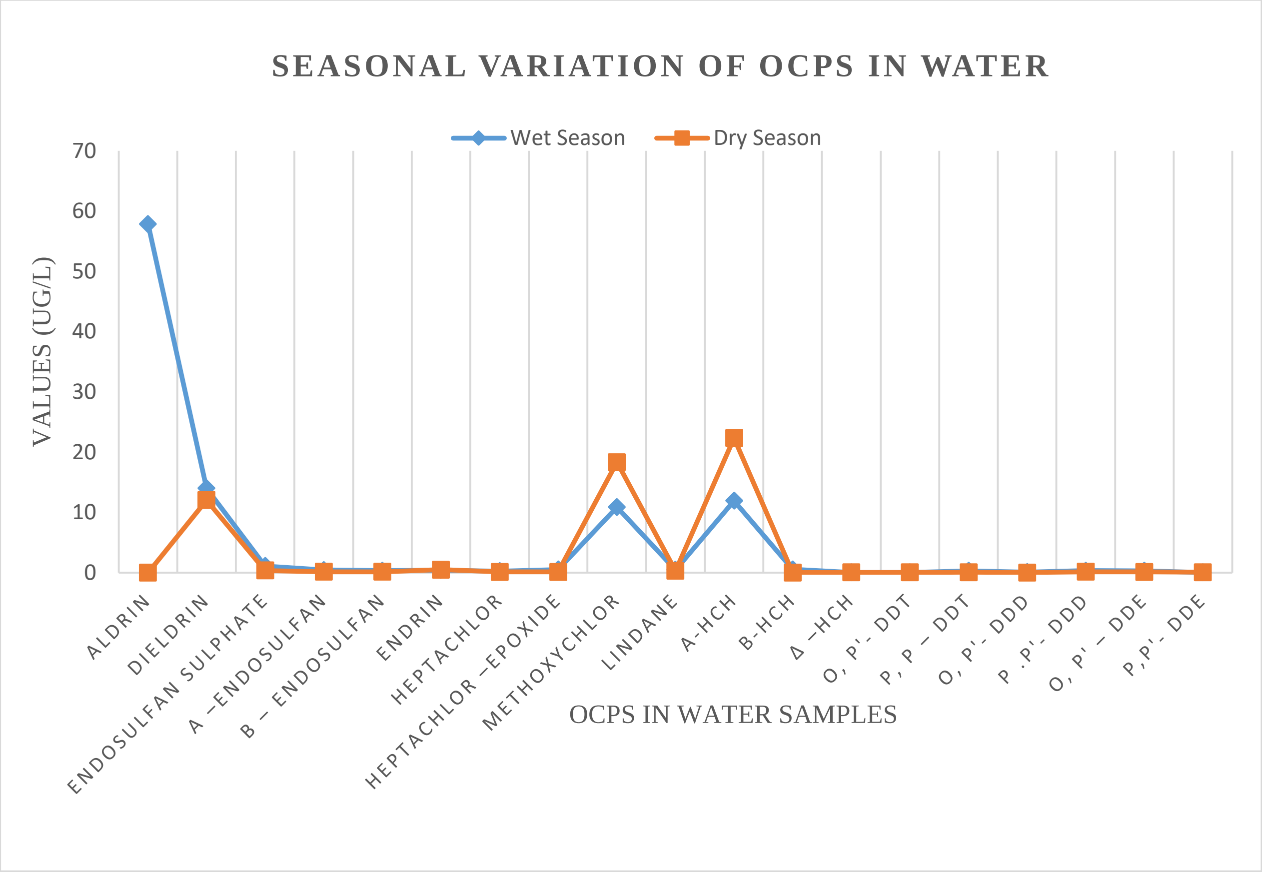


Figure 4.2: Graph showing comparison of total mean concentration of OCPs in Water (Wet and Dry Seasons)

The graph shows comparison of organochlorine pesticides between wet and dry season and illustrate that the total mean concentration of organochlorine pesticides in the water was higher during the wet or rainy season than during the dry season.

The distribution of the concentration of the pesticide in the water was presented by a violin plot (Figure 4.3)

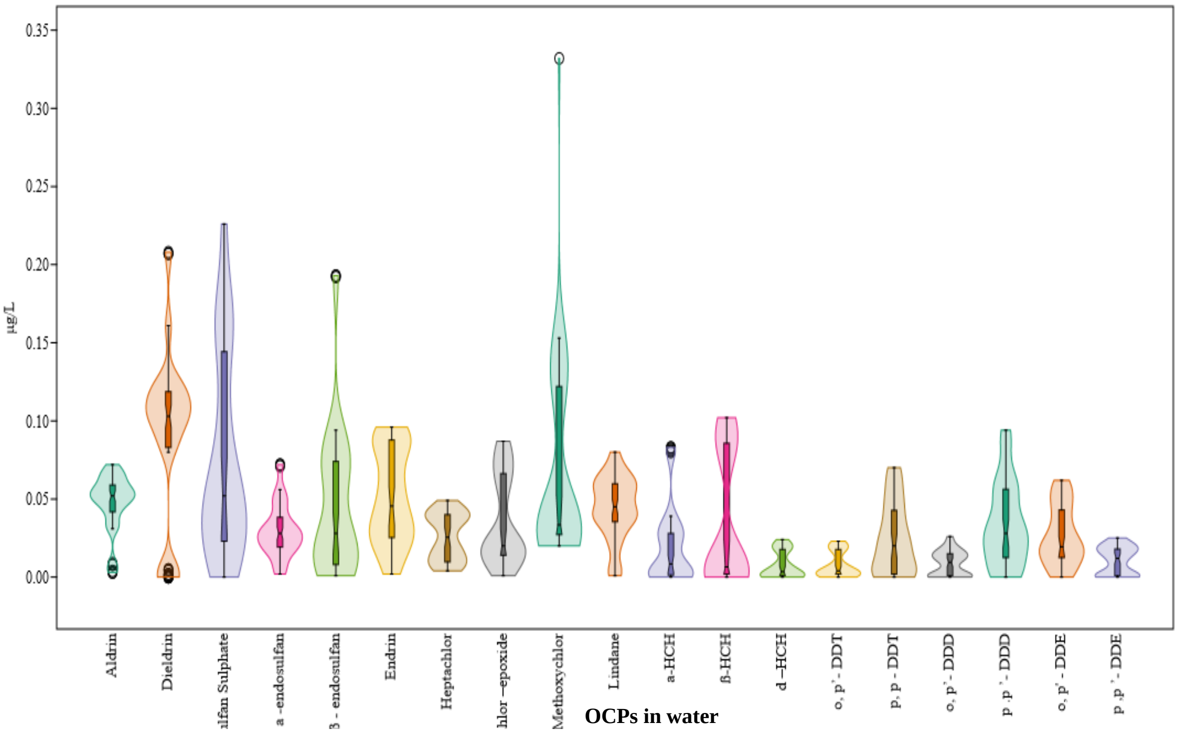


Figure 4.3: Box-and-whisker plot of mean organochlorine pesticides in water samples (Both seasons combined) results are in µg/L.

The Centerline for each plot represents the median, boxes indicate the first and third quartiles, and whiskers are set at 1.5× the interquartile range. Open circles represent outliers outside the range of the whiskers. A violin plot is superimposed on each box, depicting the data's distribution.

The results of 19 organochlorine pesticides (OCP) residues in water at different sampling points (S1-S10) (Table 4.1) on a seasonal basis and the average concentrations are presented in Table 4.1. High concentrations of Aldrin pesticide (8.33±0.58 µg/L) were observed for samples taken during the wet season relative to those for the dry season at sampling station 1

(S1). This sampling site (S1) is almost at the convergent of River Kibos & River Awach near a Guba Bridge and closer to large sugarcane farms and the agricultural research center (Table 4.1). The concentrations of aldrin in water during the wet season were higher in all sampling points and mostly significant at ($P<0.05$).

Aldrin, dieldrin, endosulfan sulphate, α–endosulfan, methoxychlor, and α-HCH were the only pesticides detected at concentrations over 0.1 µg/L in the water during the wet season. Dieldrin concentration was significantly higher ($P<0.05$) at the Olad Ouko bridge (8.67±0.58 µg/L) than all the other sampling points. This might be because of human activities or small agricultural farms nearby in which the farmers might be using this type of pesticides or dumping the used containers into the river illegally. Endosulfan sulfate was significantly higher at the entry point to Lake Victoria (S10) than at any other sampling point (Table 4.1). During the dry season, dieldrin concentrations at Nyamasaria bridge (S5) were 6.03±5.14 µg/L, while methoxychlor and α-HCH were recorded at 3.43±0.06 µg/L and 8.27±0.06 µg/L respectively at the entry point to Lake Victoria (S10) (Table 4.1). Generally, the mean aldrin pesticide residual levels were higher than all the other organochlorine pesticides detected in water (Table 4.1), regardless of the sampling season.

The findings of this study also affirmed that, in water samples, Organochlorine pesticides were more prevalent during the wet season than the dry season. OCPs concentrations in water samples, increased downstream as the river flowed towards Lake Victoria, which is in agreement with the study conducted by (Ogola *et al.*, 2023; Nyaundi *et al.*, 2021; Nyaundi *et al.*, 2020; Alex *et al.,* 2019; Onchieku, 2019; Abong'o *et al*., 2018; Ndunda *et al*., 2018; Mahugija et al., 2018; Fang *et al*., 2017; Nthusi, 2017; Osoro *et al*., 2016; Fosu-Mensah *et al*.,2016; Abong'o *et al*., 2015; Abongo, 2009). From the results of table 4.1, most OCPs pesticides residues detected in water were above 0.03 µg/L NEMA and WHO maximum residues limits (MRLs). The results are similar to previous studies by Nthusi, 2017; Abong'o *et al*., 2015 and Abongo 2009 along the river Nyando, even though, most values of organochlorine pesticides in their study were higher than those found in this study.

The same trend and similarity of the results of the study observed in Rusinga Island of Lake Victoria, Kenya (Osoro *et al*., 2016), River Kuja catchment, Kenya (Onchieku, 2019), and Nyando River catchment of Lake Victoria, Kenya (Abong'o *et al*., 2018; Nthusi, 2017; Abong'o *et al*., 2015; Abongo, 2009), Lake Naivasha, Kenya (Njogu, 2011), Nairobi river (Ndunda *et al*.2018, Koigi, 2015**)** although result from their study were higher than those attained in this study. In summary, the average levels of OCPs pesticide residues showed an increase downstream, starting from the initial sampling point upstream towards the discharge into Lake Victoria.

4.4.2 Quantification of organochlorine pesticides in sediment samples.

The peak area was used to quantify the concentration of organochlorine pesticides in sediment samples, and the results are presented in Table **4.2**.

Table 4.2: Seasonal variations in OCPs residues in sediments during wet and dry seasons at various sampling points

	Sediments																			
	Wet season - Concentration in (µg/kg)										**Dry season - Concentration in (µg/kg)**									
OCPs (µg/kg)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
Aldrin	bdl	Bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	Bdl	bdl	bdl
Dieldrin	bdl	Bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.24±0.02^{e}	0.87±0.15^{f}	0.63±0.02^{g}	1.00±0.01^{f}	1.62±0.01^{d}	4.50±0.10^{c}	4.59±0.02^{c}	5.35±0.01^{b}	5.34±0.02^{b}	5.55±0.10^{a}
Endosulfan Sulphate	0.80±0.01^{d}	0.07±0.10^{e}	0.34±0.02^{e}	0.20±0.01^{e}	0.20±0.01^{e}	2.69±0.58 ^{ab}	2.14±0.01^{c}	3.06±0.10^{a}	2.21±0.02^{bc}	2.99±0.11^{a}	0.61±0.05^{e}	0.07±0.10^{h}	0.07±0.02^{h}	0.34±0.01^{f}	0.20±0.01^{g}	2.00±0.12^{d}	2.15±0.01^{c}	2.16±0.10^{c}	2.28±0.03^{b}	3.31±0.02^{a}
α – endosulfan	bdl	Bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.57±0.08^{e}	0.58±0.05^{e}	0.36±0.04^{f}	0.63±0.01^{d}	0.67±0.03^{d}	2.08±0.13^{c}	2.08±0.01^{c}	2.19±0.10^{b}	2.31±0.11^{a}	2.37±0.01^{a}
β – endosulfan	0.75±0.10^{c}	0.20±0.01^{d}	0.63±0.01^{c}	1.50±0.21^{a}	1.25±0.02^{b}	0.23±0.10^{d}	0.31±0.01^{d}	0.39±0.02^{d}	0.35±0.01^{d}	0.33±0.12^{d}	1.62±0.02^{a}	1.62±0.03^{a}	1.48±0.12^{b}	1.62±0.10^{a}	1.25±0.01^{c}	0.28±0.11^{e}	0.30±0.02^{e}	0.31±0.10^{e}	0.36±0.01^{e}	0.44±0.02^{d}
Endrin	0.47±0.46^{d}	0.80±0.10^{d}	1.00±0.01^{c}	0.63±0.03^{cd}	1.00±0.01^{c}	2.96±0.11^{b}	3.10±0.02^{ab}	3.44±0.12^{a}	3.32±0.01^{ab}	3.33±0.01^{ab}	1.62±0.01^{f}	0.80±0.11^{h}	0.80±0.01^{h}	0.63±0.02^{i}	1.00±0.01^{g}	3.01±0.10^{e}	3.11±0.02^{d}	3.26±0.12^{c}	3.33±0.01^{b}	3.36±0.03^{a}

Table 4.2: Seasonal variations in OCPs residues in sediments during wet and dry seasons at various sampling points, continues'

OCPs (μg/kg)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
Heptachlor	1.62±0.01^{a}	0.87±0.15^{b}	0.07±0.01^{c}	0.07±0.02^{c}	0.48±0.01^{bc}	0.89±0.03^{b}	0.31±0.01^{c}	0.94±0.58^{b}	0.45±0.03^{bc}	0.51±0.02^{bc}	0.41±0.19^{c}	1.25±0.11^{a}	0.20±0.03^{d}	0.07±0.02^{d}	0.61±0.05^{b}	0.41±0.10^{c}	0.42±0.01^{c}	0.51±0.13^{bc}	0.55±0.02^{bc}	0.57±0.01^{bc}
Heptachlor–epoxide	0.63±0.02^{g}	1.62±0.04^{d}	0.20±0.02^{i}	0.34±0.10^{h}	0.20±0.01^{i}	1.11±0.02^{g}	1.16±0.01^{f}	1.89±0.03^{b}	1.81±0.20^{a}	1.77±0.01^{c}	0.56±0.08^{fg}	0.64±0.08^{f}	0.80±0.06^{e}	0.48±0.04^{g}	0.20±0.07^{h}	1.01±0.01^{d}	1.18±0.02^{c}	1.81±0.10^{b}	1.91±0.03^{a}	1.92±0.01^{a}
Methoxychlor	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	Bdl	bdl	bdl
Lindane	0.48±0.03^{g}	0.41±0.13^{g}	1.62±0.01^{e}	1.00±0.02^{f}	0.48±0.01^{g}	2.60±0.03^{d}	2.79±0.01^{c}	2.99±0.11^{b}	3.10±0.02^{b}	3.32±0.01^{a}	0.90±0.10^{f}	0.34±0.04^{i}	1.25±0.02^{e}	0.80±0.01^{g}	0.48±0.03^{h}	2.61±0.01^{d}	2.78±0.02^{c}	3.00±0.10^{b}	3.33±0.01^{a}	3.40±0.01^{a}
α-HCH	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
β-HCH	0.09±0.10^{g}	0.61±0.09^{e}	0.48±0.03^{e}	0.34±0.01^{f}	0.84±0.05^{d}	0.33±0.13^{f}	2.05±0.01^{c}	2.02±0.11^{c}	2.54±0.02^{b}	3.66±0.02^{a}	0.13±0.20^{f}	0.90±0.10^{e}	0.07±0.03^{f}	0.20±0.02^{f}	0.80±0.01^{e}	2.00±0.14^{d}	2.06±0.01^{d}	2.21±0.11^{c}	2.55±0.02^{b}	3.81±0.03^{a}
δ –HCH	1.62±0.02^{b}	0.18±0.04^{c}	0.80±0.01^{c}	0.48±0.03^{c}	1.73±0.18^{ab}	2.00±0.01^{ab}	2.20±0.02^{ab}	1.79±0.41^{ab}	2.40±0.00^{a}	2.12±0.69^{ab}	0.24±0.04^{h}	0.18±0.04^{i}	0.46±0.04^{g}	0.48±0.01^{g}	1.25±0.03^{f}	2.00±0.02^{e}	2.23±0.05^{d}	2.32±0.13^{c}	2.41±0.06^{b}	2.52±0.02^{a}
o,p'-DDT	0.48±0.01^{e}	1.62±0.11^{ab}	0.20±0.01^{g}	0.20±0.10^{g}	0.34±0.03^{f}	1.01±0.02^{d}	1.68±0.01^{a}	1.37±0.12^{c}	1.55±0.01^{b}	1.53±0.03^{b}	1.00±0.01^{g}	1.62±0.12^{d}	0.34±0.02^{h}	0.07±0.01^{i}	0.34±0.03^{h}	1.05±0.01^{f}	1.66±0.02^{b}	1.45±0.02^{e}	1.65±0.01^{c}	1.82±0.12^{a}
p,p'–DDT	1.25±0.08^{e}	1.25±0.04^{e}	0.53±0.09^{f}	0.07±0.02^{g}	0.07±0.02^{g}	1.80±0.13^{d}	2.18±0.01^{bc}	2.11±0.21^{c}	2.27±0.02^{b}	2.95±0.01^{a}	0.24±0.04^{d}	1.25±0.01^{c}	0.20±0.02^{d}	0.20±0.01^{d}	0.07±0.01^{d}	2.00±0.10^{b}	2.20±0.03^{b}	2.23±0.11^{b}	2.30±0.02^{b}	3.03±0.58^{a}
o,p'-DDD.	0.29±0.08^{e}	0.09±0.04^{f}	1.62±0.02^{a}	1.17±0.14^{b}	0.63±0.01^{c}	0.30±0.03^{e}	0.37±0.01^{e}	0.40±0.05^{e}	0.49±0.03^{d}	0.55±0.02^{c}	0.90±0.10^{b}	0.31±0.11^{f}	1.36±0.09^{a}	1.25±0.08^{a}	0.50±0.04^{cde}	0.31±0.03^{f}	0.35±0.02^{ef}	0.41±0.08^{def}	0.56±0.06^{cd}	0.61±0.02^{c}

Table 4.2: Seasonal variations in OCPs residues in sediments during wet and dry seasons at various sampling points, continues’

OCPs (µg/kg)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
p,p' DDD	0.04±0.07^{f}	0.48±0.04^{e}	0.56±0.13^{e}	0.48±0.03^{e}	0.80±0.10^{d}	2.99±0.01^{c}	3.10±0.02^{c}	3.11±0.05^{c}	3.26±0.03^{a}	3.24±0.06^{b}	1.25±0.01^{e}	0.09±0.04^{i}	1.00±0.02^{f}	0.34±0.01^{h}	0.80±0.02^{g}	3.01±0.05^{d}	3.11±0.03^{c}	3.22±0.08^{b}	3.28±0.02^{a}	3.28±0.06^{a}
o,p'–DDE	0.15±0.08^{e}	0.87±0.15^{bc}	1.00±0.03^{b}	0.80±0.02^{c}	1.62±0.04^{a}	0.24±0.01^{de}	0.24±0.03^{de}	0.21±0.08^{de}	0.27±0.05^{de}	0.32±0.02^{d}	0.80±0.01^{c}	0.43±0.11^{d}	1.00±0.03^{b}	1.00±0.02^{b}	1.62±0.01^{a}	0.22±0.10^{f}	0.23±0.13^{f}	0.24±0.10^{ef}	0.27±0.05^{ef}	0.34±0.08^{de}
p,p' DDE	0.53±0.17^{e}	0.34±0.03^{h}	1.25±0.05^{ab}	1.21±0.36^{ab}	0.97±0.06^{d}	0.26±0.02^{i}	0.28±0.01^{i}	1.03±1.15^{c}	0.38±0.08^{g}	0.40±0.03^{f}	0.22±0.04^{g}	0.53±0.04^{d}	0.63±0.02^{c}	0.80±0.01^{b}	1.00±0.03^{a}	0.29±0.01^{f}	0.30±0.02^{f}	0.33±0.10^{f}	0.39±0.02^{e}	0.43±0.0^{e}

Means within a row followed by different letters (a, b, c, d, e, f, g) are significantly different ($p < 0.05$) with respect to the sampling site and OCPs. **S=**Sampling Site; **bdl**=below detectable limit, results are in **µg/kg** and S1- S10 are sampling points

Graphical presentation of total mean concentration of OCPs in sediment samples (wet and dry season)

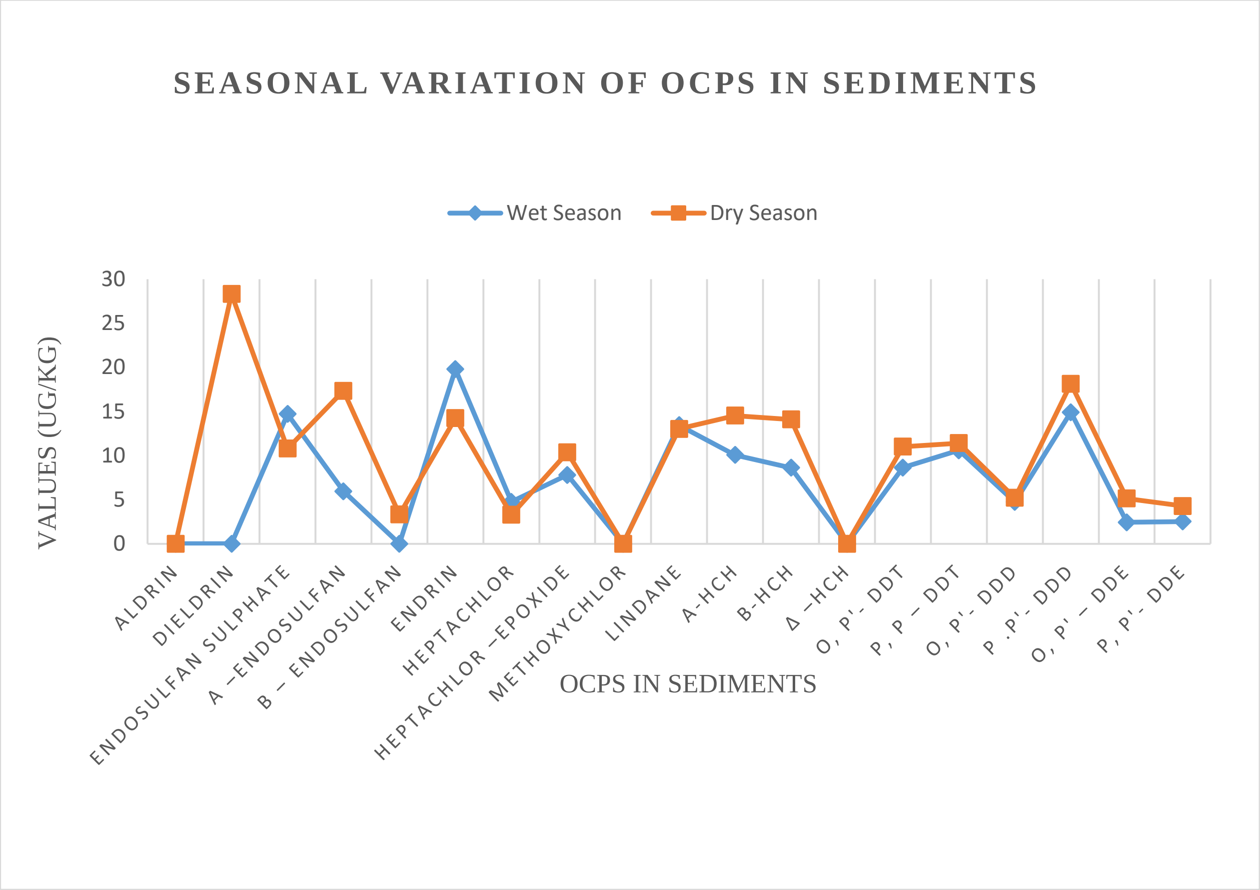


Figure 4.4: Graph showing comparison of total mean concentration of OCPs in Sediment (Wet and Dry Seasons)

The graph shows comparison of organochlorine pesticides between wet and dry season and prove or demonstrate that the total mean concentration of organochlorine pesticides in the sediment was higher during the dry season than during the wet season.

The distribution of the concentration of the pesticide in the sediment samples was presented by a violin plot (Figure 4.5)

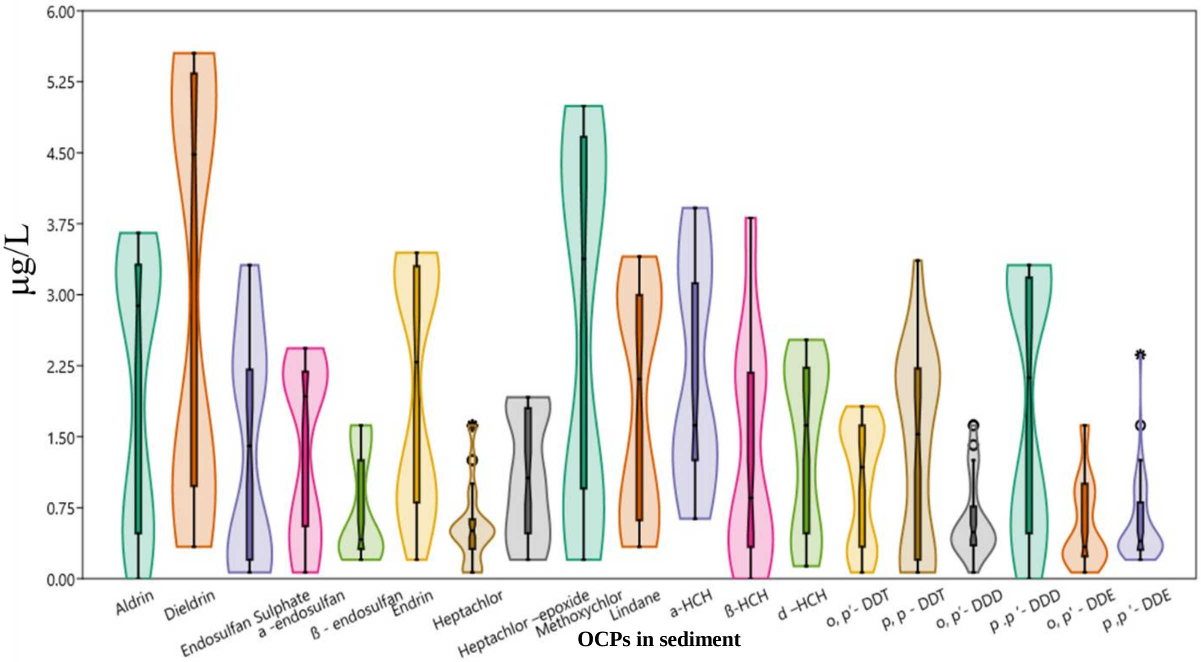


Figure 4.5: Box-and-whisker plot of mean organochlorine pesticides in sediment samples (Both seasons combined), results are in μg/kg.

The Centerline for each plot represents the median, boxes indicate the first and third quartiles, and whiskers are set at 1.5× the interquartile range. Open circles represent outliers outside the range of the whiskers. A violin plot is superimposed on each box, depicting the data's distribution.

The number of pesticides found at the sampling sites varied greatly in the two seasons. The detected organochlorine pesticides were above 0.2 μg/kg. The mean averages of OCPs in sediment for wet and dry seasons; isomers of lindane α -HCH, aldrin, and methoxychlor were lower than the detection limits <0.01 μg/kg during the two seasons (Table 4.2). However, dieldrin and α-endosulfan were detected only during the dry season because of bioaccumulation, solubility, and affinity of these pesticides in sediment during the dry season.

In the wet season, they were not detected because a large amount of water flowing due to runoff which might have deposited fresh or new sediments that were not much concentrated on top of the previous ones.

β- endosulfan recorded the highest concentration of 6.60±0.03 μg/kg at point S5 (Foot Bridge near Jamilo academy) during the dry season. Most organochlorine pesticides detected in sediments were above 0.2 μg/kg, exceeding the WHO maximum residue limit (Table 4.2). Organochlorine pesticides were more dominant in sediments during the dry season than during the rainy season, which suggests that pesticides are soluble in sediment and bioaccumulate there. However, because of increased farming activities and greater quantities of run-off from such activities along the river banks, it was anticipated that organochlorine pesticide concentrations would be higher in sediment during the rainy season.

Generally, there was an increase in organochlorine pesticide residues in sediments downstream (S1-S10) along the river to Lake Victoria. This trend is consistent with earlier research conducted on this subject by Ogola *et al*., (2023), Onchieku (2019), Abong'o *et al*. (2018), Nthusi (2017), Osoro *et al*. (2016), Abong'o *et al*. (2015) and Abongo (2009). Organochlorine pesticides banned under the Stockholm Convention as persistent organic pollutants such as; α-HCH, β-HCH, DDT and its metabolites DDE and DDD, BHC (lindane), dieldrin, and endrin were detected in the sediments (Table 4.2). β- HCH concentrations were the highest among HCH isomers.

4.5 Water and sediment physicochemical parameters

The physicochemical properties of water and soil sediment samples from the study sites were summarized, and the results are presented in Table 4.3.

Table 4.3: Physicochemical characteristics of water and sediments along River Kibos-Nyamasaria

Site	S1		S2		S3		S4		S5		S6		S7		S8		S9		S10	
Parameter	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**
Water samples																				
pH	7.10±0.05	7.05±0.04	6.96±0.02	6.93±0.06	7.34±0.08	7.10±0.10	7.42±0.10	7.18±0.04	7.50±0.10	7.33±0.12	7.50±0.17	7.26±0.16	7.61±0.12	7.40±0.21	7.61±0.09	7.45±0.18	7.90±0.02	7.88±0.01	7.89±0.09	7.86±0.05
Conductivity (µs/cm)	106.93±0.25	123.13±0.35	139.26±1.05	147±0.85	127.43±0.15	135.43±0.15	124.16±1.10	129.00±0.95	121.40±0.20	120.26±0.56	123.56±0.75	120.53±0.70	126±0.81	130.53±0.87	132.66±0.85	128.53±1.01	137.56±0.97	133±0.75	139.26±0.86	137.26±0.36
TDS (Mg/L)	101.23±1.15	93.63±1.30	110.50±0.80	118.56±1.13	108.30±0.81	113.46±0.70	113.46±0.77	106.16±0.75	103.53±1.02	99.46±1.25	105.36±0.50	101.33±0.25	111.40±1.35	107.53±0.86	117.26±1.10	115.46±1.12	115.6±0.88	113.40±0.79	120.10±0.45	118.10±0.33
TSS (Mg/L)	86.46±0.73	71.43±0.15	102.70±0.60	94.96±0.90	65.40±0.80	71.60±0.10	71.10±0.10	79.70±0.20	94.40±0.05	88.50±0.50	89.70±0.10	83.20±0.90	97.60±0.90	111.40±0.03	113.20±0.20	120.30±0.60	123.73±0.60	126.90±0.70	111.50±0.90	110.50±0.41
Turbidity (NTU)	147.23±0.96	84.23±0.41	155.33±0.85	98.43±1.06	154.30±0.81	129.43±0.75	158.20±0.95	132.30±1.05	163.93±0.61	144.33±0.65	159.10±0.80	139.36±1.15	181.46±1.05	156.13±0.80	173.30±0.91	152.40±0.88	201.46±1.12	177.06±0.61	188.50±1.08	184.30±1.19
Sediments samples																				
pH	6.73±0.09	6.55±0.15	6.20±0.05	6.21±0.01	6.39±0.15	6.27±0.04	6.57±0.10	6.33±0.14	6.57±0.13	6.5±0.17	6.9±0.08	6.73±0.07	7.03±0.07	6.92±0.07	6.20±0.15	6.83±0.10	7.26±0.06	7.16±0.15	7.25±0.02	7.23±0.05
Conductivity (µs/cm)	58.13±0.35	56.57±0.60	44.43±0.31	46.5±0.36	90.6±0.36	91.4±0.20	83.5±0.30	87.67±0.25	90.8±0.45	89.43±0.70	112.1±0.20	109.5±0.61	123.8±0.36	120.5±0.36	142.23±0.35	138.43±0.35	231.2±0.36	226.47±0.40	233.63±0.25	230.1±0.31
Moisture (%)	18.15±0.03	16.81±0.06	17.27±0.11	13.14±0.03	17.58±0.14	15.75±0.03	18.38±0.03	15.23±0.07	18.78±0.02	13.32±0.11	19.00±0.02	16.82±0.09	19.86±0.10	16.98±0.03	22.10±0.03	17.43±0.02	24.04±0.03	17.70±0.02	26.34±0.03	19.14±0.03
Organic Matter (%)	3.21±0.04	2.95±0.06	4.62±0.10	4.02±0.01	4.65±0.17	4.52±0.11	4.38±0.15	4.41±0.30	3.87±0.09	3.64±0.07	3.93±0.22	3.69±0.17	4.13±0.02	3.89±0.08	8.23±0.03	6.82±0.16	8.03±0.02	6.89±0.10	9.43±0.11	8.75±0.02
Organic carbon (%)	1.86±0.03	1.71±0.04	2.67±0.05	2.33±0.01	2.69±0.11	2.60±0.07	2.54±0.08	2.46±0.06	2.24±0.05	2.11±0.04	2.28±0.12	2.14±0.09	2.4±0.01	2.25±0.04	4.77±0.02	3.95±0.09	4.66±0.01	4.00±0.06	5.47±0.07	5.07±0.01
Clay (%)	44.05±0.03	43.83±0.14	44.44±0.04	44.05±0.08	43.27±0.03	43.15±0.02	39.73±0.02	39.55±0.13	39.87±0.05	39.64±0.11	40.35±0.03	40.74±0.66	44.05±0.09	42.94±0.14	43.28±0.06	42.93±0.21	44.32±0.02	44.77±0.15	45.51±0.07	45.99±0.19
Silt (%)	23.99±0.61	23.61±0.07	25.92±0.12	23.07±0.04	26.06±0.05	25.64±0.04	27.92±0.17	26.88±0.03	28.13±0.04	27.11±0.05	26.66±0.03	25.80±0.06	28.15±0.15	25.85±0.07	28.8±0.12	31.04±0.02	29.73±0.04	30.11±0.03	30.05±0.03	31.82±0.12
Sand (%)	31.63±0.02	32.54±0.04	6.2±0.05	6.21±0.01	6.39±0.15	6.27±0.04	6.57±0.10	33.53±0.11	31.97±0.07	33.23±0.11	32.96±0.02	33.14±0.03	30.87±0.06	31.14±0.12	27.57±0.68	26.03±0.02	25.92±0.03	25.10±0.06	22.45±0.22	22.23±0.03

Sampling Sites (S1-S10)

The pH of water samples ranged from 6.93±0.06 at Kibos Bridge near Kibos market (S2) to 7.88±0.01 at Nyalenda farms (S9) in the drier months. Conductivity during the rainy season ranged from 106.93±0.25 µs/cm (S1) to 139.26±0.86 µs/cm (S10), while total suspended solids (TSS) ranged from 65.40±0.80 mg/L (S3) to 123.73±0.60 mg/L (S9). During the dry season, the pH of water samples ranged from 6.93±0.06 at the Kibos Bridge near Kibos market (S2) to 7.86±0.05 at the point of entry to Lake Victoria (S10). The soils' sediment pH ranged from 6.55±0.15 at the convergent of River Kibos and Awach near Guba Bridge Kibos (S1) to 7.23±0.05 at the point of entry to Lake Victoria (S10) in the drier months. Although during the wet season, the pH of sediment ranged from 6.20±0.05 at the Nyalenda wastewater treatment plant (S8) to 7.25±0.02 at the point of entry to Lake Victoria (S10), indicating that the soils sediment was generally weakly acidic to basic.

It's worth noting that the pH values for both water and sediment samples generally fell within the WHO allowable limits of 6.5 to 8.5. Conductivity and TDS levels were also within acceptable limits. However, turbidity and TSS exceeded the recommended levels, particularly downstream, indicating a potential pollution issue. Dissolved ionic solids such as inorganic substances present in river water as a result of pollution leads to increase in conductivity downstream. Soil pH influences pesticide bioavailability and transport in soils (Idowu et al., 2022). Conversion of DDT to DDE requires soil pH levels close to 10 as DDT transformation becomes faster in naturally occurring alkaline soils than in acid soils (Ahmad *et al*., 2000). Soil sediment conductivity during dry season ranged from 56.57±0.60 µs/cm (S1) to 230.1±0.31 µs/cm (S10), while the dry season's clay and silt composition varied from 43.83±0.14 % (S1) to 45.99±0.19 % (S10) and 23.61±0.07 % (S1) to 31.82±0.12% (S10) respectively.

4.5.1 The graphical presentation of results of physicochemical parameters of river water

Figure 4.6 illustrates a consistent trend of increasing water physicochemical parameters downstream, observed in both the wet and dry seasons across the ten selected sampling sites, which span from the river's first sampling point (S1) to Lake Victoria (S10). This pattern indicates heightened human, industrial, and agricultural activities downstream along the river Kibos-Nyamasaria, potentially leading to increased pollution levels in the downstream river. Notably, this trend is more pronounced during the wet season, likely attributed to runoff from human settlements, industries, and agricultural activities occurring both upstream and downstream, ultimately culminating at the point where the river flows into Lake Victoria.

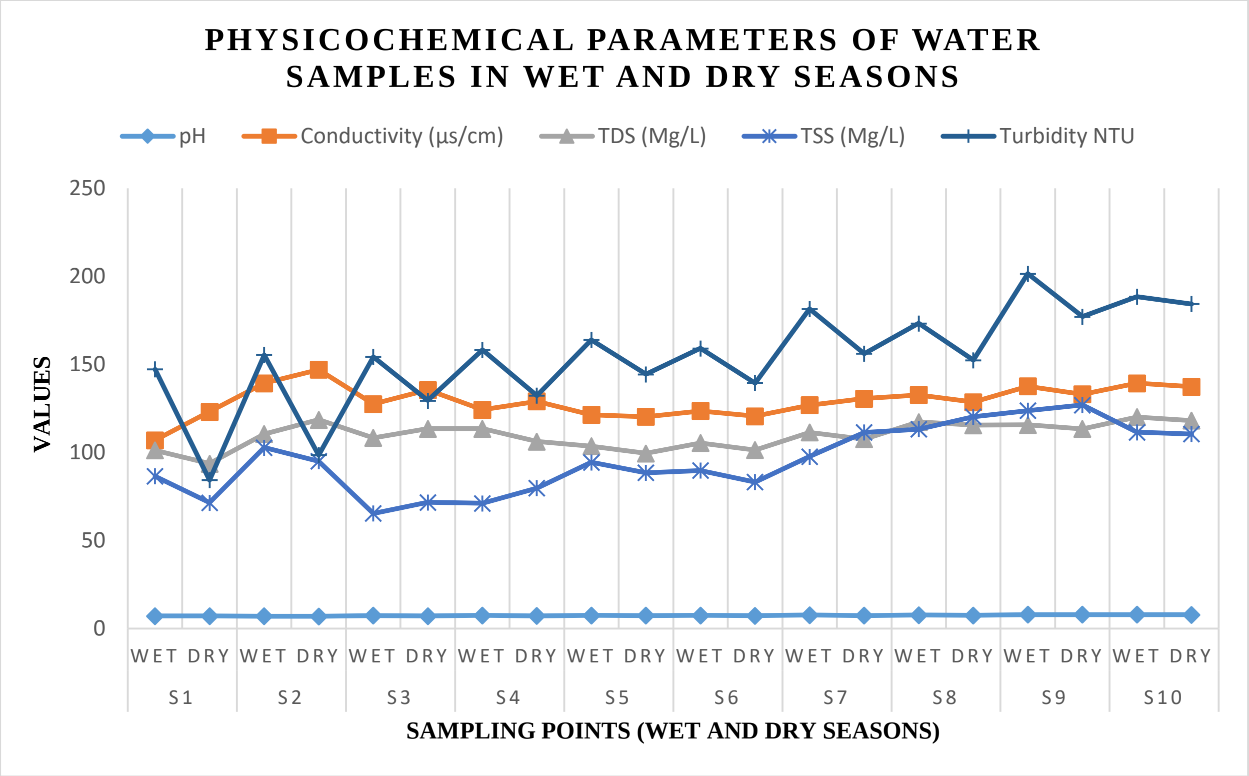


Figure 4.6: Graph showing increase in water physicochemical parameters downstream

4.5.2 The graphical presentation of results of physicochemical parameters of sediments

Figure 4.7 show a general trend in the increase of the soil sediment physicochemical parameters downstream from ten sampling point along the river, which extent from the river's first sampling point (S1) to where river drained into Lake Victoria (S10) indicating increased human, industrial and agricultural activities downstream along the river. The trend was much more during the wet season; this could be attributed to surface run-off from human settlement and industrial and agricultural activities upstream and downstream to the point where the river drains into Lake Victoria.

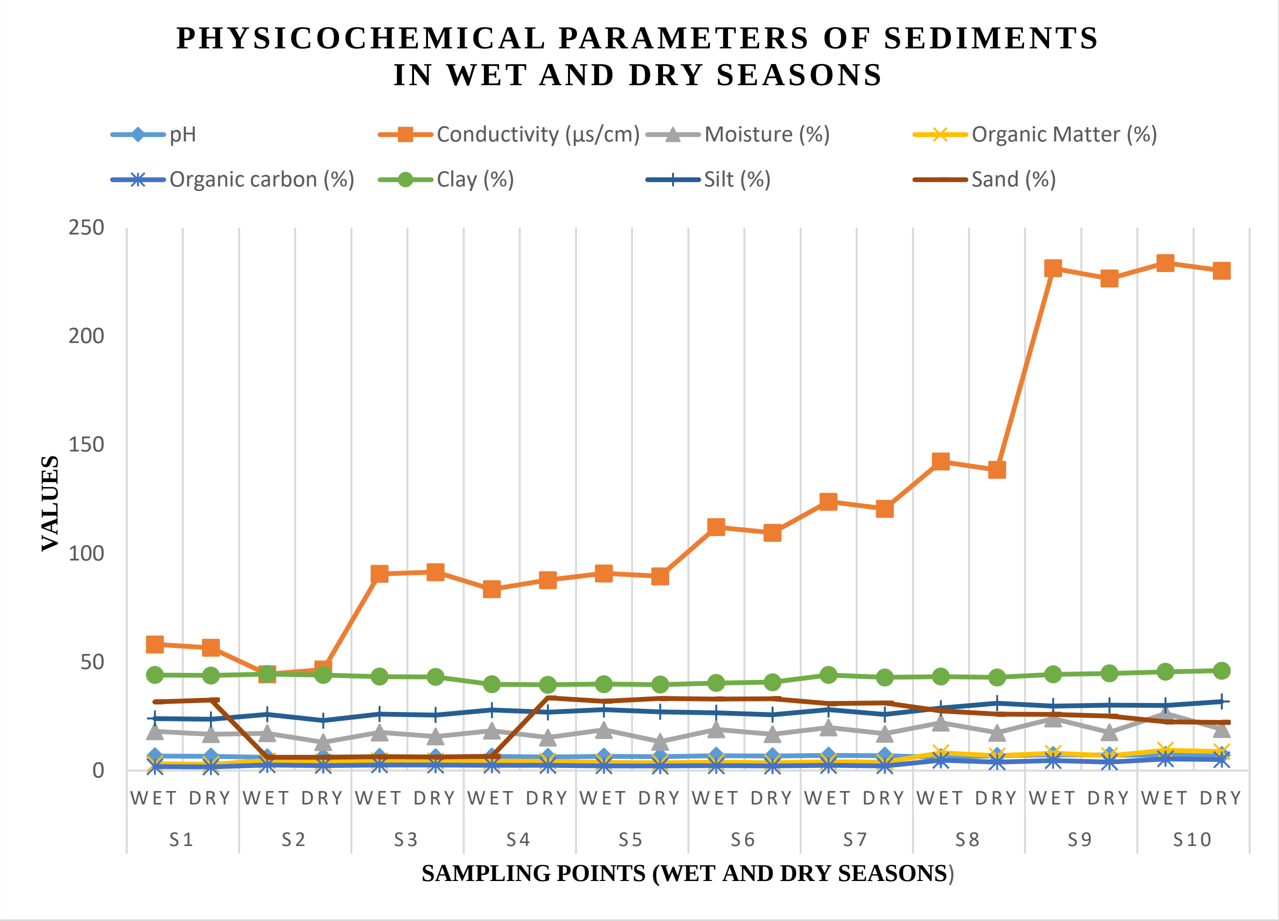


Figure 4.7: Graph showing increase in sediment physicochemical parameters downstream

4.6 Correlation Analysis results between Physicochemical Parameters and organochlorine pesticide residues (in wet and dry season)

The results in table 4.1, 4.2 and 4.3 were used for correlation analysis. The physicochemical parameters of the water and sediments were compared and correlated with those of OCPs, and their results of correlation analysis given in Tables 4.4 and 4.5.

Table 4.4: Pearson's correlation analysis between selected water physicochemical parameters and organochlorine pesticides during the wet and dry season

	Water (Wet season)																		
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
pH	0.893**	0.763**	0.933**	0.901**	0.831**	0.954**	0.950**	0.935**	0.652**	0.887**	0.975**	0.917**	0.870**	0.897**	0.767**	0.966**	0.992**	0.864**	0.940**
Conductivity (us/cm)	0.686**	0.252	0.407*	0.729**	0.574**	0.665**	0.391*	0.502**	0.244	0.704**	0.216	0.332	0.644**	0.662**	0.825**	0.516**	0.315	0.698**	0.468*
TDS (mg/l)	0.710**	0.481**	0.607**	0.806**	0.726**	0.826**	0.513**	0.665**	0.380*	0.810**	0.497**	0.553**	0.795**	0.808**	0.806**	0.664**	0.562**	0.729**	0.690**
TSS (mg/l)	0.407*	0.099	0.595**	0.674**	0.616**	0.661**	0.593**	0.573**	0.374*	0.507**	0.486**	0.471**	0.825**	0.795**	0.827**	0.525**	0.513**	0.744**	0.731**
Turbidity (NTU)	0.769**	0.530**	0.794**	0.880**	0.784**	0.923**	0.808**	0.800**	0.540**	0.854**	0.788**	0.734**	0.870**	0.914**	0.874**	0.839**	0.825**	0.852**	0.906**

	Water (Dry season)																		
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
pH	0.899**	0.838**	0.947**	0.768**	0.732**	0.824**	0.917**	0.793**	0.774**	0.884**	0.799**	0.862**	0.750**	0.759**	0.029	0.822**	0.419*	0.965**	0.764**
Conductivity (us/cm)	0.714**	-0.183	0.227	0.845**	0.681**	0.573**	0.555**	0.781**	0.560**	0.671**	0.738**	0.636**	0.747**	0.807**	0.816**	0.844**	0.023	0.144	0.428*
TDS (mg/l)	0.748**	0.302	0.628**	0.811**	0.844**	0.662**	0.763**	0.788**	0.842**	0.760**	0.669**	0.742**	0.856**	0.848**	0.553**	0.849**	-0.012	0.502**	0.579**
TSS (mg/l)	0.513**	0.151	0.644**	0.728**	0.805**	0.640**	0.748**	0.465**	0.563**	0.450*	0.685**	0.688**	0.816**	0.802**	0.654**	0.800**	-0.314	0.542**	0.621**
Turbidity (NTU)	0.802**	0.551**	0.828**	0.773**	0.819**	0.755**	0.919**	0.701**	0.739**	0.804**	0.825**	0.826**	0.798**	0.754**	0.364	0.828**	0.115	0.780**	0.712**

** Correlation was significant at the 0.01 level (2-tailed). * Correlation was significant at the 0.05 level (2-tailed). (1) Aldrin (2) Dieldrin (3) Endosulfan Sulphate (4) α –endosulfan (5) β – endosulfan (6) Endrin (7) Heptachlor (8) Heptachlor –epoxide (9) Methoxychlor (10) Lindane (11) α-HCH (12) β-HCH (13) δ –HCH (14) o, p'- DDT (15) p, p' – DDT (16) o, p'- DDD (17) p, p'- DDD (18) o, p' – DDE (19) p, p '- DDE

Table 4.5: Pearson's correlation analysis between selected sediment physicochemical parameters and organochlorine pesticides during the wet and dry season

	Soil sediment (wet Season)																		
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Soil pH	0.585**	0.593**	0.880**	0.761**	0.800**	0.825**	0.870**	0.776**	0.559**	0.667**	0.885**	0.768**	0.887**	0.882**	0.692**	0.837**	0.903**	0.727**	0.923**
Conductivity (us/cm)	0.780**	0.727**	0.836**	0.888**	0.881**	0.957**	0.829**	0.788**	0.516**	0.864**	0.834**	0.724**	0.929**	0.966**	0.808**	0.875**	0.913**	0.787**	0.896**
Moisture (%)	0.400*	0.678**	0.681**	0.573**	0.701**	0.665**	0.580**	0.504**	0.338	0.548**	0.665**	0.483**	0.756**	0.739**	0.476**	0.639**	0.745**	0.418*	0.692**
Organic matter (%)	0.671**	0.592**	0.651**	0.817**	0.797**	0.864**	0.606**	0.646**	0.371*	0.804**	0.568**	0.527**	0.919**	0.922**	0.800**	0.670**	0.679**	0.717**	0.744**
Organic carbon (%)	0.671**	0.592**	0.651**	0.817**	0.797**	0.864**	0.606**	0.646**	0.371*	0.804**	0.568**	0.527**	0.919**	0.922**	0.800**	0.670**	0.679**	0.717**	0.744**
Clay (%)	0.016	0.194	0.089	0.298	0.385*	0.278	0.004	-0.067	-0.136	0.294	0.009	-0.201	0.486*	0.480**	0.408*	0.168	0.134	0.141	0.250
Silt (%)	0.893**	0.634**	0.859**	0.915**	0.796**	0.940**	0.847**	0.922**	0.617**	0.899**	0.890**	0.877**	0.881**	0.884**	0.828**	0.884**	0.888**	0.912**	0.915**
Sand (%)	-0.539**	-0.544**	-0.546**	-0.759**	-0.815**	-0.773**	-0.485**	-0.481**	-0.232	-0.723**	-0.474*	-0.349	-0.846**	-0.867**	-0.751**	-0.619**	-0.592**	-0.610**	-0.664**
	Soil sediment (dry Season)																		
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Soil pH	0.624**	0.759**	0.959**	0.559**	0.773**	0.790**	0.905**	0.479**	0.687**	0.643**	0.773**	0.866**	0.772**	0.755**	0.067	0.815**	0.118	0.961**	0.897**
Conductivity (us/cm)	0.785**	0.695**	0.880**	0.754**	0.881**	0.806**	0.924**	0.758**	0.748**	0.819**	0.944**	0.955**	0.900**	0.872**	0.284	0.923**	0.112	0.885**	0.811**
Moisture (%)	0.405*	0.773**	0.832**	0.301	0.718**	0.692**	0.735**	0.300	0.656**	0.532**	0.655**	0.902**	0.769**	0.711**	0.008	0.783**	0.030	0.841**	0.948**
Organic matter (%)	0.703**	0.456*	0.731**	0.823**	0.956**	0.717**	0.830**	0.791**	0.815**	0.746**	0.787**	0.874**	0.986**	0.984**	0.558**	0.980**	-0.193	0.656**	0.674**
Organic carbon (%)	0.703**	0.456*	0.731**	0.823**	0.956**	0.717**	0.830**	0.791**	0.815**	0.746**	0.787**	0.874**	0.986**	0.984**	0.558**	0.980**	-0.193	0.656**	0.674**

Table 4.5: Pearson's correlation analysis continues’

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Clay (%)	0.024	0.014	0.227	0.149	0.581**	0.197	0.346	0.090	0.259	0.187	0.604**	0.616**	0.684**	0.577**	0.649**	0.672**	-0.524**	0.204	0.571**
Silt (%)	0.921**	0.634**	0.906**	0.888**	0.760**	0.727**	0.880**	0.893**	0.809**	0.869**	0.701**	0.806**	0.849**	0.762**	0.256	0.860**	0.271	0.850**	0.571**
Sand (%)	-0.548**	-0.303	-0.599**	-0.696**	-0.922**	-0.560**	-0.734**	-0.706**	-0.624**	-0.617**	-0.886**	-0.875**	-0.926**	-0.899**	-0.670**	-0.942**	0.297	-0.581**	-0.610**

** Correlation was significant at the 0.01 level (2-tailed). * Correlation was significant at the 0.05 level (2-tailed). (1) Aldrin (2) Dieldrin (3) Endosulfan Sulphate (4) α –endosulfan (5) β – endosulfan (6) Endrin (7) Heptachlor (8) Heptachlor –epoxide (9) Methoxychlor (10) Lindane (11) α-HCH (12) β-HCH (13) δ –HCH (14) o, p’- DDT (15) p, p’ – DDT (16) o, p’- DDD (17) p, p’- DDD (18) o, p’ – DDE (19) p, p’- DDE

The physicochemical parameters and organochlorine pesticides in water between the dry and wet seasons were compared by Pearson's correlation analysis and found to give a positive correlation (Table 4.3), except that for p, p'- DDD with TDS and TSS during the dry season, which was negative and not significant ($P>0.01$). Pearson's correlation between conductivity and dieldrin, methoxychlor, α-HCH, β-HCH, p, p'- DDD (wet season) and dieldrin, endosulfan sulphate, p, p'- DDD, and o, p'-DDE (dry season) were not statistically significant ($P\leq0.01$). The correlation between the water pH with all the 19 organochlorine pesticides was significantly positive ($P\leq0.01$) (Table 4.4) during wet and dry seasons except for p, p'-DDT ($r = 0.029$), which was not significant during the dry season.

In addition, the correlation between turbidity with all organochlorine pesticides analyzed was significantly positive except p, p' – DDT, and p, p' – DDD, which were insignificant at ($P\leq0.01$). Correlation between conductivity and endosulfan Sulphate, heptachlor, p, p'-DDE, between TDS and methoxychlor, between TSS and aldrin, and methoxychlor were significantly positive ($P\leq0.05$) in the rainy season. When the weather is dry, the correlation between conductivity and p, p'- DDE, TSS, and lindane were significantly positive ($P\leq0.05$) (Table 4.4).

Furthermore, the correlation between soil pH, conductivity, soil moisture content, organic matter, and organic carbon with all 19 organochlorine pesticides was significantly positive ($P\leq0.01$) (Table 7) during wet and dry seasons except the correlation between moisture content and aldrin, o, p' – DDE, organic matter and methoxychlor, organic carbon and methoxychlor, clay and β – endosulfan, δ –HCH, p, p' – DDT, sand, and lindane which were significant at $P\leq0.05$ during the wet season. During the dry season, the correlation between moisture and aldrin, organic matter and dieldrin, and organic carbon and dieldrin were significantly positive ($P \leq 0.05$). The correlation between clay content and aldrin, dieldrin, endosulfan sulphate, α–endosulfan, and endrin was not statistically significant ($P > 0.01$).

The pH of rivers and soils influences the bioavailability and transport of pesticides in water and sediments (Ogola *et al*., 2023; Idowu *et al*., 2022; Drevenkar *et al*., 1996). Pesticides containing organochlorines respond variably in water and soil, depending on their specific properties and the water-soil physicochemical parameters. The significant negative correlation between pH and p, p'-DDD and the significant positive correlation between water/soil pH and organochlorine pesticides during the wet and dry seasons both imply that hydrolysis, a chemical reaction in which water reacts with a compound to produce other compounds, may have increased pesticide adsorption and desorption due to pH. Hydrolysis involves splitting the OCPs bond and adding the hydrogen cation and hydroxide anion. This implies that the pesticides degrade more quickly in alkaline water (Ogola *et al*., 2023).

When the pH of the water is greater (above 7) or alkaline, hydrolysis might happen very quickly. The rate of hydrolysis increases ten times for every unit increase in pH (Ogola *et al*., 2023; Ahmad *et al*., 2000). Some organochlorine pesticides degrade immediately when mixed with high-pH water (Ahmad *et al*., 2000). This would lead to increase in organochlorine pesticides in water due to increase in pH. The pH and speciation of dissolved ions also affect an organochlorine pesticide's capacity to coagulate or sorb ions (Ogola *et al*., 2023).This finding is similar to Fosu-Mensah *et al*. (2016), who reported a significant increase in lindane, dieldrin, and beta-HCH concentrations with an increase in soil pH. In this study, water and soil pH were within the range of most natural rivers, streams, or lakes between 6.5 and 7.5, while the WHO allowable pH range for water and soil is 6.5-8.5 (Rehman *et al*., 2015). The sorption, transport, and transformation of pesticides are significantly influenced by the organic matter composition of the soil (Ogola *et al*., 2023; Tariq *et al*., 2016). The organic matter in this study varied from 2.95±0.06 % at the convergent of River Kibos & Awach near Guba Bridge Kibos (S1) to 9.43 ± 0.11 % at the downstream point of entry to Lake Victoria (S10). Depending on the type of pesticides and the organic matter, soil with an organic carbon concentration of greater than 5% facilitates the sorption of pesticides (Ogola *et al*., 2023; Rehman *et al*., 2015).

Organochlorine pesticide residue levels in the soils are associated with high conductivity, organic matter, and organic carbon of the soil, as shown by a strong positive correlation between conductivity (both water and soil), organic matter, and organic carbon with the detection of organochlorine pesticides in both dry and wet seasons (Tables 4.2 and 4.5). This might be explained by the fact that, like the fats, oils, or lipids found in plants and animals, pesticide molecules have a high propensity to attach to organic matter and carbon in soil (Fosu-Mensah *et al*. 2016). The negative connection between organic matter, organic carbon, and p, p'-DDD, on the other hand, demonstrates that a rise in organic matter or organic carbon of the soils led to a drop in p, p'-DDD, and vice versa.

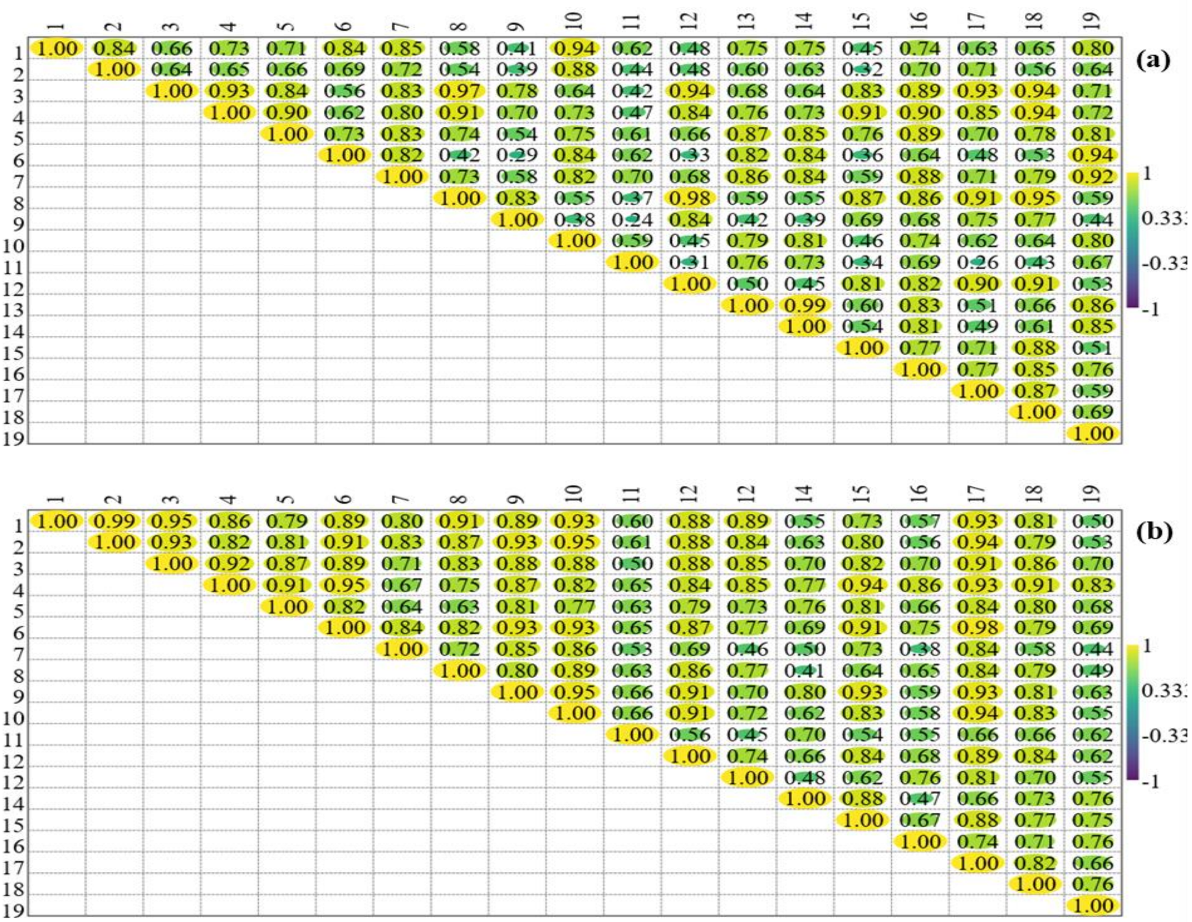
These results are essentially identical to those researched by Fosu-Mensah *et al.* (2016) and Aiyesanmi & Idowu (2012), which revealed nearly the same trend of significant ($p>0.05$) associations between total organochlorine pesticides assessed in soil samples and organic carbon, organic matter, and those two variables. Additionally, although organic carbon is known to be the most important OCP sorbent on the soil surface, other parameters such as the composition of organic matter, particle-size characteristics, and physicochemical properties of OCPs are also implicated in pesticide retention (Ogola *et al*., 2023; Fosu-Mensah *et al*. 2016).

The texture of the soil affects how organochlorine pesticides behave in the soil, according to Fosu-Mensah *et al*. (2016). Sandy soils promote the leaching of pesticides, whereas clay soils aid in accumulating OCPs through colloid formation. Sand impacts extractable pesticides in soils, as evidenced by the strong negative association between the amount of sand in soils during dry and wet seasons and practically with every organochlorine pesticide found (Ogola *et al*., 2023). As a result, when the amount of sand increased, the number of organochlorine pesticides discovered decreased proportionally (Table 4.5).

Our findings concur with those made public by Idowu et al., 2022 and Fosu-Mensah *et al*. (2016). The negative correlation between the percentage of clay soil and Heptachlor-epoxide, methoxychlor, and β-HCH during the wet season and p, p'- DDD during the dry season shows that the amount of clay in the soil has a significant impact on the dispersion of organochlorine pesticides (Ogola *et al*., 2023). As a result, heptachlor-epoxide, methoxychlor, and β-HCH decreased proportion to an increase in the percentage of clay soils and vice versa (Fosu-Mensah *et al*., 2016). Most of the examined organochlorine pesticides have a high positive and significant connection ($p > 0.05$) with the percentage of silt, indicating that as the percentage of silt increased, so did the concentrations of these pesticides (Table 4.5). This discovery is comparable to that made by Fosu-Mensah *et al*. (2016), who found a connection between the percentage of silt and the OCPs found in soil samples ($p>0.05$).

4.7 Relationship between OCPs residues in water and sediments

Comparison of the organochlorine pesticide residues in river water with sediments by Pearson’s correlation tests at a 95% confidence level revealed significant positive correlations (Figure 4.8). In river water, there were strong positive correlations between aldrin and lindane (r=0.91, $p \leq 0.05$), endosulfan sulphate and; heptachlor-epoxide (r=0.91, $p \leq 0.05$), α-HCH (r=0.94, $p \leq 0.05$), p, p, -DDD (r=0.93, $p \leq 0.05$), p, p,’ -DDE (r=0.94, $p \leq 0.05$) (Figure 4.8a). Only methoxychlor and β-HCH correlation were not significant ($p \geq 0.05$). However, in water, the remaining OCPs had significant positive correlations ($p \leq 0.05$). In the sediments, there was a strong to weak positive statistically significant relation between all the organochlorine pesticides (Figure 4.8b). Aldrin showed a strong positive correlation with dieldrin (r=0.99, $p \leq 0.05$) and with endosulfan sulphate (r=0.93, $p \leq 0.05$). Lindane and p, p,’ -DDD had strong positive correlations with most organochlorine pesticides under study (Figure 4.8).



(a)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	1.00	0.84	0.66	0.73	0.71	0.84	0.85	0.58	0.41	0.94	0.62	0.48	0.75	0.75	0.45	0.74	0.63	0.65	0.80
2		1.00	0.64	0.65	0.66	0.69	0.72	0.54	0.39	0.88	0.44	0.48	0.60	0.63	0.32	0.70	0.71	0.56	0.64
3			1.00	0.93	0.84	0.56	0.83	0.97	0.78	0.64	0.42	0.94	0.68	0.64	0.83	0.89	0.93	0.94	0.71
4				1.00	0.90	0.62	0.80	0.91	0.70	0.73	0.47	0.84	0.76	0.73	0.91	0.90	0.85	0.94	0.72
5					1.00	0.73	0.83	0.74	0.54	0.75	0.61	0.66	0.87	0.85	0.76	0.89	0.70	0.78	0.81
6						1.00	0.82	0.42	0.29	0.84	0.62	0.33	0.82	0.84	0.36	0.64	0.48	0.53	0.94
7							1.00	0.73	0.58	0.82	0.70	0.68	0.86	0.84	0.59	0.88	0.71	0.79	0.92
8								1.00	0.83	0.55	0.37	0.98	0.59	0.55	0.87	0.86	0.91	0.95	0.59
9									1.00	0.38	0.24	0.84	0.42	0.39	0.69	0.68	0.75	0.77	0.44
10										1.00	0.59	0.45	0.79	0.81	0.46	0.74	0.62	0.64	0.80
11											1.00	0.31	0.76	0.73	0.34	0.69	0.26	0.43	0.67
12												1.00	0.50	0.45	0.81	0.82	0.90	0.91	0.53
13													1.00	0.99	0.60	0.83	0.51	0.66	0.86
14														1.00	0.54	0.81	0.49	0.61	0.85
15															1.00	0.77	0.71	0.88	0.51
16																1.00	0.77	0.85	0.76
17																	1.00	0.87	0.59
18																		1.00	0.69
19																			1.00

(b)

	1	2	3	4	5	6	7	8	9	10	11	12	12	14	15	16	17	18	19
1	1.00	0.99	0.95	0.86	0.79	0.89	0.80	0.91	0.89	0.93	0.60	0.88	0.89	0.55	0.73	0.57	0.93	0.81	0.50
2		1.00	0.93	0.82	0.81	0.91	0.83	0.87	0.93	0.95	0.61	0.88	0.84	0.63	0.80	0.56	0.94	0.79	0.53
3			1.00	0.92	0.87	0.89	0.71	0.83	0.88	0.88	0.50	0.88	0.85	0.70	0.82	0.70	0.91	0.86	0.70
4				1.00	0.91	0.95	0.67	0.75	0.87	0.82	0.65	0.84	0.85	0.77	0.94	0.86	0.93	0.91	0.83
5					1.00	0.82	0.64	0.63	0.81	0.77	0.63	0.79	0.73	0.76	0.81	0.66	0.84	0.80	0.68
6						1.00	0.84	0.82	0.93	0.93	0.65	0.87	0.77	0.69	0.91	0.75	0.98	0.79	0.69
7							1.00	0.72	0.85	0.86	0.53	0.69	0.46	0.50	0.73	0.38	0.84	0.58	0.44
8								1.00	0.80	0.89	0.63	0.86	0.77	0.41	0.64	0.65	0.84	0.79	0.49
9									1.00	0.95	0.66	0.91	0.70	0.80	0.93	0.59	0.93	0.81	0.63
10										1.00	0.66	0.91	0.72	0.62	0.83	0.58	0.94	0.83	0.55
11											1.00	0.56	0.45	0.70	0.54	0.55	0.66	0.66	0.62
12												1.00	0.74	0.66	0.84	0.68	0.89	0.84	0.62
12													1.00	0.48	0.62	0.76	0.81	0.70	0.55
14														1.00	0.88	0.47	0.66	0.73	0.76
15															1.00	0.67	0.88	0.77	0.75
16																1.00	0.74	0.71	0.76
17																	1.00	0.82	0.66
18																		1.00	0.76
19																			1.00

Figure 4.8: Correlation analysis of organochlorine pesticides in (a) water and (b) sediments

The correlation coefficients (*r*) values are shown in each eclipse.
1=Aldrin; **2**=Dieldrin; **3**=Endosulfan Sulphate; **4**= α –endosulfan; **5**= β – endosulfan; **6**= Endrin; **7**= eptachlor; **8**= Heptachlor – epoxide; **9**= Methoxychlor; **10**= Lindane; **11**= α-HCH; **12**= β-HCH; **13**= δ –HCH; **14**= o, p’-DDT; **15**= p, p’ – DDT; **16**= o, p’- DDD; **17**= p, p’- DDD; **18**= o, p’ – DDE; **19**= p, p’- DDE.

In this study, aldrin and dieldrin recorded the highest concentration of 8.33±0.58 μg/L (S1) and 8.67±0.58 μg/L (S4), respectively, during the wet season, while during the dry season, α-HCH recorded the highest concentration of 8.27±0.06 μg/L (S10) in river water. Aldrin, dieldrin, endosulfan sulphate, α-endosulfan, methoxychlor, and α-HCH were the only pesticides detected individually at concentrations over 0.1 μg/L in water samples. During the dry season, dieldrin, 6.03±5.14 μg/L at S5, methoxychlor, 3.43±0.06 μg/L at S10, and α-HCH, 8.27±0.06 μg/L (S10) were the only pesticide residues detected above 0.1 μg/L which exceed

WHO maximum residues limits (MRLs) in the dry season with the highest mean levels recorded near the river mouths (Table 4.1). In sediment, Dieldrin recorded the highest concentration (5.55±0.10 µg/kg) at S10 during the dry season (Table 4.2).

In water and sediment samples, there was a general increase in organochlorine pesticide residues along the river downstream to the lake. This may be due to the continuous addition and general bioaccumulation of pesticides downstream due to human, industrial, and agricultural activities along the river. Higher concentrations of organochlorine pesticides were observed in sediment compared to water samples because of higher affinity and bioaccumulation of organochlorine pesticides in sediment than in water samples (Ogola et al., 2023; Nyaundi *et al*., 2021; Nyaundi *et al*., 2020; Alex *et al.*, 2019; Onchieku, 2019; Abong'o *et al*., 2018; Ndunda *et al*., 2018).

Organochlorine pesticides were more in sediment samples during the dry season than in wet seasons because of the bioaccumulation of the pesticides in sediment. Organochlorine pesticides in sediments were less during the wet season due to the large volume of water flowing due to the runoffs, hence washing and dissolving some organochlorine pesticides from sediment as water drains into Lake Victoria, reducing their concentration from sediments (Ogola *et al.*, 2023). In addition, less concentration of organochlorine pesticides in sediments during wet seasons might have been contributed by the fresh deposition of new sediments with low pesticide concentration than the previous ones at the bottom because of large moving volume of water downstream to the Lake (Ogola *et al*., 2023).

Moreover, organochlorine pesticides were more in water samples in wet season because of large volume of water flowing due to runoff and washing of OCPs sprayed in agriculture farms, industrial, human settlements, building sites, public health, mosquitoes, and termite control sites during rainy season to the river (Ogola *et al*., 2023). The increase of OCPs in water samples is also contributed by washing and dissolving of some organochlorine pesticide from sediment as water drains into the Lake reducing its concentration from sediments and increasing it in river water (Ogola et al., 2023).

The study also found that OCPs are more prevalent in water samples during wet or rainy seasons than during dry seasons, while sediment samples contained more OCPs during dry seasons than during wet seasons, and their concentrations rose downstream. These findings are consistent with those of other researchers (Nyaundi *et al*., 2021; Nyaundi *et al*., 2020; Alex *et al.,* 2019; Onchieku, 2019; Abong'o *et al*., 2018; Ndunda *et al*., 2018; Fang *et al*., 2017; Nthusi, 2017; Osoro *et al*., 2016; Fosu-Mensah *et al*.,2016; Abong'o *et al*., 2015; Abongo, 2009).

In the study, most organochlorine pesticides detected in sediment were above 0.2 μg/kg, which exceeds the maximum residues limits (MRLs) of WHO. The results are similar to those reported by Nthusi (2017), Abong'o *et al*.(2015) and Abongo (2009) along the river Nyando, even though most of the pesticides concentrations in their studies were higher.

The same trend of the results were also observed in Rusinga Island of Lake Victoria, Kenya Osoro *et al*.(2016) and River Kuja catchment by Onchieku (2019). The high concentrations of organochlorine pesticides reported in sediments compared to river water samples could be attributed to higher solubility, affinity, and bioaccumulation of organochlorine pesticides in soil sediments. These compounds are persistent and move longer distances in surface run-off or groundwater. They have a low solubility in water and therefore tend to adsorb onto the sediment particles. (Ogola *et al.*, 2023; Nyaundi *et al*., 2021; Nyaundi *et al*., 2020; Alex *et al.,* 2019; Onchieku, 2019; Abong'o *et al*., 2018; Ndunda *et al*., 2018; Fang *et al*., 2017).

The variations in organochlorine pesticide residues observed at different sampling points along the river in different seasons might have resulted from human or industrial activities along the river. Some of the human activities involving pesticides along the river line include; the treatment of fence lines poles, the foundations of homes and new construction sites, public health to control mosquitoes around the lake region, treatment of woods or timber around Nyamasaria and Kibos area to control termites and ants by wood venders and also dumping of used pesticides containers into the river (Ogola *et al*., 2023).

Run-off or leaching of organochlorine pesticides into the river could have also occurred when too much pesticides were applied or were spilled on the surface carelessly, highly water soluble pesticides were used, or too much rainwater or irrigation water which occurred in a short period washed the pesticides to the river (Ogola *et al*., 2023; Fosu-Mensah *et al*. 2016). Dieldrin had the highest mean concentration of (5.55 µg/kg) amongst the organochlorine pesticides in sediments, while endosulfan sulfate (0.15 µg/L) and dieldrin (0.17 µg/L) had the highest mean concentration in water samples when mean of both seasons combined.

Dieldrin is an insecticide commonly used on fruits, seeds, and soil; it persists in the soil with a half-life period of almost five years in temperate latitudes (Fosu-Mensah *et al*. 2016). Aldrin and dieldrin may be volatilized from sediment and redistributed by air currents, contaminating areas far from their sources. According to a report by the Pest Control Products Board of Kenya (PCPB) (2008), many of the pesticides under investigation are no longer imported or used. Studies by Ogola *et al.*, (2023), Onyango *et al.* (2014) and Gitahi *et al*. (2002) have suggested that these pesticides may be used in the Lake Basin to control mosquitoes. The presence of DDT and its isomers or metabolites in our study may be explained by the frequent use of agricultural pesticides and human settlements along the malaria-prone sample points (S1-S10), which has benefited from mosquitoes and termite control initiatives

4.8 Comparisons of mean organochlorine pesticides (OCPs) residues in water and soil sediments between wet and dry Seasons

The variation in organochlorine pesticide concentration between the wet and dry seasons may be seen in Table 4.6, paired t-test (mean and standard deviation). Except for α-HCH (t (29) = 0.737, p = 0.467) and endrin (t (29) = -0.493, p = 0.626), the concentration of organochlorine pesticides in the water was considerably more significant during the wet season than during the dry season. In sediments, the concentrations of endosulfan sulphate (t (29) =19.434, p = 0.000), β-endosulfan (t (29) = 3.194, p =0.003), methoxychlor (t (26) = -5.816, p =0.000), α-HCH (t (23) = -3.338, p=0.003), β-HCH (t (29) = -2.443, p=0.021), p, p'-DDT (t (29) = -2.094, p = 0.045) and o, p'- DDD (t (29) = -2.010, p= 0.054 were significantly higher during the dry season as compared to wet season (Table 4.6).

In water, Endosulfan Sulphate recorded the highest mean of 0.113±0.073 (t (29) = 7.638, p= 0.000) during the wet season. It was statistically significant between the wet and dry seasons (p< 0.005). Endrin, on the other hand, reported the highest mean during the dry season (0.520±0.033; t (29) = -0.493; p=0.626); however, there was no statistically significant difference between the dry and wet seasons (p> 0.05). Additionally, during the rainy season, in sediment, Dieldrin had a higher mean of 2.880±2.519 (t (27) = 1.551, p=0.133). In contrast, Methoxychlor recorded the highest mean of 2.761±2.044 during the dry season (t (26) = -5.816, p = 0.000) and was statistically significant between the wet and dry seasons (p> 0.05) (Table 4.6).

Table 4.6: Paired t-test for organochlorine pesticides (OCPs) residues in water and sediments between wet and dry Seasons

	OCPs in water					**OCPs in sediments**				
Pesticide	**Means ± S.D. (μg/L)**					**Means ± S.D. (μg/kg)**				
	Wet season	**Dry season**	***t*-value**	**df**	***p*-value**	**Wet season**	**Dry season**	***t*-value**	**df**	***p*-value**
Aldrin	0.050±0.017	0.046±0.018	7.562	29	0.000	2.070±1.550	1.888±1.584	1.859	22	0.076
Dieldrin	0.103±0.061	0.083±0.043	3.789	29	0.001	2.880±2.519	2.720±2.685	1.551	27	0.133
Endosulfan Sulphate	0.113±0.073	0.038±0.020	7.638	29	0.000	1.362±1.345	0.589±0.952	19.434	29	0.000
α – endosulfan	0.039±0.018	0.020±0.008	9.134	29	0.000	0.556±2.922	1.328±1.209	1.782	23	0.088
β – endosulfan	0.063±0.053	0.029±0.032	6.443	29	0.000	0.233±0.707	0.589±0.952	3.194	29	0.003
Endrin	0.051±0.027	0.520±0.033	0.493	29	0.626	1.939±1.370	2.094±1.170	1.411	29	0.169
Heptachlor	0.300±0.015	0.022±0.014	7.540	29	0.000	0.013±0.794	0.009±0.593	0.236	29	0.815
Heptachlor –epoxide	0.055±0.028	0.016±0.006	9.003	29	0.000	0.671±1.082	0.723±0.989	0.761	29	0.453
Methoxychlor	0.104±0.065	0.028±0.005	6.672	29	0.000	2.398±2.035	2.761±2.044	5.816	26	0.000
Lindane	0.047±0.021	0.042±0.019	5.892	29	0.000	1.797±1.290	1.889±1.198	1.662	29	0.107
α – HCH	0.022±0.013	0.018±0.032	0.737	29	0.467	1.972±1.060	2.251±1.229	3.338	23	0.003
β – HCH	0.065±0.040	0.003±0.003	8.849	29	0.000	0.844±1.529	1.080±1.578	2.443	29	0.021
δ – HCH	0.009±0.008	0.006±0.008	7.489	29	0.000	1.241±1.200	1.223±1.191	0.168	29	0.868
o, p’- DDT	0.009±0.008	0.007±0.008	4.133	29	0.000	0.835±0.824	0.831±0.962	0.106	29	0.916
p, p’- DDT	0.040±0.021	0.009±0.010	10.267	29	0.000	1.184±1.275	1.372±1.085	2.094	29	0.045
o, p’- DDD	0.013±0.007	0.004±0.006	9.175	29	0.000	0.169±0.730	0.028±0.766	2.010	29	0.054
p, p’- DDD	0.049±0.030	0.018±0.011	6.411	29	0.000	1.802±1.376	1.939±1.302	1.744	29	0.092
o, p’- DDE	0.039±0.018	0.014±0.008	12.637	29	0.000	0.318±0.674	0.356±0.687	0.778	29	0.443
p, p’- DDE	0.012±0.009	0.009±0.009	3.645	29	0.001	0.128±0.833	0.040±0.556	1.028	29	0.312

All the 19 Organochlorine pesticides residues and their isomers, such as aldrin, dieldrin, endosulfan sulphate, α-endosulfan, β-endosulfan, endrin, heptachlor, heptachlor-epoxide, methoxychlor, lindane, gamma-hexachlorocyclohexane (γ-HCH) or benzene hexachloride (BHC), α-HCH, β-HCH, δ -HCH, o, p'- DDT, p, p' - DDT, o, p'- DDD, p .p'-DDD, o, p'- DDE, p, p'- DDE were detected in water and sediment samples in the ten sampling points at different concentrations. Due to the bioaccumulation, solubility, and affinity of dieldrin and α -endosulfan in sediment during the dry season, these pesticides were only detected in dry season. Farmers might not have utilized Dieldrin and α -endosulfan during the sampling period; hence, they were not found during the wet season.

4.9 Principal Component Analysis for Organochlorine Pesticide Residues

The results of the principal component analysis (PCA) for organochlorine pesticide residues in River Kibos-Nyamasaria are presented in Figure 4.9.

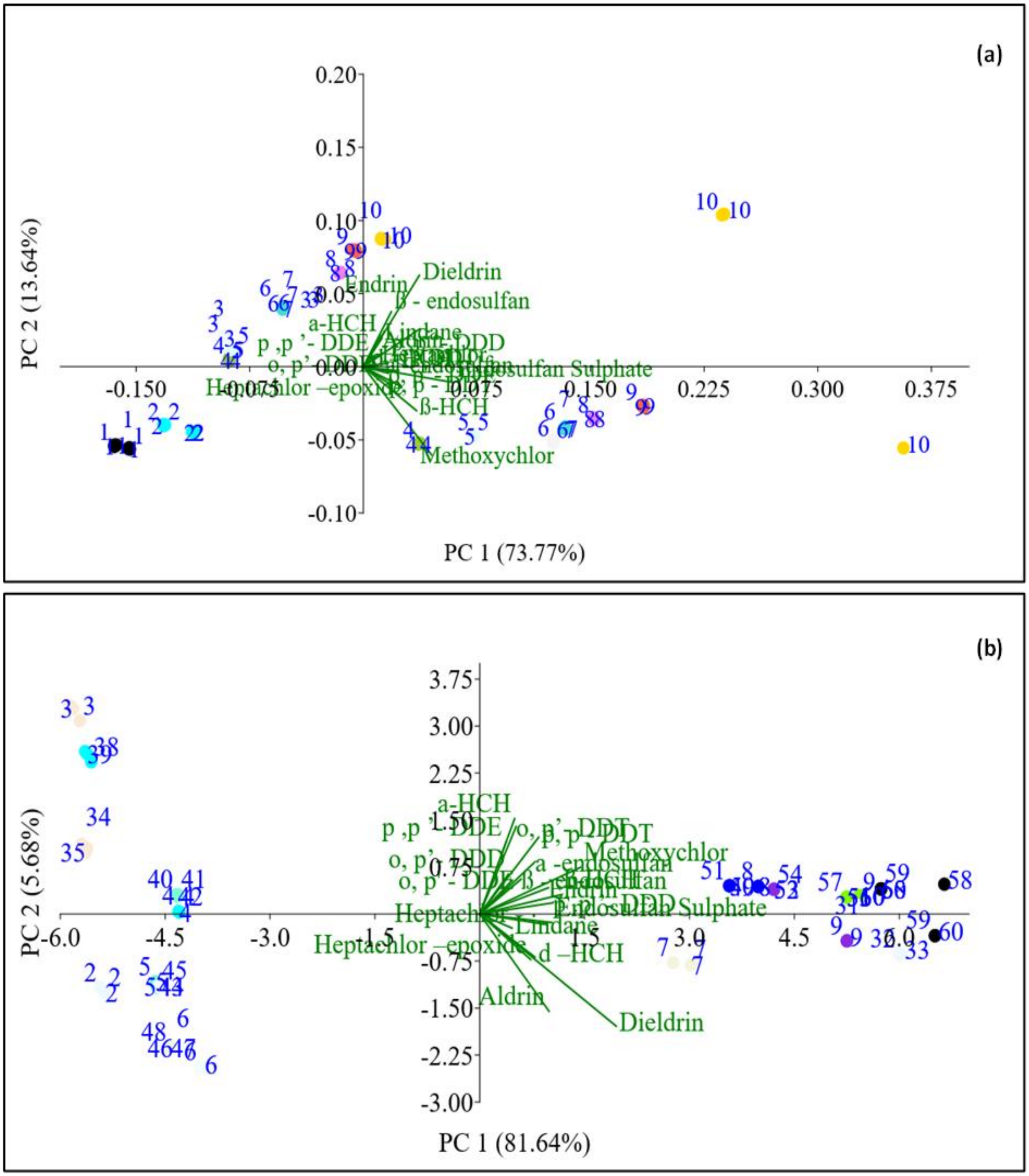


Figure 4.9: Principal composite analysis of Organochlorine Pesticide residues in (a) water and (b) sediments; numbers indicate sampling sites.

In this study, principal component analysis (PCA) was used to analyze the correlate matrix for organochlorine pesticide concentrations in the water and sediments to ascertain or determine the distribution pattern of pesticides. Figure 4.9 (a) shows that the first principal component (PC1) explained 73.77% of the total variance in water and was dominated by positive loadings on dieldrin, aldrin, endrin, heptachlor, lindane, α- HCH, p, p’ -DDT, o, p’-DDD, and p, p’- DDE and further negative loading on endosulfan sulphate, heptachlor-epoxide, methoxychlor, and β-HCH. The organochlorine pesticide residues with the same association possibly suggest that they come from the same source or have similar properties (Nyantakyi *et al*., 2022) and may be related to influences from sugarcane growing agricultural activities in the area as well as activities related to National research center around the region.

In contrast, the first principal component (PC1) and the second principal component (PC2) for pesticides in sediment, Figure 4.9 (b), accounted for 81.64% of the total variance in sediment and were dominated by 12 organochlorine pesticide residues. The first major component explains 81.64% of the overall variation in sediments. It is dominated by positive loadings of α-endosulfan, β- endosulfan, endrin, methoxychlor, α-HCH, β-HCH, o, p'- DDT, p, p' -DDT, o, p'- DDD, p, p'- DDD, o, p' -DDE and p, p'- DDE and negative loadings on aldrin, dieldrin, endrin, endosulfan sulphate, heptachlor, heptachlor-epoxide, lindane and δ – HCH.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

Nineteen OCPs residues and their isomers were detected in water and sediment samples from ten sampling points at different concentrations. The presence of residues from outlawed OCPs in water and soil sediment samples from the research area suggests that some people continue to use these OCPs illegally, endangering aquatic, animals and human health. The concentration of organochlorine pesticides in the water was higher during the wet or rainy season than during the dry season, while sediment samples contained more OCPs during dry seasons than during wet seasons, and their concentrations increased downstream as the river drained into Lake Victoria.

Higher levels of organochlorine pesticides were linked to human, industrial, and agricultural activity along the Kibos-Nyamasaria River. The residues of organochlorine pesticides may have entered the soils through spray drift, wash-off from sprayed agricultural land, accidental spills on the ground, improper disposal of leftover spray solution, dumping of used pesticide containers into rivers, misuse or overuse of the pesticide, sprayer wash water and pesticide containers. Some of the human activities involving the use of pesticides along the river line included; the treatment of fence lines poles, the foundations of homes and new construction sites, public health in controlling mosquitoes, treatment of woods or timber around the Nyamasaria and Kibos area and dumping of used pesticides containers into the river.

Aldrin, methoxychlor, and α -HCH were not detected in any season, while dieldrin and α -endosulfan were detected only during the dry season due to their nature of bioaccumulation, affinity and solubility in sediment. In the wet season, dieldrin and α -endosulfan were not detected because a large amount of water flowing due to runoff which might have deposited fresh or new sediments that were not much concentrated on top of the previous ones.

OCPs in the soils contaminate nearby water bodies through leaching and surface runoff, endangering soil organisms, aquatic and human health. Frequent monitoring of pesticide residues in this study area is necessary for preventing, controlling, and reducing environmental pollution to minimize health risks. Furthermore, most organochlorine pesticides detected in sediment were above 0.2 μg/kg, which exceeded the maximum residues limits (MRLs) of WHO. Dieldrin had the highest concentration amongst the organochlorine pesticides in sediments, while endosulfan sulfate and dieldrin had the highest concentration in water samples.

There was an increase in the water and soil sediment physicochemical parameters downstream along the river towards Lake Victoria. This indicated increased human, industrial, and agricultural activities downstream along the river. The trend was much more during the wet season, which could be attributed to surface run-off from human settlement, industrial and agricultural activities upstream and downstream to the point where the river drains into Lake Victoria.

The specific properties and physicochemical parameters of water and soil sediments and concentrations of the organochlorine pesticides residues determined at specific sampling points. The pH and speciation of dissolved ions in river water and soil sediment affect organochlorine pesticide's capacity to coagulate or sorb ions and influence the bioavailability and transport of pesticides in water and sediments. The rate of hydrolysis increases ten times for every unit increase in pH, leading to the degradation of pesticides. Depending on the type of pesticides and the organic matter, soil with an organic carbon concentration of greater than 5% facilitates the sorption of pesticides.

Organochlorine pesticide levels in the soil's sediments were found to be associated with high conductivity, organic matter, and organic carbon of the soil, as shown by a strong positive correlation between conductivity (of both water and soil), organic matter, and organic carbon in the dry and wet seasons. Pesticide molecules attach to organic matter and carbon in the soil, enhancing OCPs retention. The soil texture was found to affect the soil organochlorine pesticide behavior; sandy soils promote the leaching of pesticides, whereas clay soils aid in accumulating OCPs through colloid formation. As a result, when the amount of sand increased, the amount of organochlorine pesticides in the soil decreased.

Most of the organochlorine pesticides in this study had a high positive and significant difference with the percentage of silt, indicating that as the percentage of silt increased, so did the concentrations of these pesticides in sediments ($p > 0.05$). Significant positive correlations existed between most OCPs in water and the soil sediments ($p \leq 0.05$). In the sediments, there was a vital to weak positive statistically significant relation between all the organochlorine pesticides. The study showed a need to control bioaccumulation and pesticide pollution to relieve possible aquatic, animal, and human health calamities.

5.2 RECOMMENDATIONS

As a result of an increase in organochlorine pesticide residues and water and soil physicochemical parameters then contamination and pollution downstream, the study indicated that river water, sediment as well as Lake Victoria waters in which the river drains into are contaminated with organochlorine pesticide residues. Hence, it is recommended that,

Recommendations from research study objective:

- The point and non-point sources of organochlorine pesticide and other classes of pesticides in the water and sediments along the river need to be investigated, analyzed then managed, prevented and controlled to avoid further contamination and pollution.
- The bioavailability and bioaccumulation of the pesticides from the river water and the sediments and other rivers in the Lake Victoria basin be determined, quantified and documented in every five years.
- Before water from agricultural farms, industrial sites, sewage treatment plants, and human settlements is discharged into a river, preventive measures, control measures, and remediation measures should be implemented to clean and recycle surface water runoff.
- The pesticide residue in water and sediments along the rivers draining into Lake Victoria for the dry and wet seasons and further work on speciation and correlation on additional physicochemical parameters and pesticide residues from River Kibos-Nyamasaria and Lake Victoria waters and sediments, be conducted frequently or every five years focusing on bioaccumulation of the pesticides.
- Regular monitoring of pesticide residues in this study area is crucial to prevent, manage, and reduce environmental pollution and associated aquatic, animals and human health hazards.

- The government agencies such as NEMA should strictly enforce laws on pesticide use and pollution, and help farmers and industries along the river to improve their agricultural practices and wastewater treatment systems, including the use of soak pits and wetland construction.

Recommendations for further research studies:

- The contamination levels of food products, vegetables, and plants grown in farms along the river banks be determined, and studies on the bioaccessibility, bioavailability, and bioaccumulation of pesticide residues in plants, animal products, and fish harvested within the study site should be done to quantify the exposure risks. Various plant species should be planted in the region, and those found to have high concentrations of pesticide be used for phytoremediation.
- The effect of the bioavailability, bioaccessibility and bioaccumulation of the pesticides from the water and the sediments, on aquatic life, human health and possible diseases be investigated further including study on other rivers draining into Lake Victoria.
- Bioavailability, bioaccessibility, and bioaccumulation of other classes of pesticides like organophosphate pesticide residues in vegetables, fruits, food products and in river water and sediment of river Kibos-Nyamasaria and other rivers draining into the Lake Victoria basin be studied, investigated and documented.
- Studies on best scientific methods for recycling or cleaning contaminated water or surface runoff with chemicals from industrial setup, agricultural farms, sewage treatment, and human settlement before water is discharged to the river is highly recommended to manage, control and prevent further pesticides and other toxic chemicals pollution.

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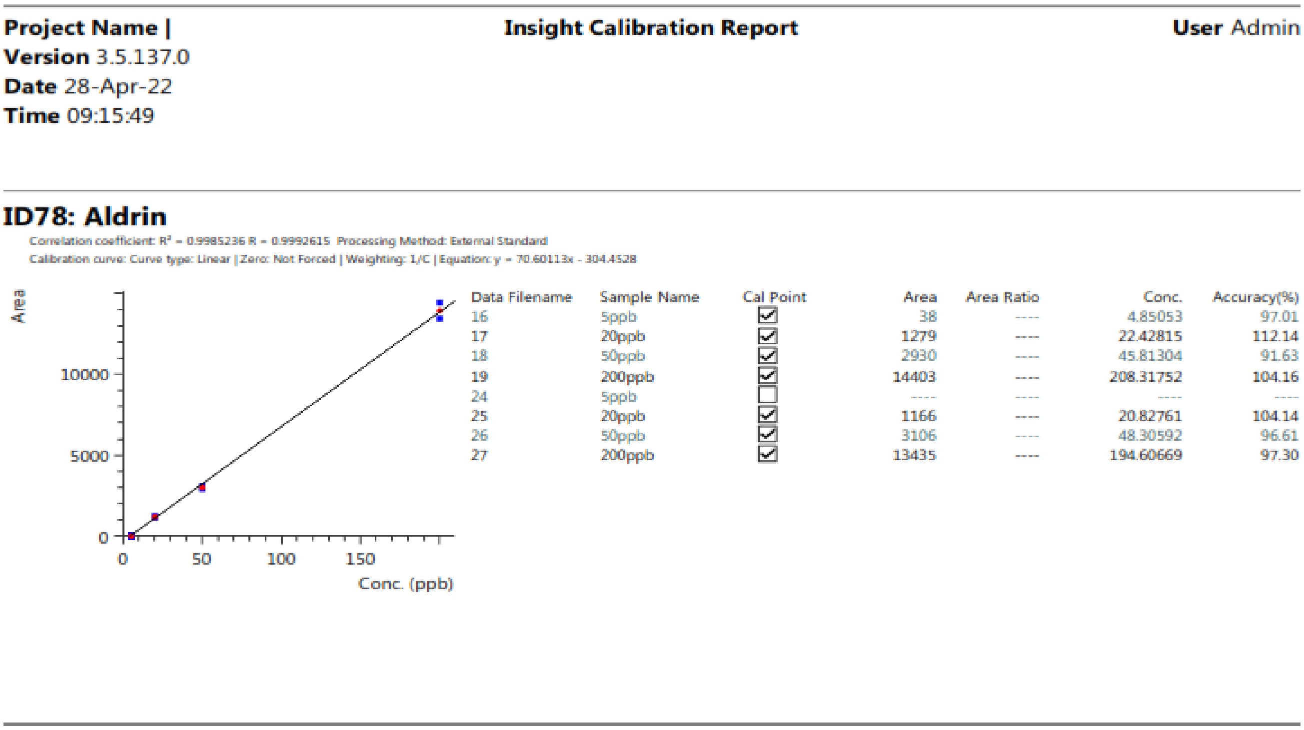
APPENDICES

Appendix I: Calibration curves of studied Organochlorine pesticides

1. Calibration curves of Dieldrin



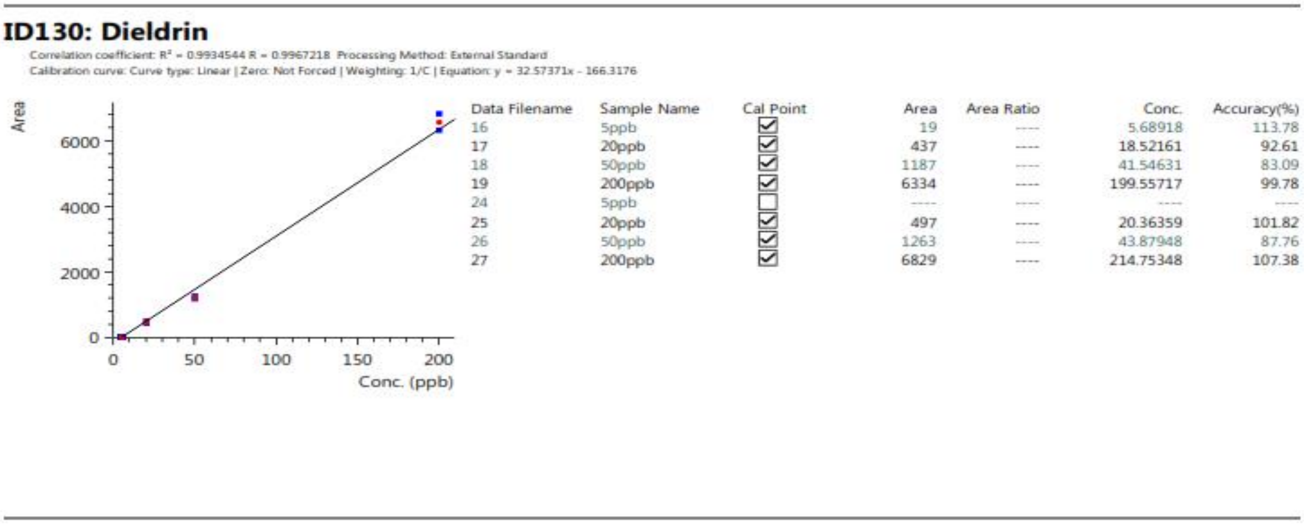
Project Name | **Insight Calibration Report** **User** Admin
Version 3.5.137.0
Date 28-Apr-22
Time 09:15:49

ID78: Aldrin

Correlation coefficient: R^2 = 0.9985236 R = 0.9992615 Processing Method: External Standard
Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 70.60113x - 304.4528

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	38	----	4.85053	97.01
17	20ppb	☑	1279	----	22.42815	112.14
18	50ppb	☑	2930	----	45.81304	91.63
19	200ppb	☑	14403	----	208.31752	104.16
24	5ppb	☐	----	----	----	----
25	20ppb	☑	1166	----	20.82761	104.14
26	50ppb	☑	3106	----	48.30592	96.61
27	200ppb	☑	13435	----	194.60669	97.30

2. Calibration curves of Dieldrin

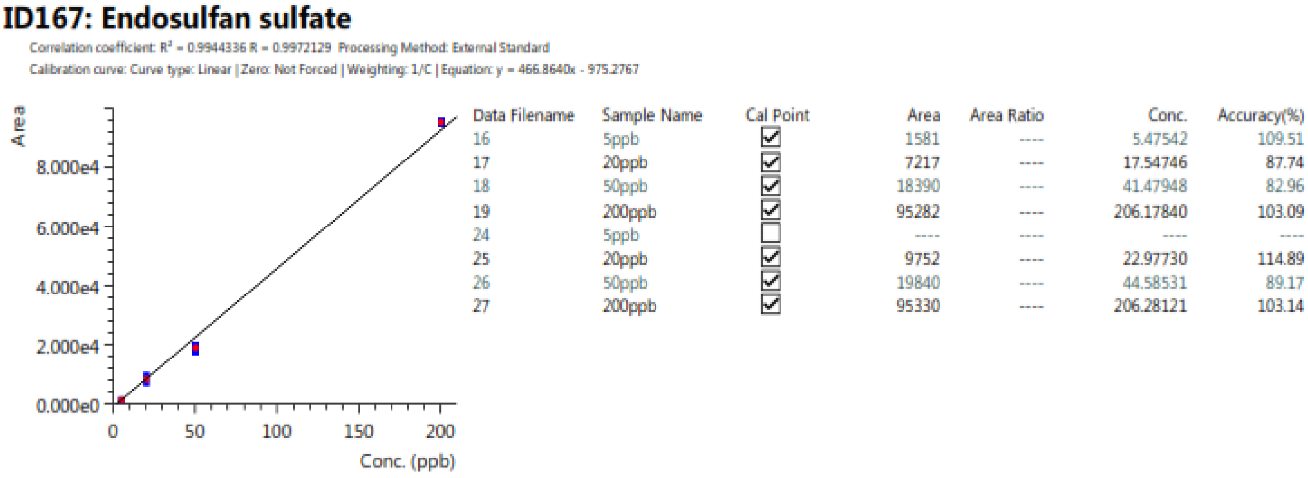


ID130: Dieldrin

Correlation coefficient: R^2 = 0.9934544 R = 0.9967218 Processing Method: External Standard
Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 32.57371x - 166.3176

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	19	----	5.68918	113.78
17	20ppb	☑	437	----	18.52161	92.61
18	50ppb	☑	1187	----	41.54631	83.09
19	200ppb	☑	6334	----	199.55717	99.78
24	5ppb	☐	----	----	----	----
25	20ppb	☑	497	----	20.36359	101.82
26	50ppb	☑	1263	----	43.87948	87.76
27	200ppb	☑	6829	----	214.75348	107.38

3. Calibration curves of Endosulfan Sulfate



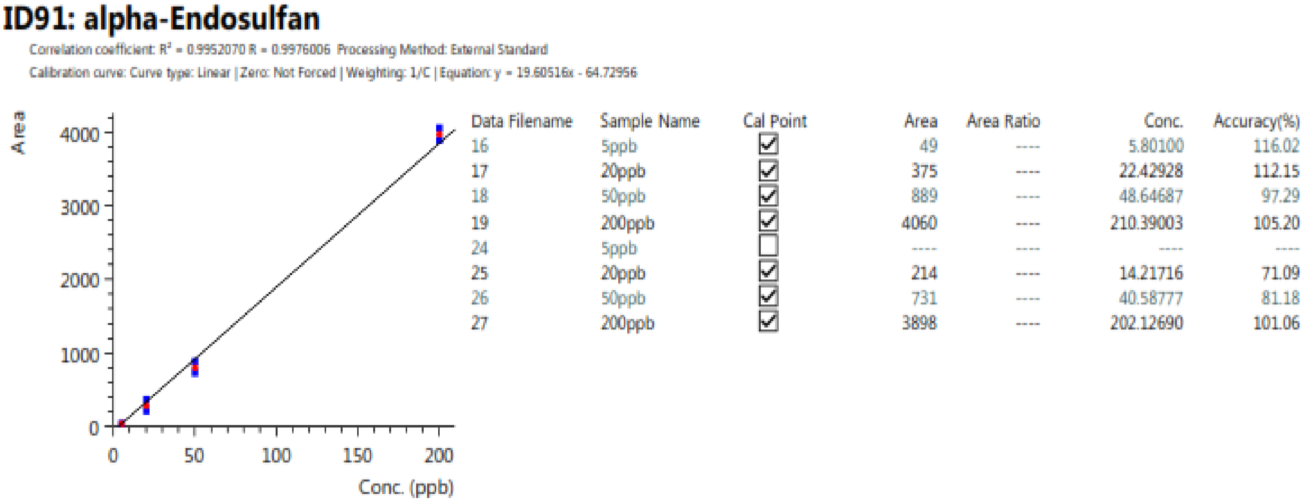
ID167: Endosulfan sulfate

Correlation coefficient: R^2 = 0.9944336 R = 0.9972129 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 466.8640x - 975.2767

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	1581	----	5.47542	109.51
17	20ppb	☑	7217	----	17.54746	87.74
18	50ppb	☑	18390	----	41.47948	82.96
19	200ppb	☑	95282	----	206.17840	103.09
24	5ppb	☐	----	----	----	----
25	20ppb	☑	9752	----	22.97730	114.89
26	50ppb	☑	19840	----	44.58531	89.17
27	200ppb	☑	95330	----	206.28121	103.14

4. Calibration curves of alpha-Endosulfan



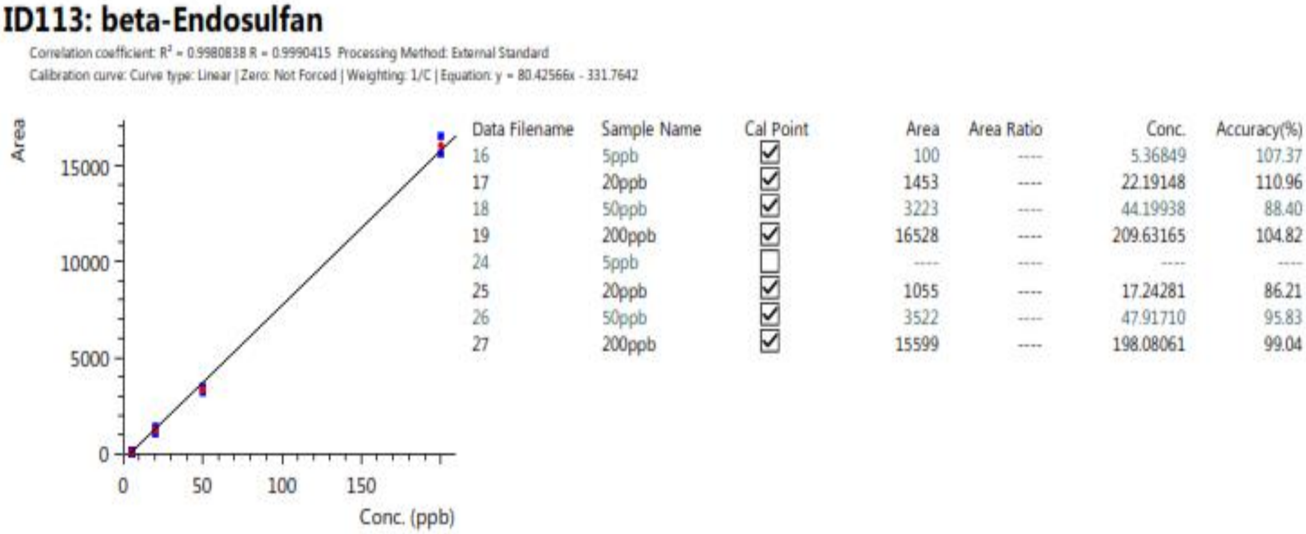
ID91: alpha-Endosulfan

Correlation coefficient: R^2 = 0.9952070 R = 0.9976006 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 19.60516x - 64.72956

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	49	----	5.80100	116.02
17	20ppb	☑	375	----	22.42928	112.15
18	50ppb	☑	889	----	48.64687	97.29
19	200ppb	☑	4060	----	210.39003	105.20
24	5ppb	☐	----	----	----	----
25	20ppb	☑	214	----	14.21716	71.09
26	50ppb	☑	731	----	40.58777	81.18
27	200ppb	☑	3898	----	202.12690	101.06

5. Calibration curves of beta-Endosulfan



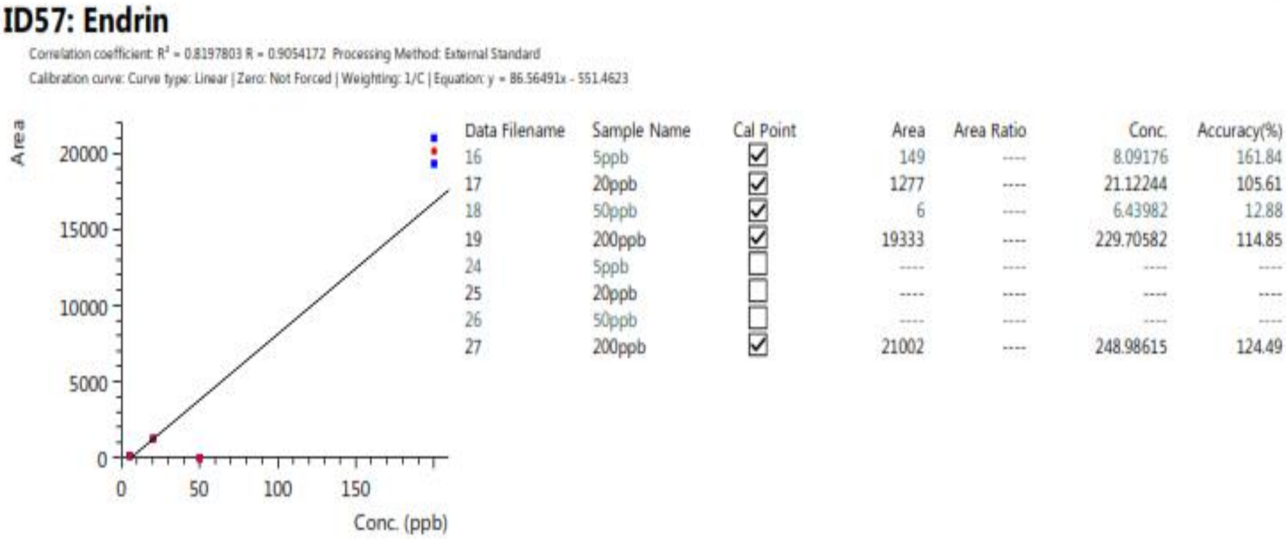
ID113: beta-Endosulfan

Correlation coefficient: R^2 = 0.9980838 R = 0.9990415 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 80.42566x - 331.7642

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	100	----	5.36849	107.37
17	20ppb	☑	1453	----	22.19148	110.96
18	50ppb	☑	3223	----	44.19938	88.40
19	200ppb	☑	16528	----	209.63165	104.82
24	5ppb	☐	----	----	----	----
25	20ppb	☑	1055	----	17.24281	86.21
26	50ppb	☑	3522	----	47.91710	95.83
27	200ppb	☑	15599	----	198.08061	99.04

6. Calibration curves of Endrin



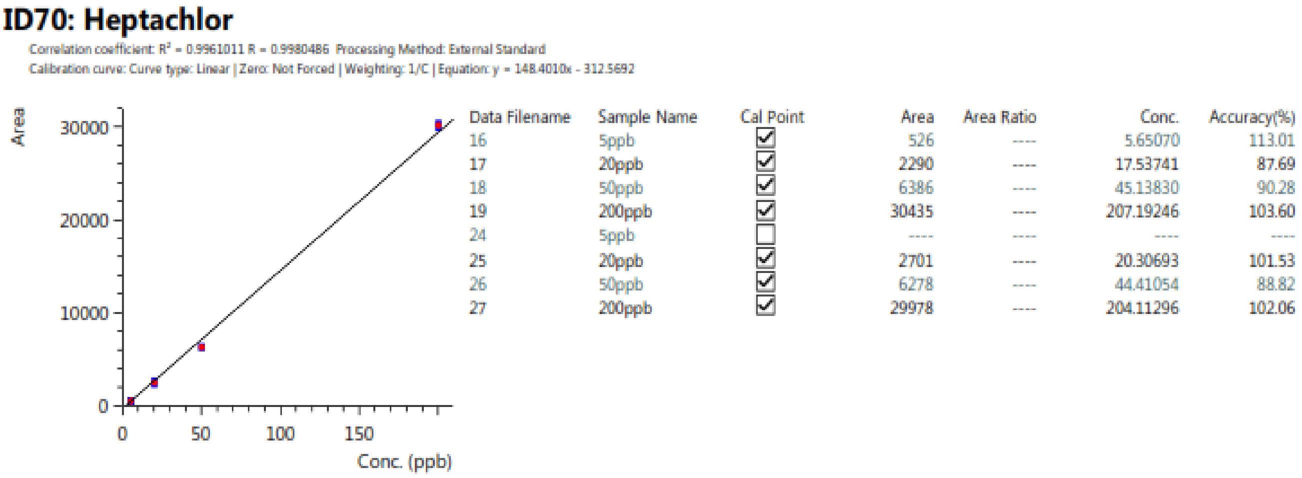
ID57: Endrin

Correlation coefficient: R^2 = 0.8197803 R = 0.9054172 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 86.56491x - 551.4623

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	149	----	8.09176	161.84
17	20ppb	☑	1277	----	21.12244	105.61
18	50ppb	☑	6	----	6.43982	12.88
19	200ppb	☑	19333	----	229.70582	114.85
24	5ppb	☐	----	----	----	----
25	20ppb	☐	----	----	----	----
26	50ppb	☐	----	----	----	----
27	200ppb	☑	21002	----	248.98615	124.49

7. Calibration curves of Heptachlor



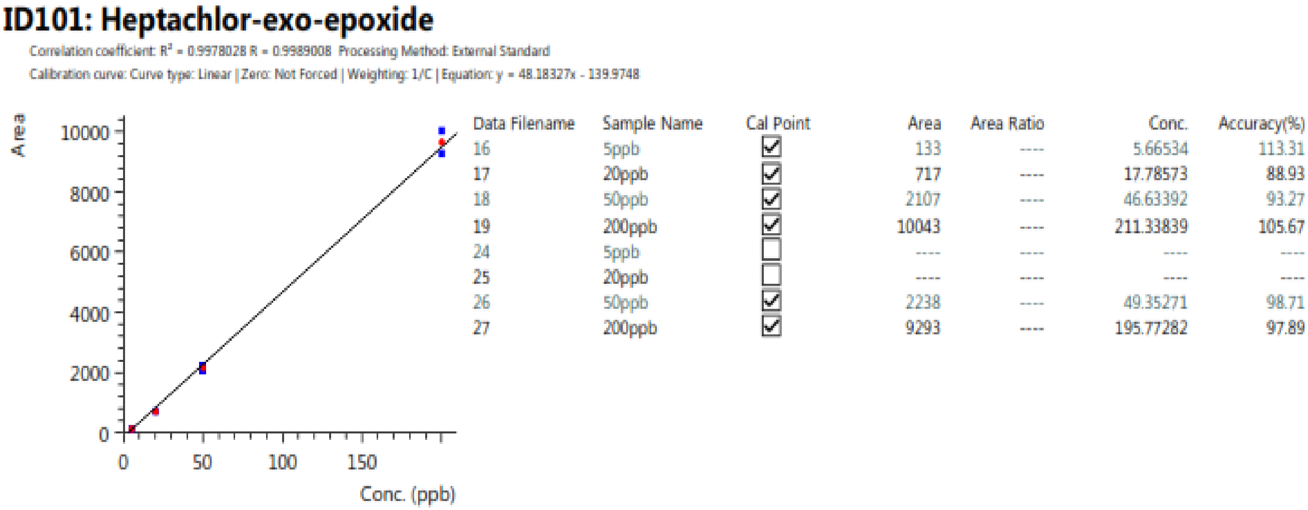
ID70: Heptachlor

Correlation coefficient: R^2 = 0.9961011 R = 0.9980486 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 148.4010x - 312.5692

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	526	----	5.65070	113.01
17	20ppb	☑	2290	----	17.53741	87.69
18	50ppb	☑	6386	----	45.13830	90.28
19	200ppb	☑	30435	----	207.19246	103.60
24	5ppb	☐	----	----	----	----
25	20ppb	☑	2701	----	20.30693	101.53
26	50ppb	☑	6278	----	44.41054	88.82
27	200ppb	☑	29978	----	204.11296	102.06

8. Calibration curves of Heptachlor-epoxide



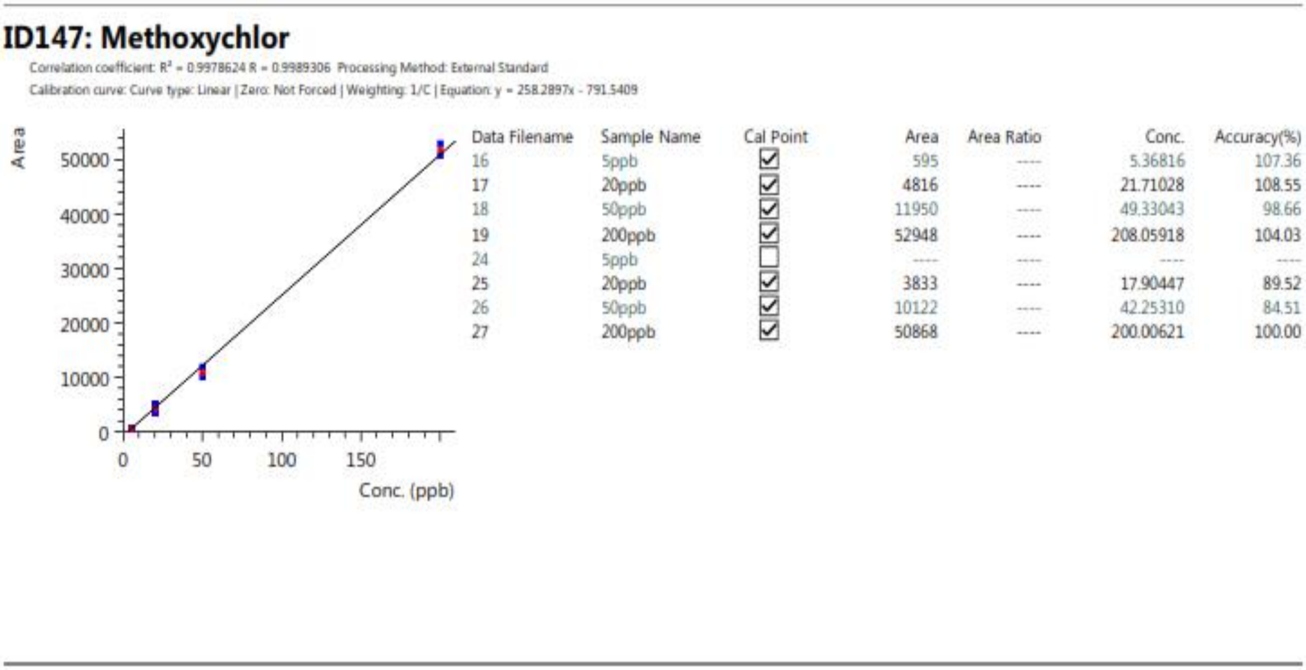
ID101: Heptachlor-exo-epoxide

Correlation coefficient: R^2 = 0.9978028 R = 0.9989008 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 48.18327x - 139.9748

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	133	----	5.66534	113.31
17	20ppb	☑	717	----	17.78573	88.93
18	50ppb	☑	2107	----	46.63392	93.27
19	200ppb	☑	10043	----	211.33839	105.67
24	5ppb	☐	----	----	----	----
25	20ppb	☐	----	----	----	----
26	50ppb	☑	2238	----	49.35271	98.71
27	200ppb	☑	9293	----	195.77282	97.89

9. Calibration curves of Methoxychlor



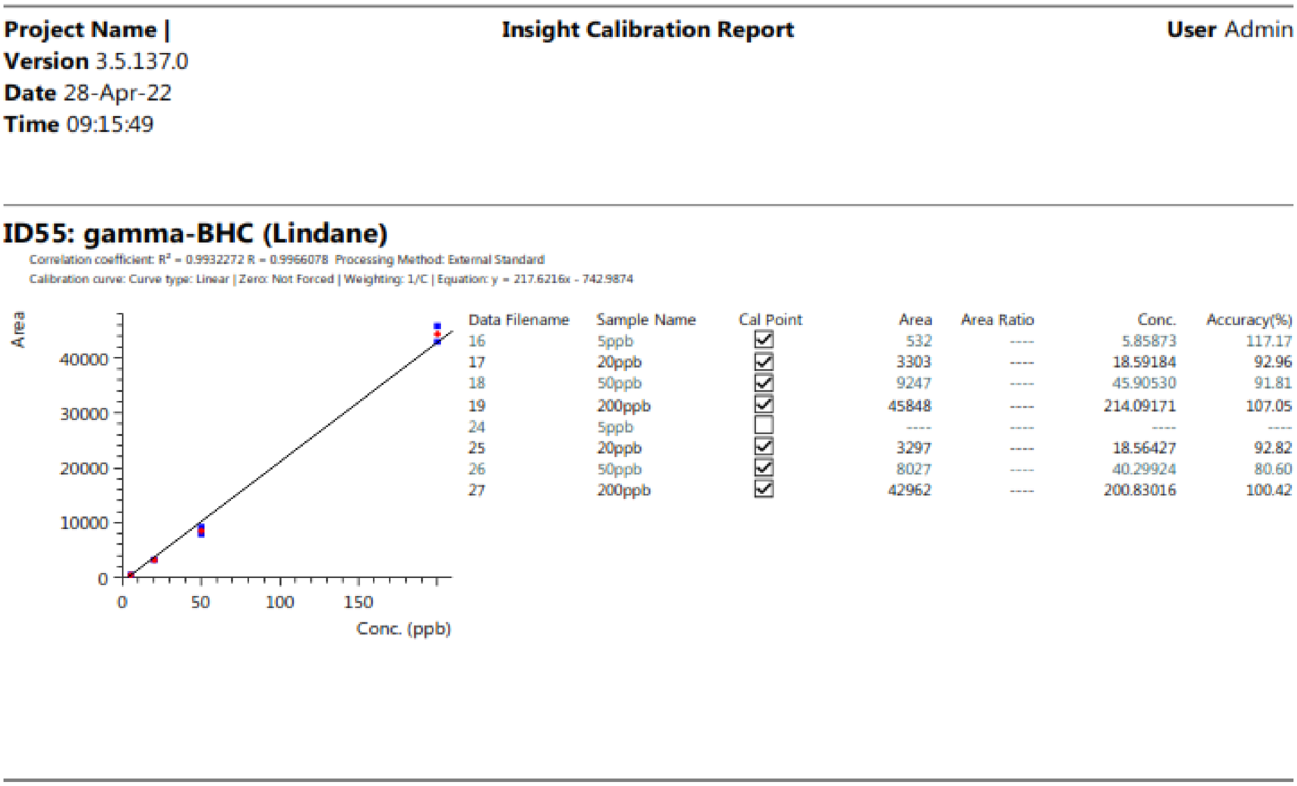
ID147: Methoxychlor

Correlation coefficient: R^2 = 0.9978624 R = 0.9989306 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 258.2897x - 791.5409

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	595	----	5.36816	107.36
17	20ppb	☑	4816	----	21.71028	108.55
18	50ppb	☑	11950	----	49.33043	98.66
19	200ppb	☑	52948	----	208.05918	104.03
24	5ppb	☐	----	----	----	----
25	20ppb	☑	3833	----	17.90447	89.52
26	50ppb	☑	10122	----	42.25310	84.51
27	200ppb	☑	50868	----	200.00621	100.00

10. Calibration curves of gamma-BHC (Lindane)



Project Name | **Insight Calibration Report** **User** Admin

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Date 28-Apr-22

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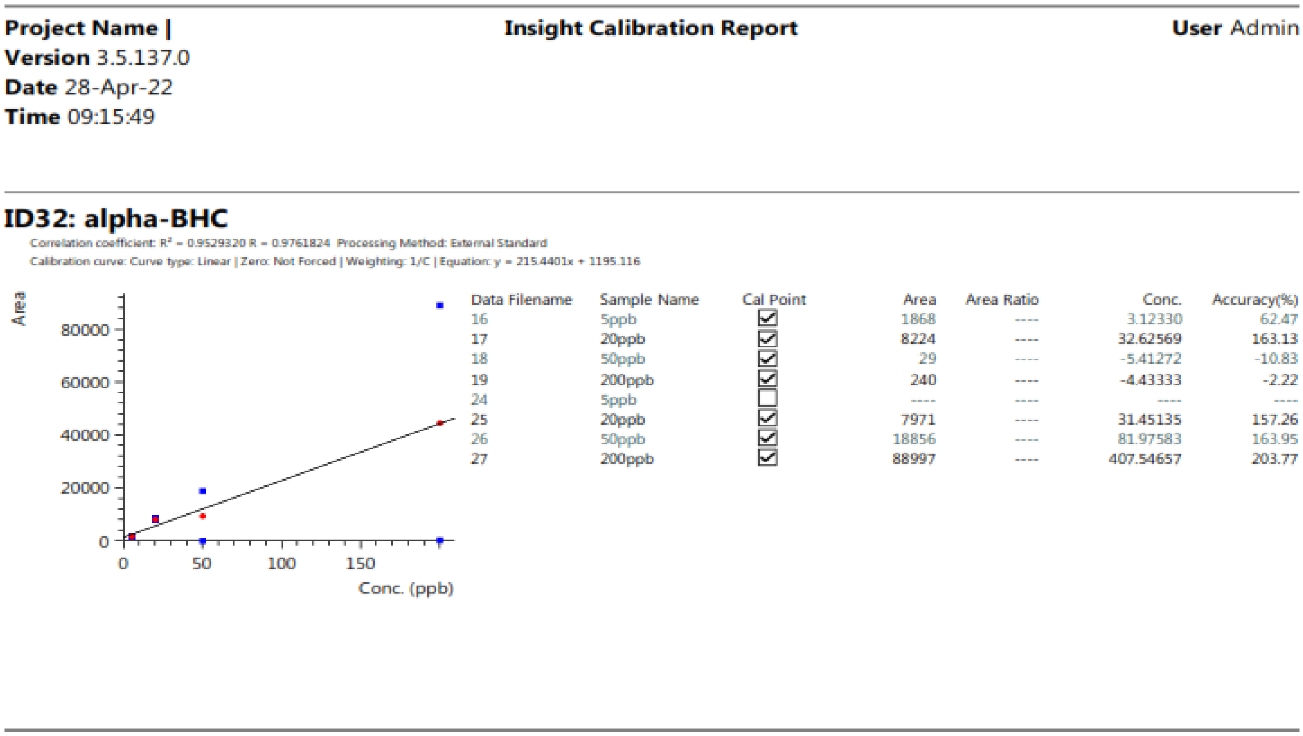
ID55: gamma-BHC (Lindane)

Correlation coefficient: R^2 = 0.9932272 R = 0.9966078 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 217.6216x - 742.9874

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	532	----	5.85873	117.17
17	20ppb	☑	3303	----	18.59184	92.96
18	50ppb	☑	9247	----	45.90530	91.81
19	200ppb	☑	45848	----	214.09171	107.05
24	5ppb	☐	----	----	----	----
25	20ppb	☑	3297	----	18.56427	92.82
26	50ppb	☑	8027	----	40.29924	80.60
27	200ppb	☑	42962	----	200.83016	100.42

11. Calibration curves of alpha-BHC (α-HCH)



Project Name | **Insight Calibration Report** **User** Admin

Version 3.5.137.0

Date 28-Apr-22

Time 09:15:49

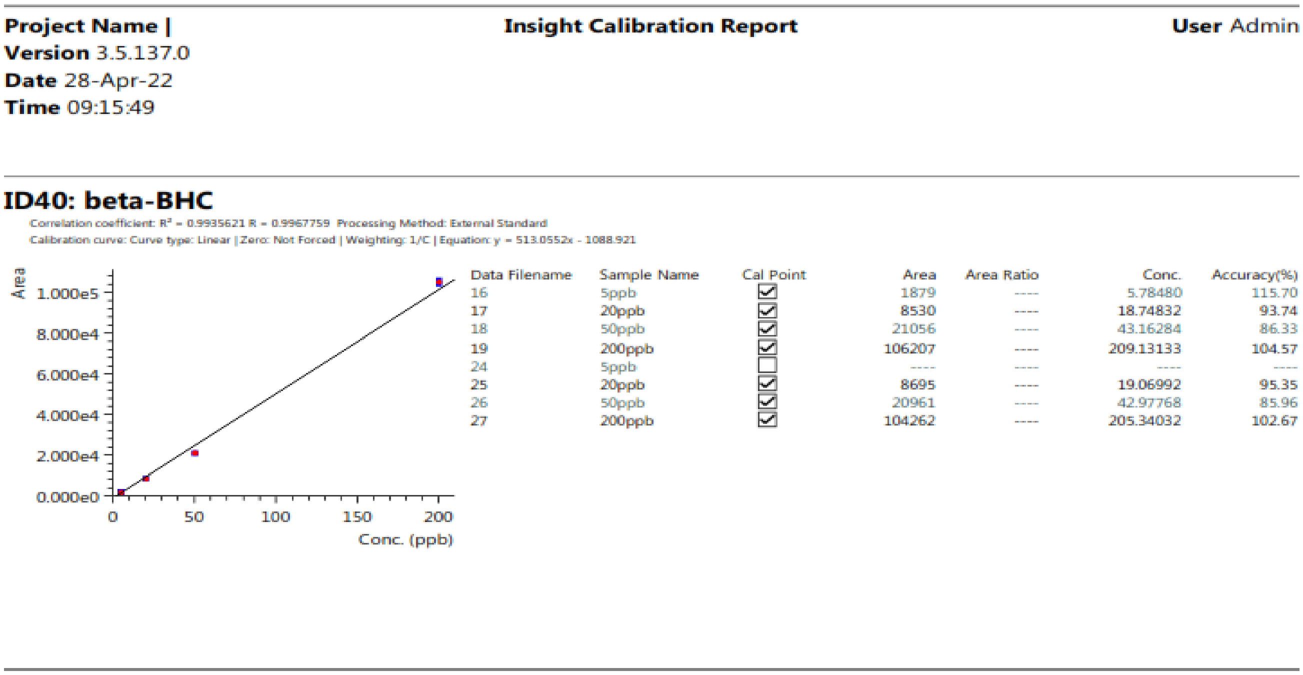
ID32: alpha-BHC

Correlation coefficient: R^2 = 0.9529320 R = 0.9761824 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 215.4401x + 1195.116

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	1868	----	3.12330	62.47
17	20ppb	☑	8224	----	32.62569	163.13
18	50ppb	☑	29	----	-5.41272	-10.83
19	200ppb	☑	240	----	-4.43333	-2.22
24	5ppb	☐	----	----	----	----
25	20ppb	☑	7971	----	31.45135	157.26
26	50ppb	☑	18856	----	81.97583	163.95
27	200ppb	☑	88997	----	407.54657	203.77

12. Calibration curves of beta-BHC (beta- hexachlorobenzene)



Project Name | **Insight Calibration Report** **User** Admin

Version 3.5.137.0

Date 28-Apr-22

Time 09:15:49

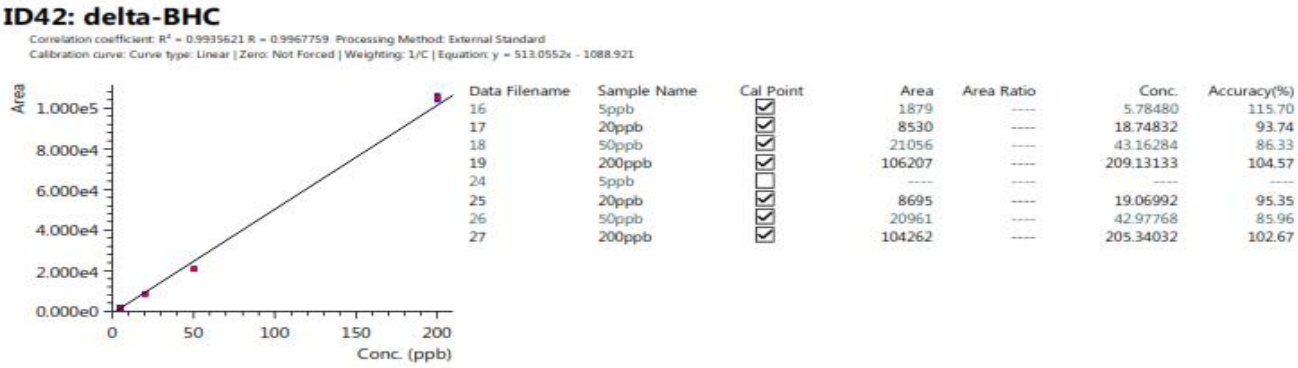
ID40: beta-BHC

Correlation coefficient: R^2 = 0.9935621 R = 0.9967759 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 513.0552x - 1088.921

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	1879	----	5.78480	115.70
17	20ppb	☑	8530	----	18.74832	93.74
18	50ppb	☑	21056	----	43.16284	86.33
19	200ppb	☑	106207	----	209.13133	104.57
24	5ppb	☐	----	----	----	----
25	20ppb	☑	8695	----	19.06992	95.35
26	50ppb	☑	20961	----	42.97768	85.96
27	200ppb	☑	104262	----	205.34032	102.67

13. Calibration curves of delta-BHC (delta- hexachlorobenzene)



ID42: delta-BHC

Correlation coefficient: R^2 = 0.9935621 R = 0.9967759 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 513.0552x - 1088.921

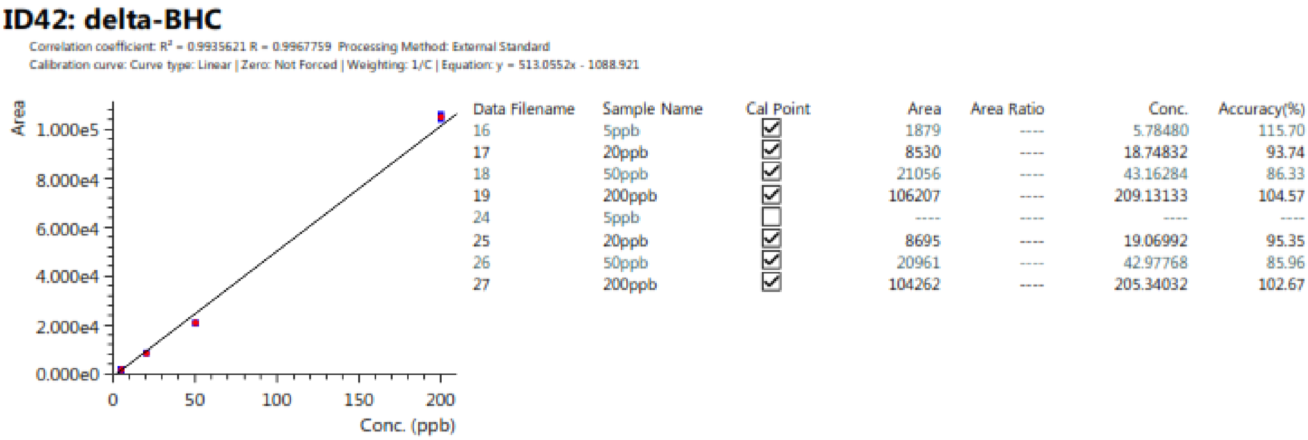
Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	1879	----	5.78480	115.70
17	20ppb	☑	8530	----	18.74832	93.74
18	50ppb	☑	21056	----	43.16284	86.33
19	200ppb	☑	106207	----	209.13133	104.57
24	5ppb	☐	----	----	----	----
25	20ppb	☑	8695	----	19.06992	95.35
26	50ppb	☑	20961	----	42.97768	85.96
27	200ppb	☑	104262	----	205.34032	102.67

Data path E:\GCMSMS_02\Data\2022\APRIL \1304202201 **Page 19 of 88** **Verified by**

Processing file 1304202201.damlp

Batch file

13. Calibration curves of delta-BHC



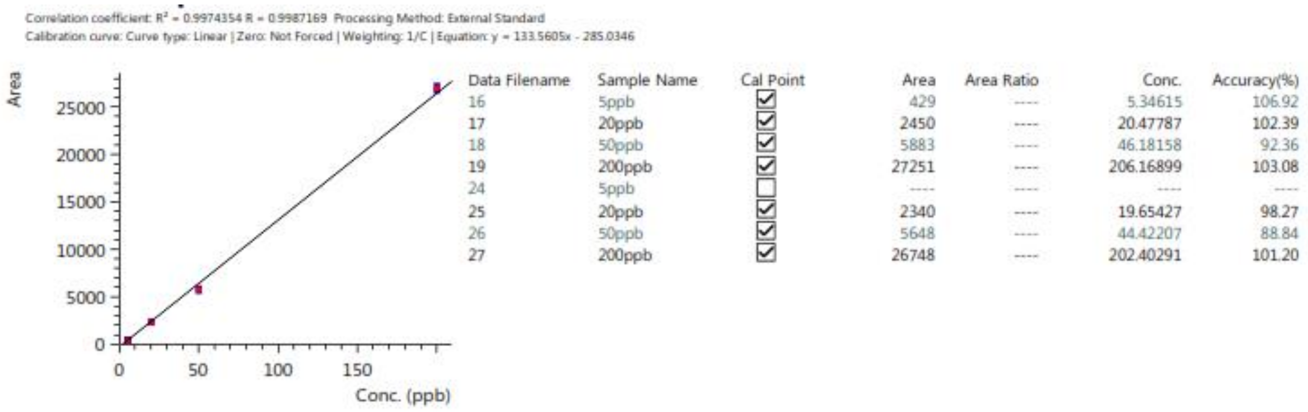
ID42: delta-BHC

Correlation coefficient: R^2 = 0.9935621 R = 0.9967759 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 513.0552x - 1088.921

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	1879	----	5.78480	115.70
17	20ppb	☑	8530	----	18.74832	93.74
18	50ppb	☑	21056	----	43.16284	86.33
19	200ppb	☑	106207	----	209.13133	104.57
24	5ppb	☐	----	----	----	----
25	20ppb	☑	8695	----	19.06992	95.35
26	50ppb	☑	20961	----	42.97768	85.96
27	200ppb	☑	104262	----	205.34032	102.67

14: **Calibration curves of o, p’- DDT**



Correlation coefficient: $R^2 = 0.9974354$ $R = 0.9987169$ Processing Method: External Standard

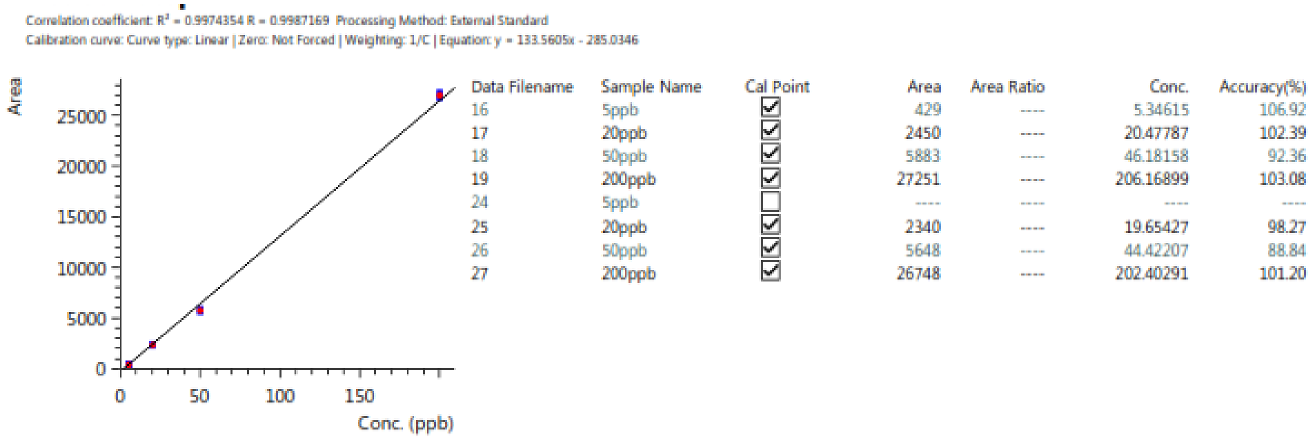
Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: $y = 133.5605x - 285.0346$

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	429	----	5.34615	106.92
17	20ppb	☑	2450	----	20.47787	102.39
18	50ppb	☑	5883	----	46.18158	92.36
19	200ppb	☑	27251	----	206.16899	103.08
24	5ppb	☐	----	----	----	----
25	20ppb	☑	2340	----	19.65427	98.27
26	50ppb	☑	5648	----	44.42207	88.84
27	200ppb	☑	26748	----	202.40291	101.20

Data path E:\GCMSMS_02\Data\2022\APRIL \1304202201 **Page 13 of 88** **Verified by**

Processing file 1304202201.damlp

Batch file

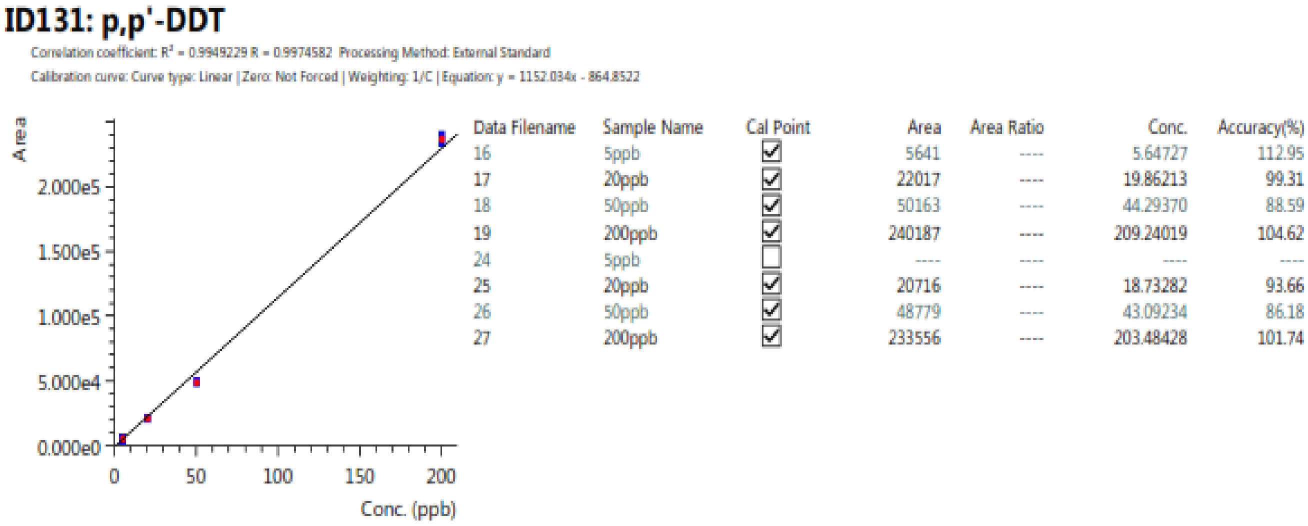


Correlation coefficient: $R^2 = 0.9974354$ $R = 0.9987169$ Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: $y = 133.5605x - 285.0346$

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	429	----	5.34615	106.92
17	20ppb	☑	2450	----	20.47787	102.39
18	50ppb	☑	5883	----	46.18158	92.36
19	200ppb	☑	27251	----	206.16899	103.08
24	5ppb	☐	----	----	----	----
25	20ppb	☑	2340	----	19.65427	98.27
26	50ppb	☑	5648	----	44.42207	88.84
27	200ppb	☑	26748	----	202.40291	101.20

15. Calibration curves of p, p'-DDT

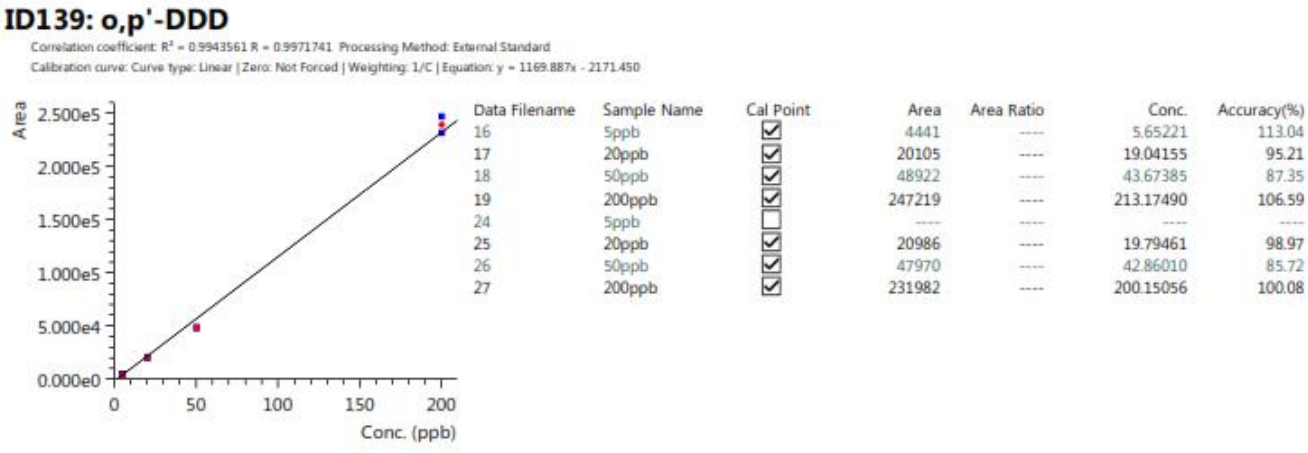

ID131: p,p'-DDT

Correlation coefficient: R^2 = 0.9949229 R = 0.9974582 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 1152.034x - 864.8522

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	5641	----	5.64727	112.95
17	20ppb	☑	22017	----	19.86213	99.31
18	50ppb	☑	50163	----	44.29370	88.59
19	200ppb	☑	240187	----	209.24019	104.62
24	5ppb	☐	----	----	----	----
25	20ppb	☑	20716	----	18.73282	93.66
26	50ppb	☑	48779	----	43.09234	86.18
27	200ppb	☑	233556	----	203.48428	101.74

16. Calibration curves of o, p'-DDD

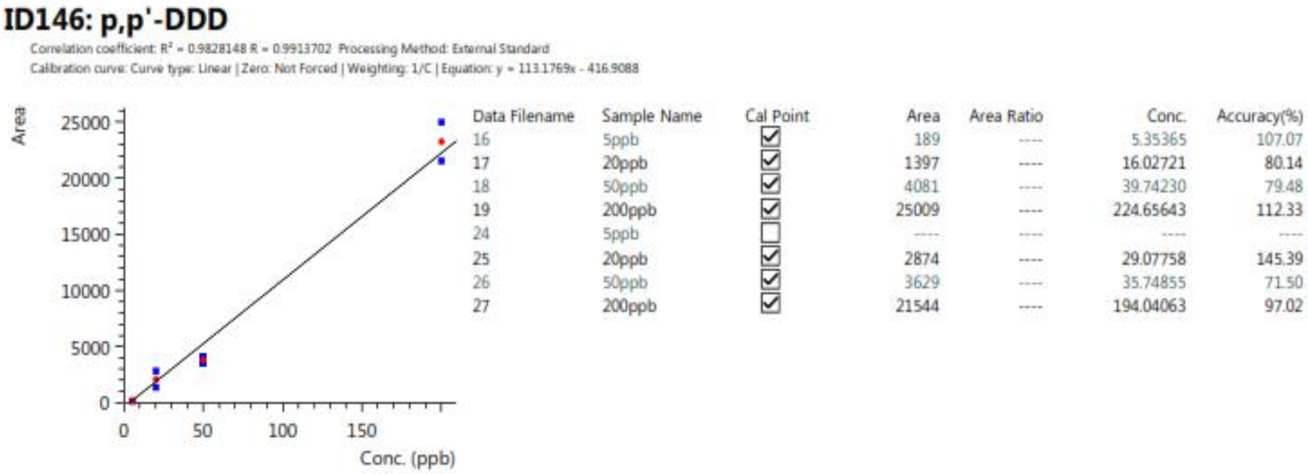

ID139: o,p'-DDD

Correlation coefficient: R^2 = 0.9943561 R = 0.9971741 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 1169.887x - 2171.450

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	4441	----	5.65221	113.04
17	20ppb	☑	20105	----	19.04155	95.21
18	50ppb	☑	48922	----	43.67385	87.35
19	200ppb	☑	247219	----	213.17490	106.59
24	5ppb	☐	----	----	----	----
25	20ppb	☑	20986	----	19.79461	98.97
26	50ppb	☑	47970	----	42.86010	85.72
27	200ppb	☑	231982	----	200.15056	100.08

17. Calibration curves of p, p’-DDD



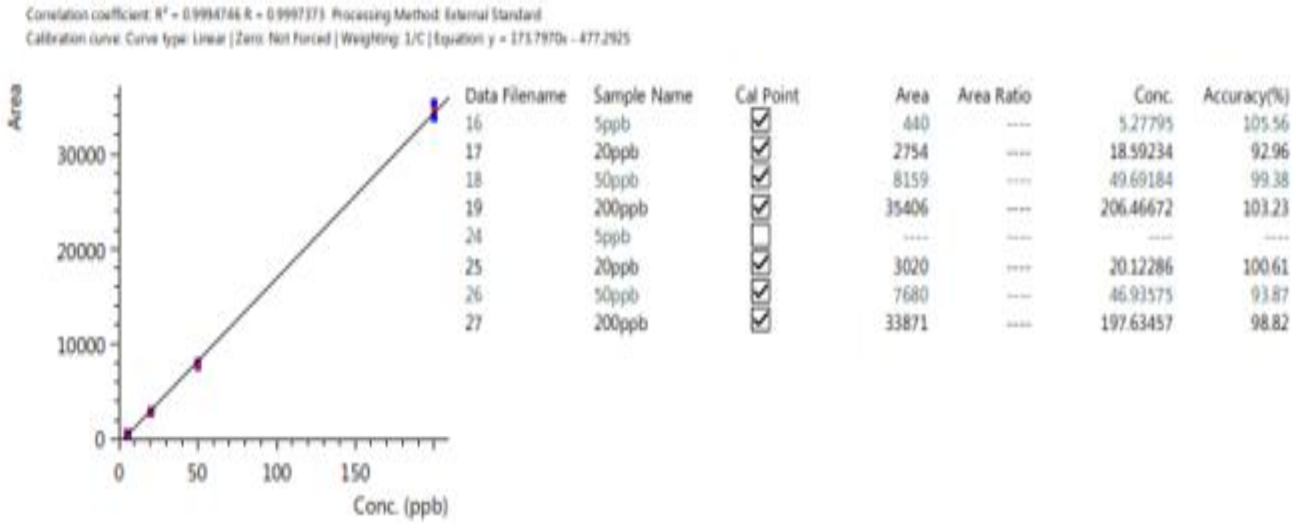
ID146: p,p'-DDD

Correlation coefficient: R^2 = 0.9828148 R = 0.9913702 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 113.1769x - 416.9088

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	189	----	5.35365	107.07
17	20ppb	☑	1397	----	16.02721	80.14
18	50ppb	☑	4081	----	39.74230	79.48
19	200ppb	☑	25009	----	224.65643	112.33
24	5ppb	☐	----	----	----	----
25	20ppb	☑	2874	----	29.07758	145.39
26	50ppb	☑	3629	----	35.74855	71.50
27	200ppb	☑	21544	----	194.04063	97.02

18. Calibration curves of o, p’-DDE

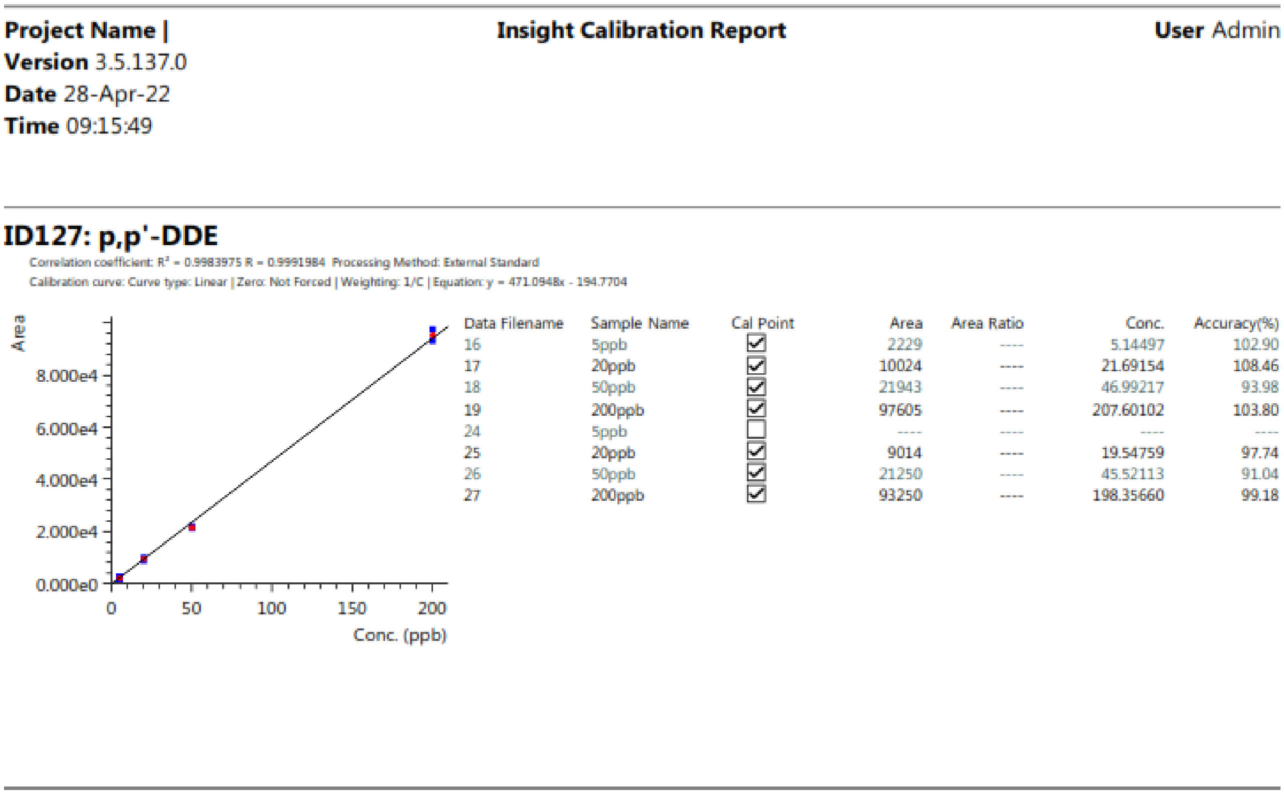


Correlation coefficient: R^2 = 0.9994746 R = 0.9997373 Processing Method: External Standard

Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 173.7970x - 477.2925

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	440	----	5.27795	105.56
17	20ppb	☑	2754	----	18.59234	92.96
18	50ppb	☑	8159	----	49.69184	99.38
19	200ppb	☑	35406	----	206.46672	103.23
24	5ppb	☐	----	----	----	----
25	20ppb	☑	3020	----	20.12286	100.61
26	50ppb	☑	7680	----	46.93575	93.87
27	200ppb	☑	33871	----	197.63457	98.82

19. Calibration curves of p, p'-DDE



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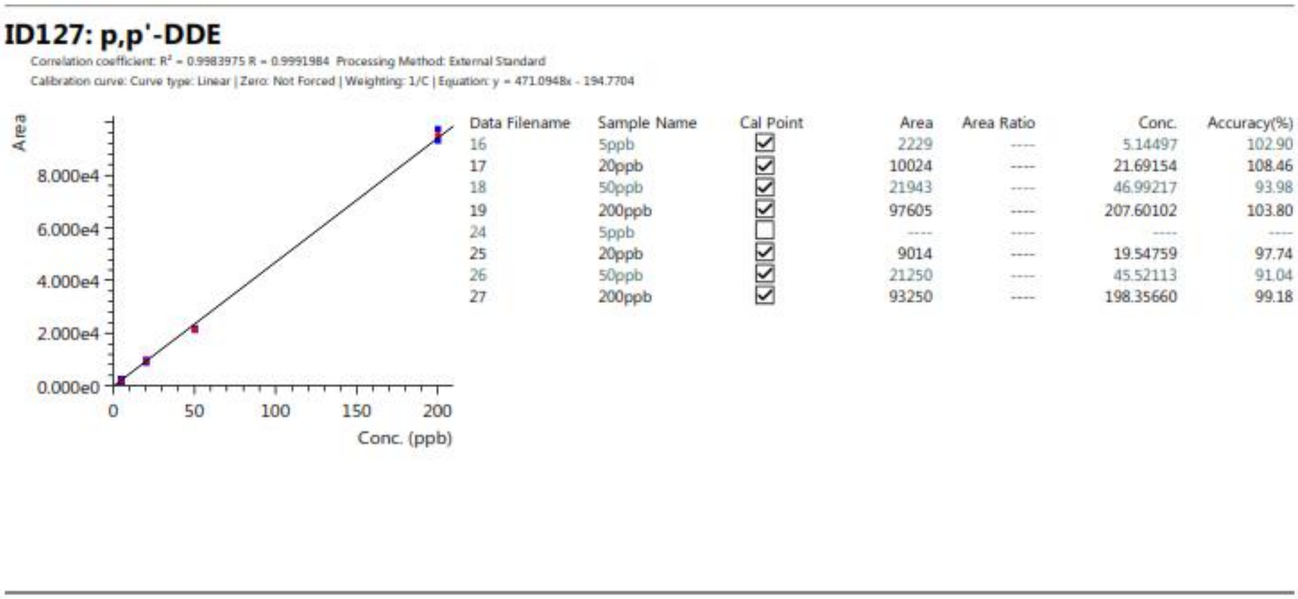
User Admin

ID127: p,p'-DDE

Correlation coefficient: R^2 = 0.9983975 R = 0.9991984 Processing Method: External Standard
Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 471.0948x - 194.7704

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	2229	----	5.14497	102.90
17	20ppb	☑	10024	----	21.69154	108.46
18	50ppb	☑	21943	----	46.99217	93.98
19	200ppb	☑	97605	----	207.60102	103.80
24	5ppb	☐	----	----	----	----
25	20ppb	☑	9014	----	19.54759	97.74
26	50ppb	☑	21250	----	45.52113	91.04
27	200ppb	☑	93250	----	198.35660	99.18

19. Calibration curves of p, p'-DDE



ID127: p,p'-DDE

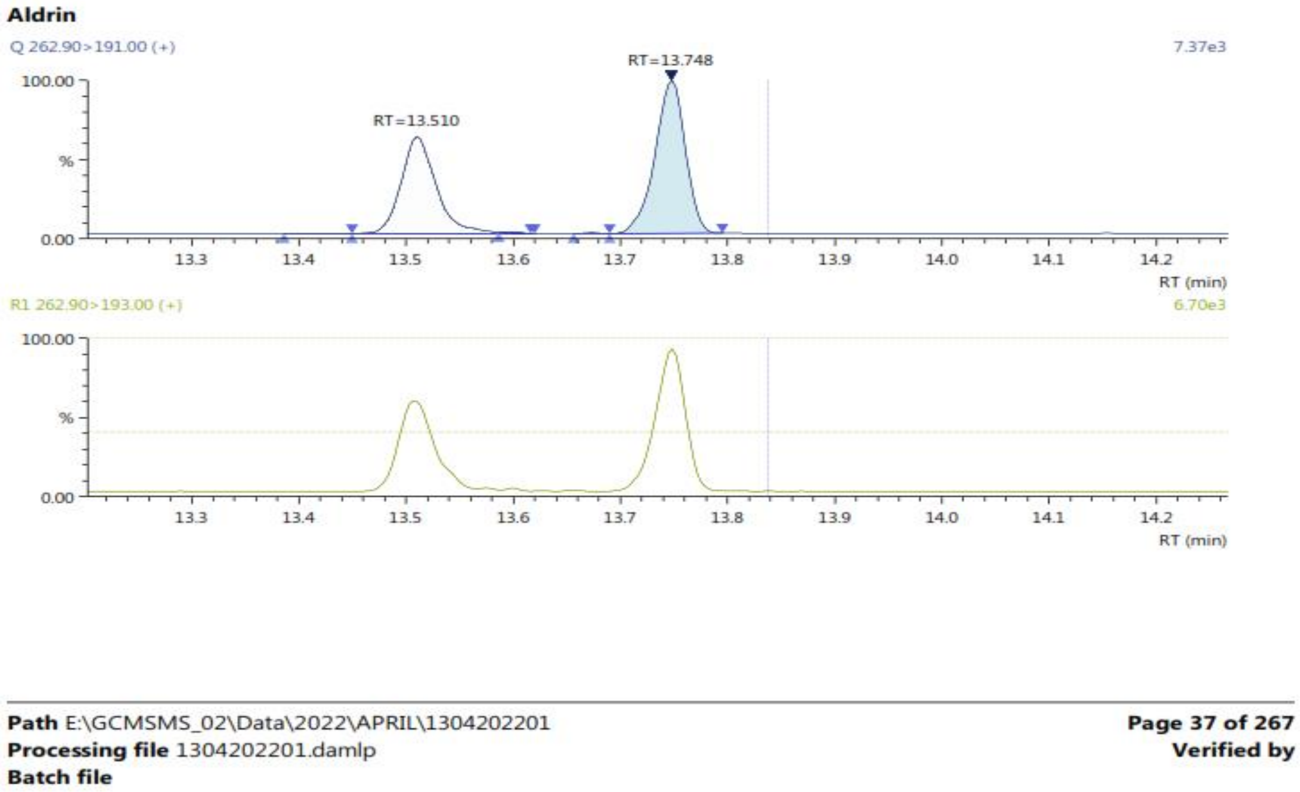
Correlation coefficient: R^2 = 0.9983975 R = 0.9991984 Processing Method: External Standard
Calibration curve: Curve type: Linear | Zero: Not Forced | Weighting: 1/C | Equation: y = 471.0948x - 194.7704

Data Filename	Sample Name	Cal Point	Area	Area Ratio	Conc.	Accuracy(%)
16	5ppb	☑	2229	----	5.14497	102.90
17	20ppb	☑	10024	----	21.69154	108.46
18	50ppb	☑	21943	----	46.99217	93.98
19	200ppb	☑	97605	----	207.60102	103.80
24	5ppb	☐	----	----	----	----
25	20ppb	☑	9014	----	19.54759	97.74
26	50ppb	☑	21250	----	45.52113	91.04
27	200ppb	☑	93250	----	198.35660	99.18

Appendix II: Mean percentage recoveries, Limit of Detection (LOD), and Limit of Quantification (LOQ) for organochlorine pesticide residues

ORGANO CHLORINE PESTICIDES RESIDUES (OCPs)	**OCPs IN WATER SAMPLES**				**OCPs IN SEDIMENT SAMPLES**			
	Water sample(µg/L)				**Sediment samples (µg/kg dry wt)**			
	Mean value±SD	**%Recovery in water sample**	**LOD in Water samples**	**LOQ in Water samples**	**Mean value ±SD**	**%Recovery in sediment samples**	**LOD in sediment sample**	**LOQ in sediment sample**
Aldrin	0.0483±0.00057	87.21 ± 0.33	0.00188	0.0057	1.9941±0.00068	78.08 ± 2.04	0.00224	0.0068
Dieldrin	0.0931±0.00061	91.35 ± 1.06	0.00201	0.0061	2.8971±0.00079	80.13 ± 1.61	0.00260	0.0079
Endosulfan Sulphate	0.0754±0.00057	79.11 ± 0.82	0.00188	0.0057	1.4538±0.02963	84.07 ± 0.95	0.09748	0.2963
α - endosulfan	0.0296±0.00062	81.54 ± 1.16	0.00204	0.0062	1.3307±0.00071	79.92 ± 1.33	0.00234	0.0071
β - endosulfan	0.0461±0.00057	83.78 ± 1.31	0.00188	0.0057	0.2744±0.00070	80.04 ± 2.27	0.00230	0.0070
Endrin	0.0512±0.00059	88.26 ± 2.03	0.00194	0.0059	1.9080±0.00553	75.51 ± 1.12	0.01819	0.0553
Heptachlor	0.0260±0.00061	76.12 ± 0.46	0.00201	0.0061	0.4029±0.02959	81.97 ± 0.78	0.09735	0.2959
Heptachlor -epoxide	0.0351±0.00057	94.08 ± 0.27	0.00188	0.0057	0.9515±0.00066	79.05 ± 0.96	0.00217	0.0066
Methoxychlor	0.0663±0.00917	90.44 ± 1.05	0.03017	0.0917	2.5354±0.00077	93.18 ± 0.89	0.00253	0.0077
Lindane	0.0446±0.00058	82.03± 2.11	0.00191	0.0058	1.8896±0.00066	88.01 ± 2.14	0.00217	0.0066
α - HCH	0.0200±0.00055	78.70 ± 0.92	0.00181	0.0055	1.9637±0.08734	90.43 ± 2.07	0.02873	0.8734
β - HCH	0.0342±0.00052	77.56 ± 0.88	0.00171	0.0052	1.2861±0.00082	82.75 ± 1.93	0.00269	0.0082
δ - HCH	0.0078±0.00049	79.82 ± 1.12	0.00161	0.0049	1.4074±0.05537	83.32 ± 2.11	0.01822	0.5537
o, p’- DDT	0.0081±0.00040	83.14 ± 2.57	0.00132	0.0040	0.8948±0.00646	78.94 ± 0.88	0.02125	0.0646
p, p’- DDT	0.0247±0.00059	80.25 ± 1.09	0.00194	0.0059	1.3646±0.02976	91.55 ± 1.75	0.09791	0.2976
o, p’- DDD	0.0088±0.00051	79.91 ± 0.98	0.00168	0.0051	0.3347±0.00075	87.01 ± 1.09	0.00247	0.0075
p, p’- DDD	0.0336±0.00057	92.13 ± 1.87	0.00188	0.0057	1.8500±0.00673	84.44 ± 1.72	0.02214	0.0673
o, p'- DDE	0.0265±0.00060	94.01 ± 2.21	0.00197	0.0060	0.2350±0.00150	92.06 ± 0.95	0.00494	0.0150
p, p’- DDE	0.0107±0.00045	78.55 ± 0.69	0.00148	0.0045	0.3206±0.00587	89.93 ± 1.09	0.01932	0.0587

Appendix III: Chromatograms of some of the organochlorine pesticides studied



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Batch file

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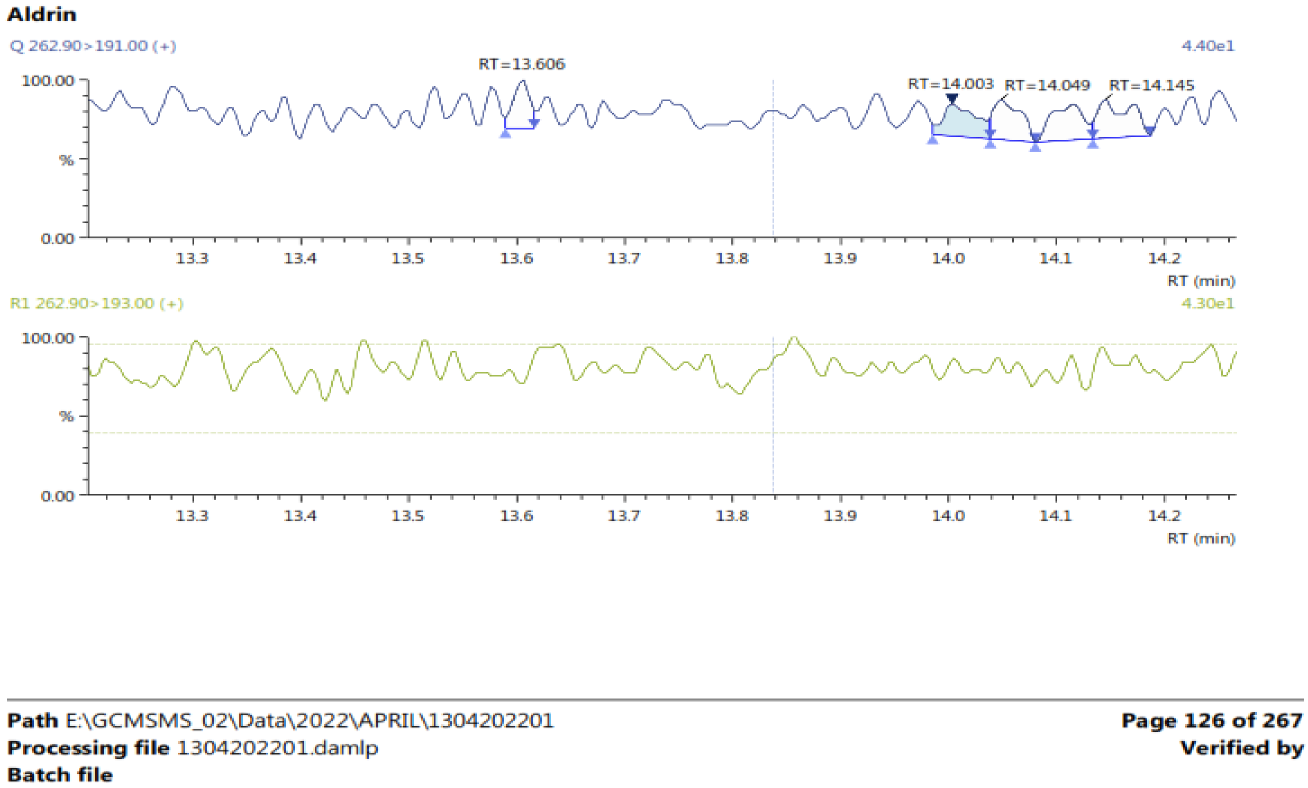

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Processing file 1304202201.damlp
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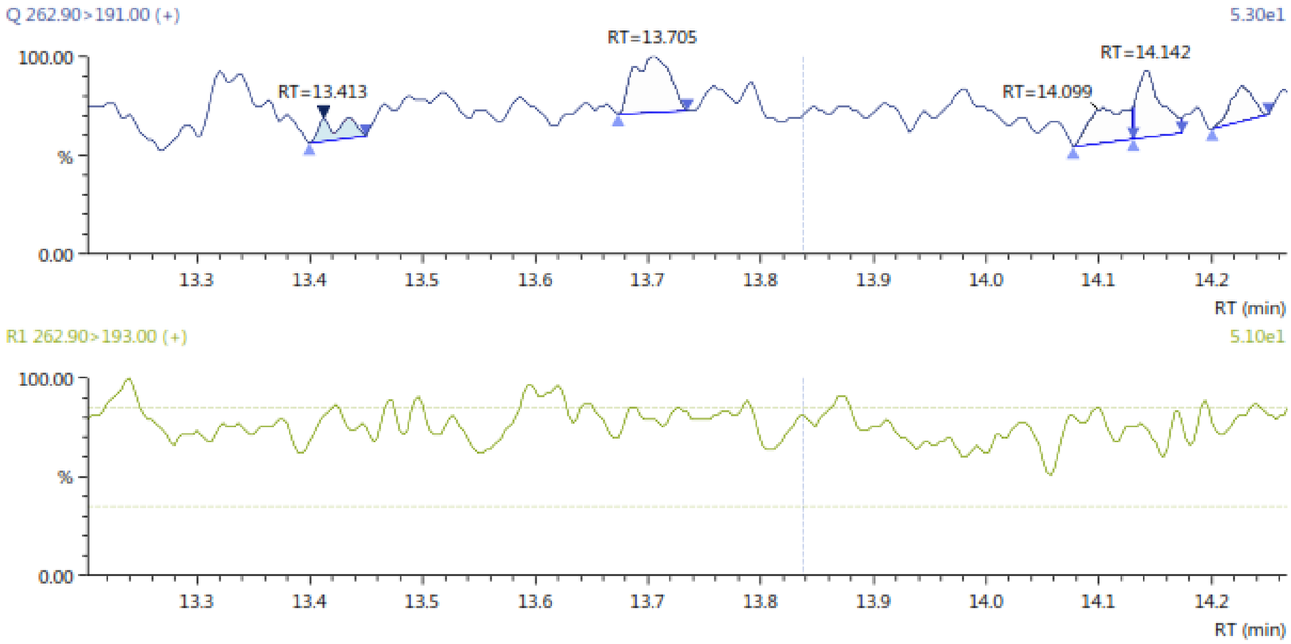
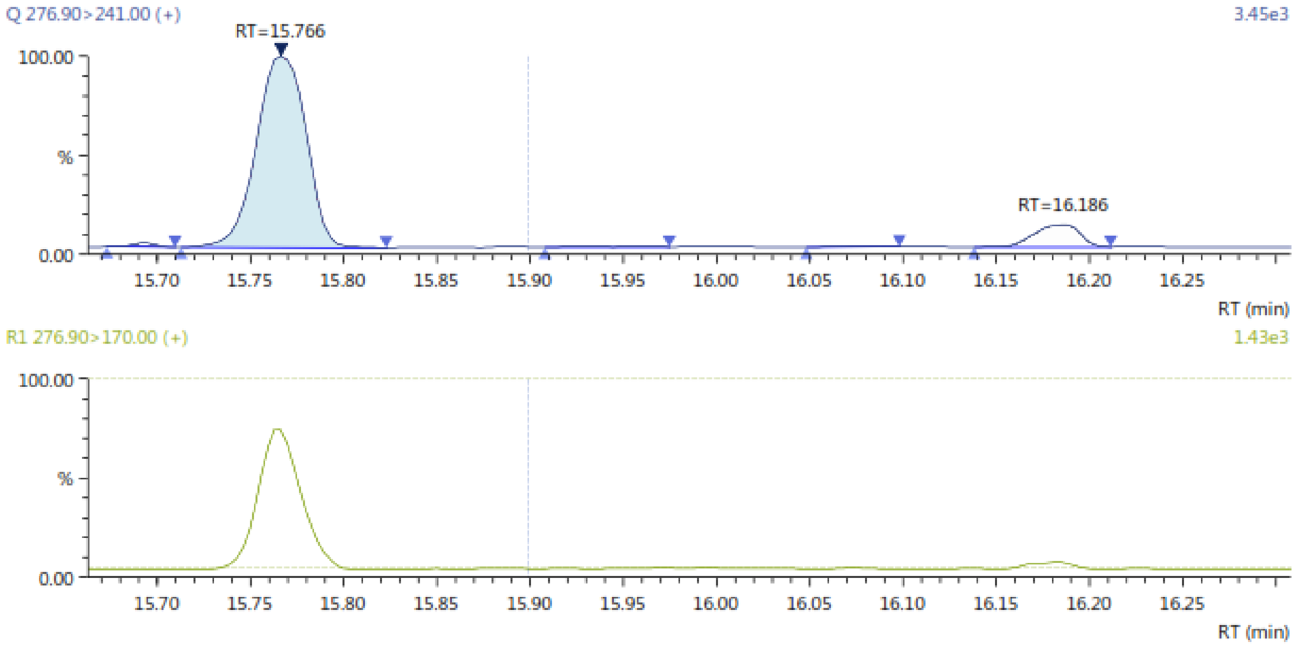
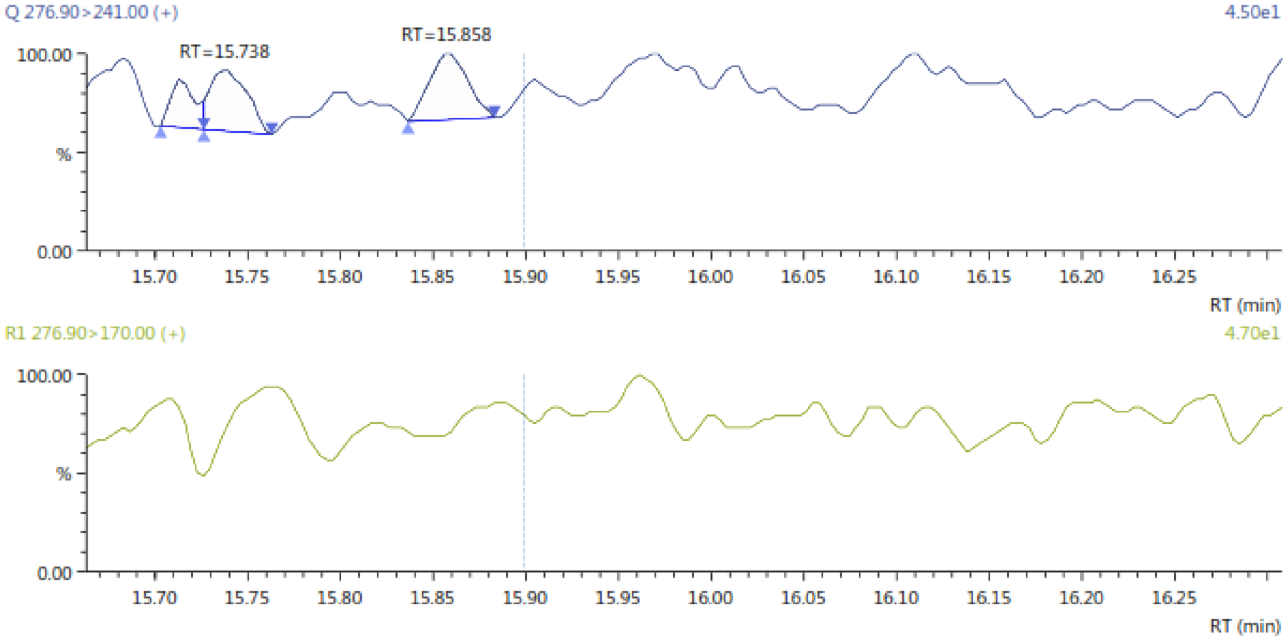
Aldrin



Dieldrin



Dieldrin



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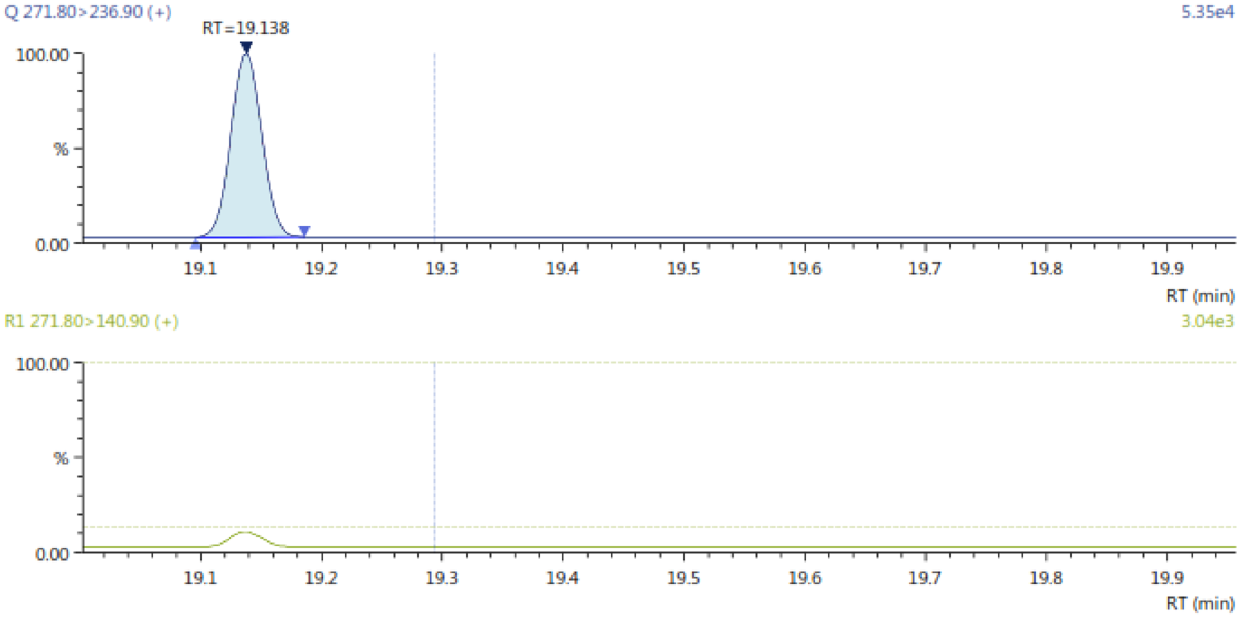
Endosulfan sulfate



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Insight Chromatogram Report

User ID Admin

Date 28-Apr-22

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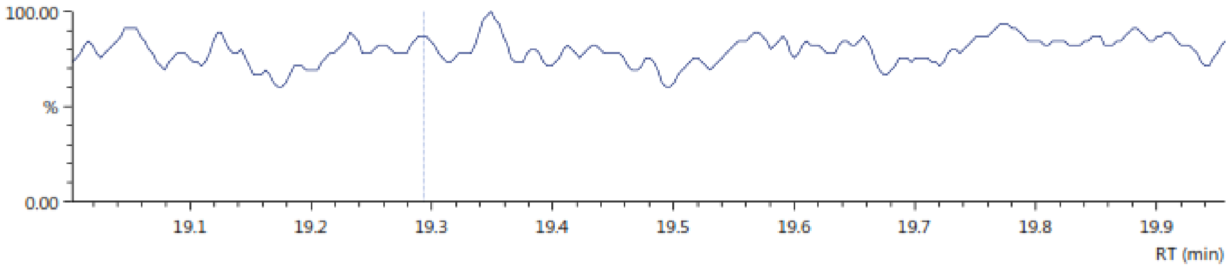
Endosulfan sulfate

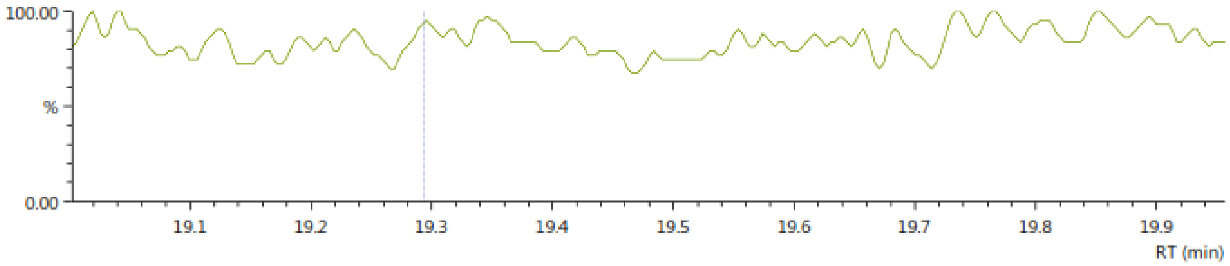
Q 271.80>236.90 (+)

4.40e1



R1 271.80>140.90 (+)

4.20e1



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Insight Chromatogram Report

User ID Admin

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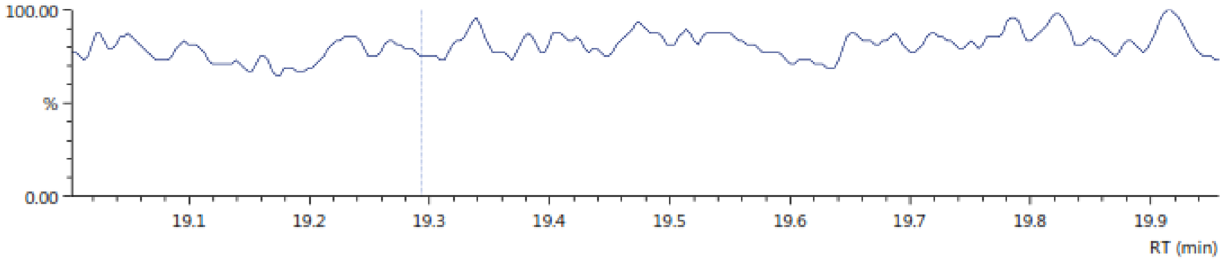
Endosulfan sulfate

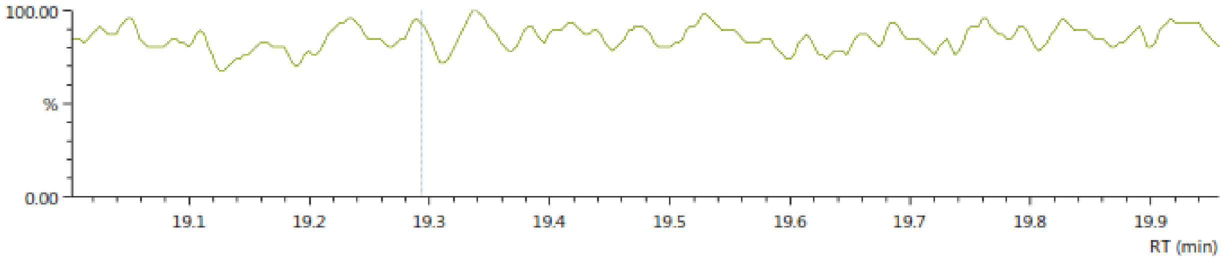
Q 271.80>236.90 (+)

4.70e1



R1 271.80>140.90 (+)

4.50e1



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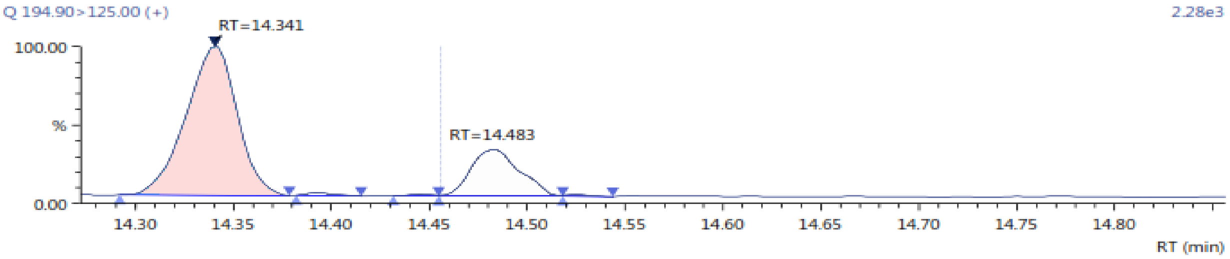
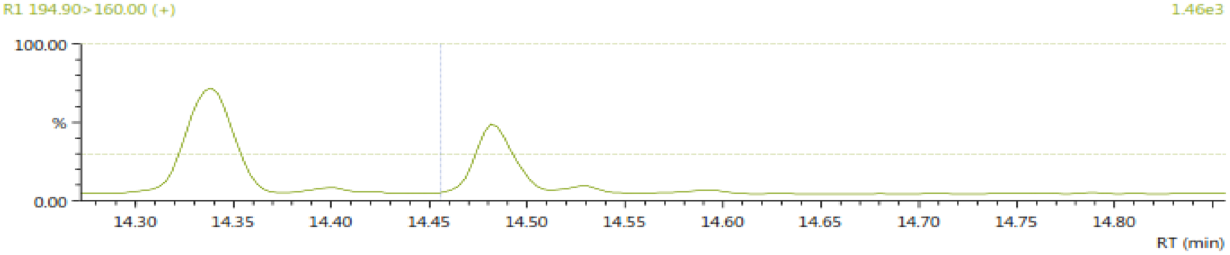
alpha-Endosulfan





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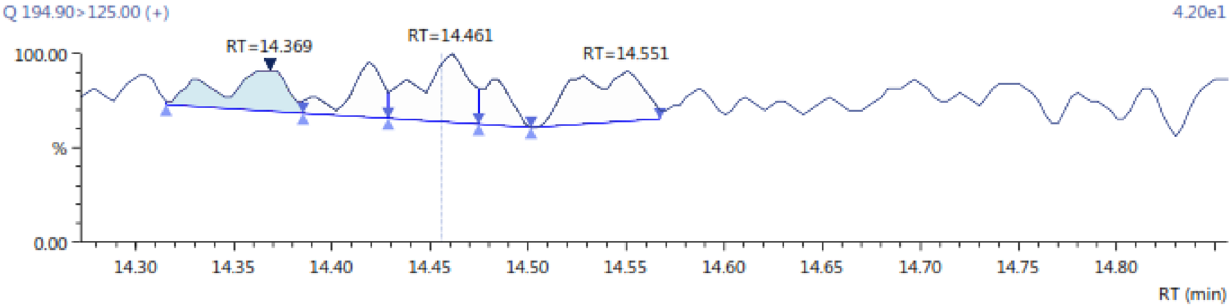
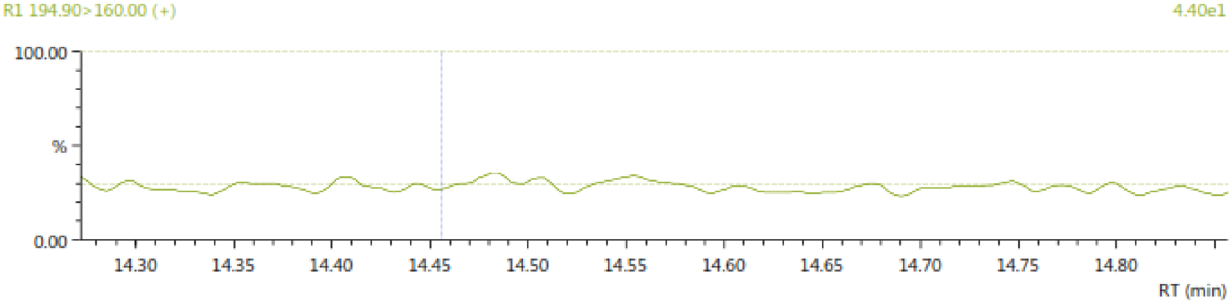
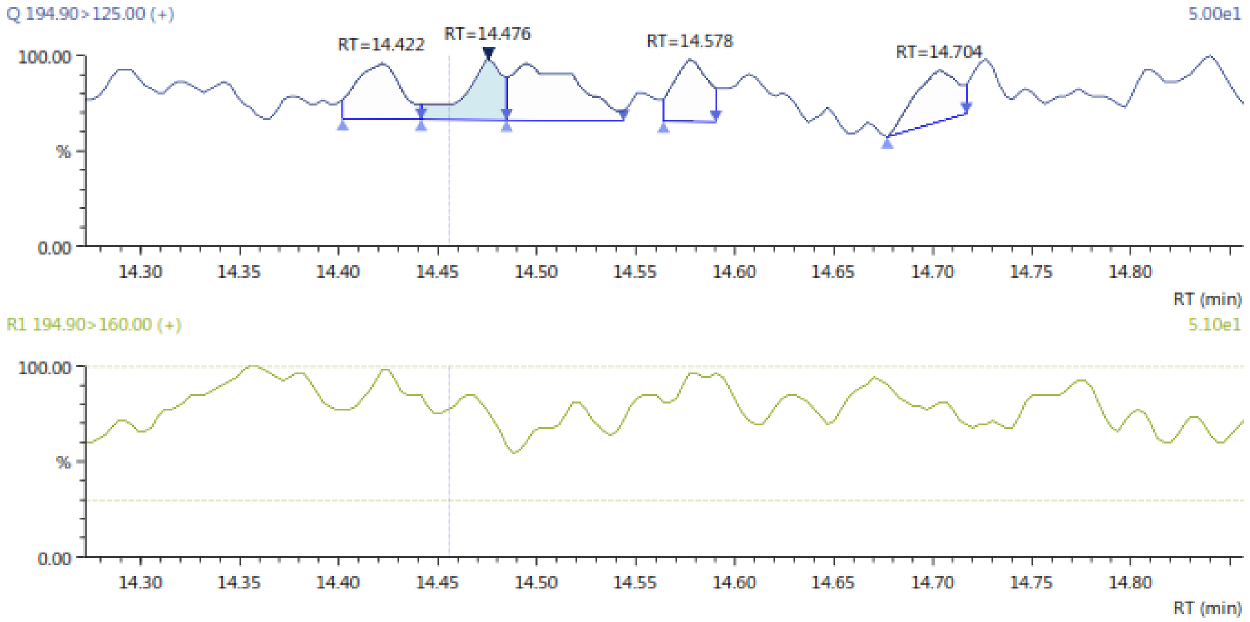
alpha-Endosulfan

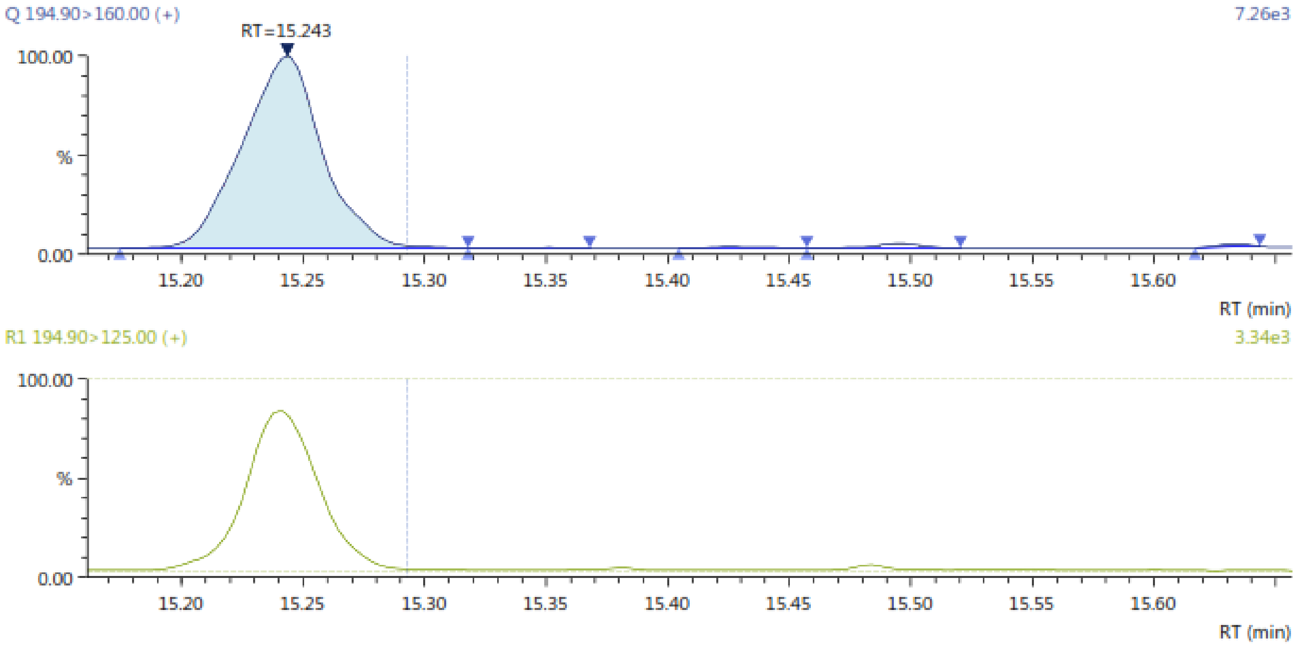




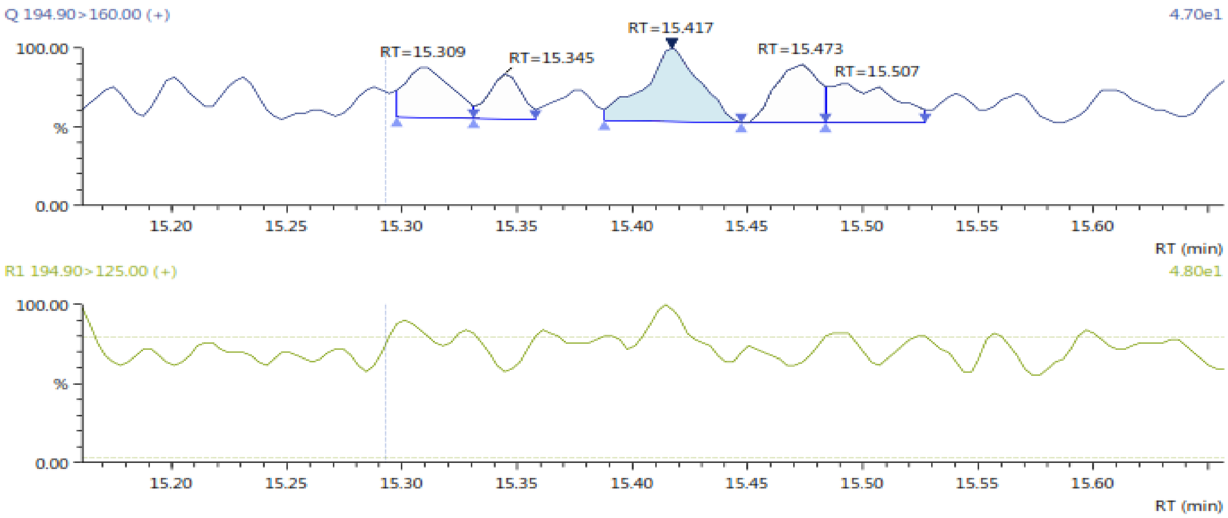
alpha-Endosulfan



beta-Endosulfan



beta-Endosulfan



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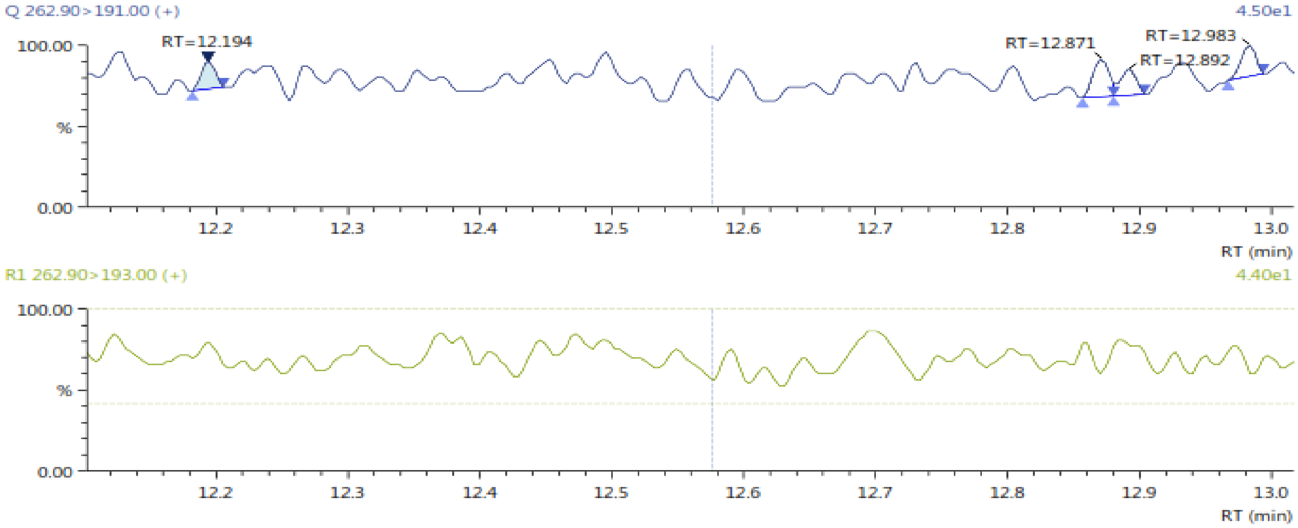
Endrin



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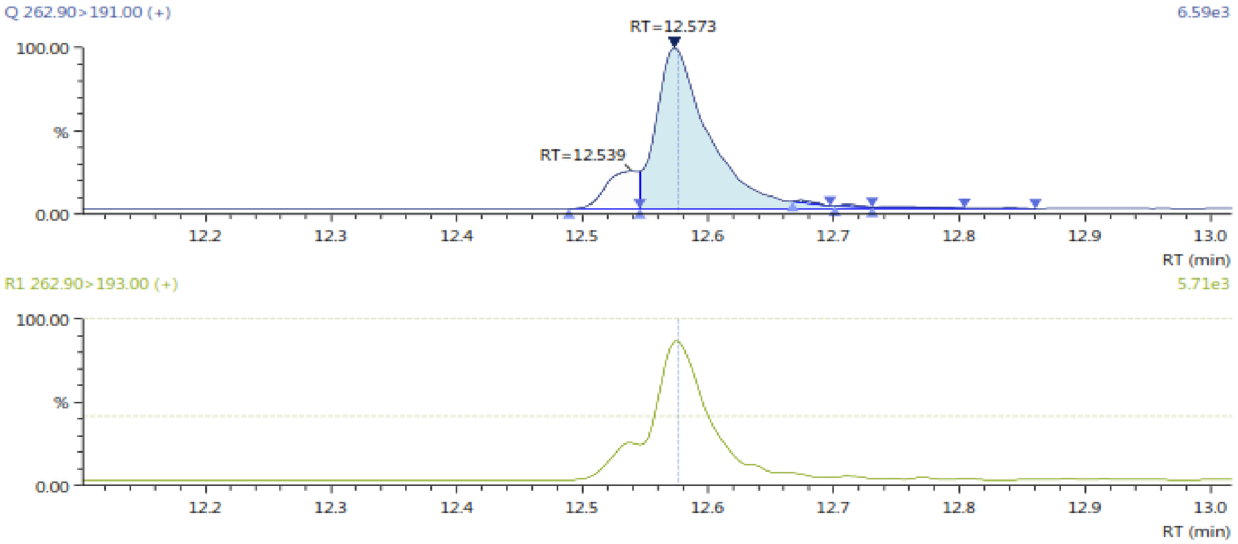

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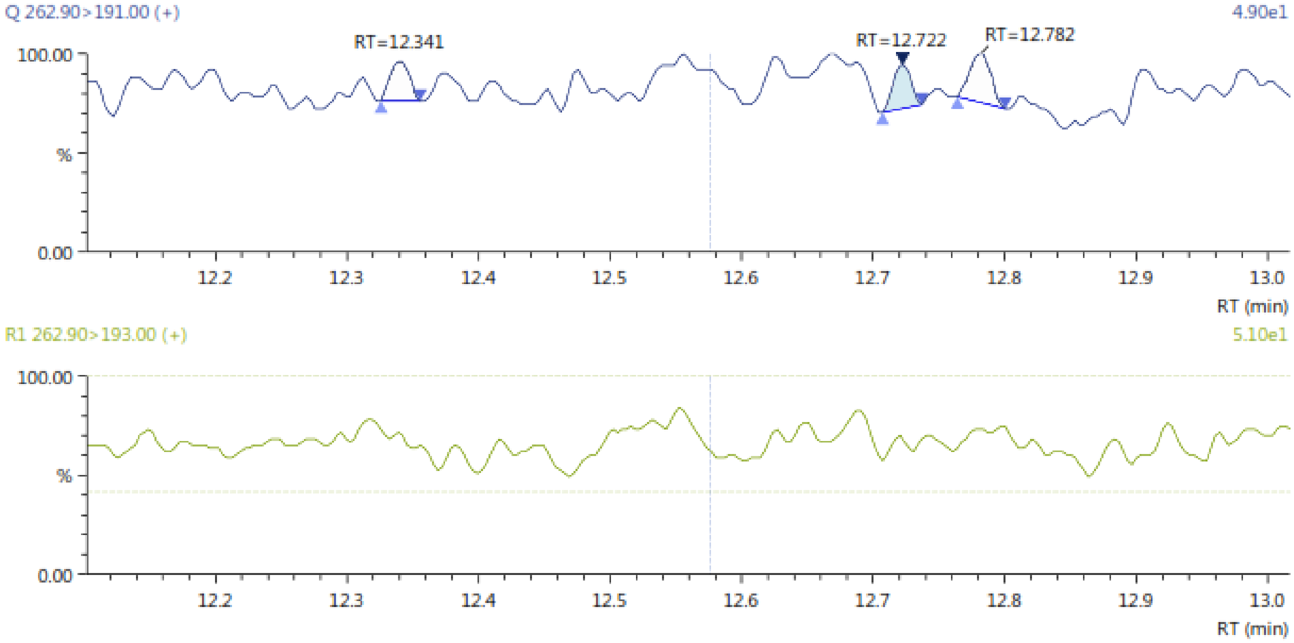
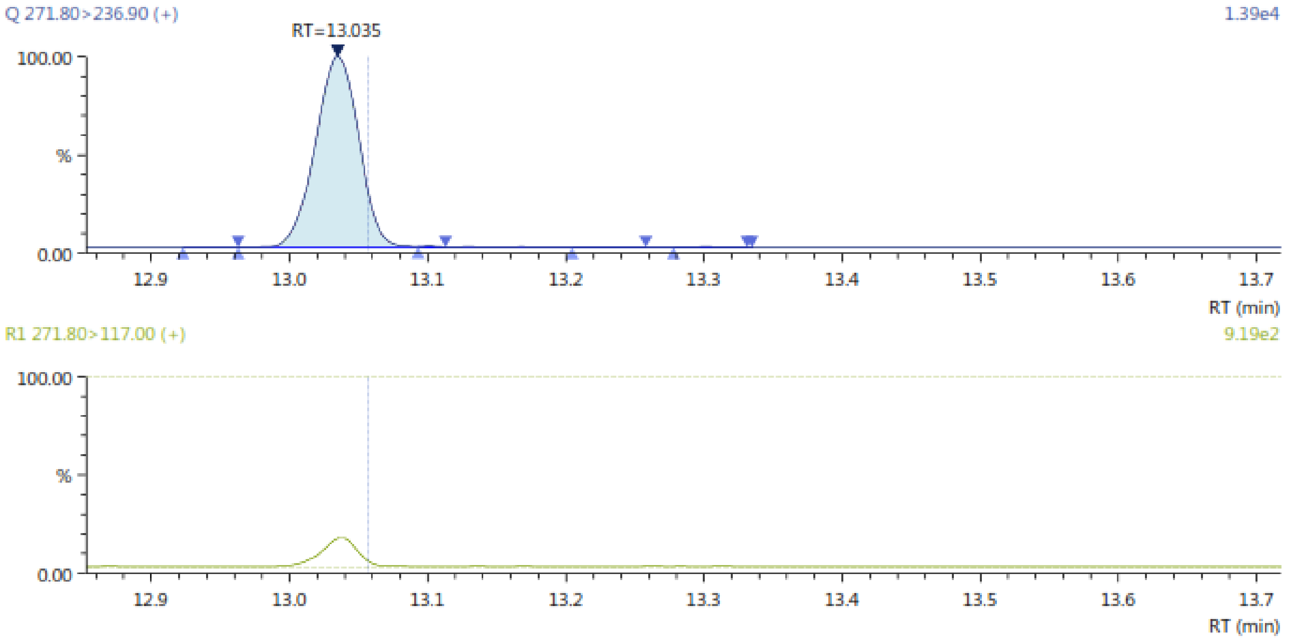
Endrin



Heptachlor



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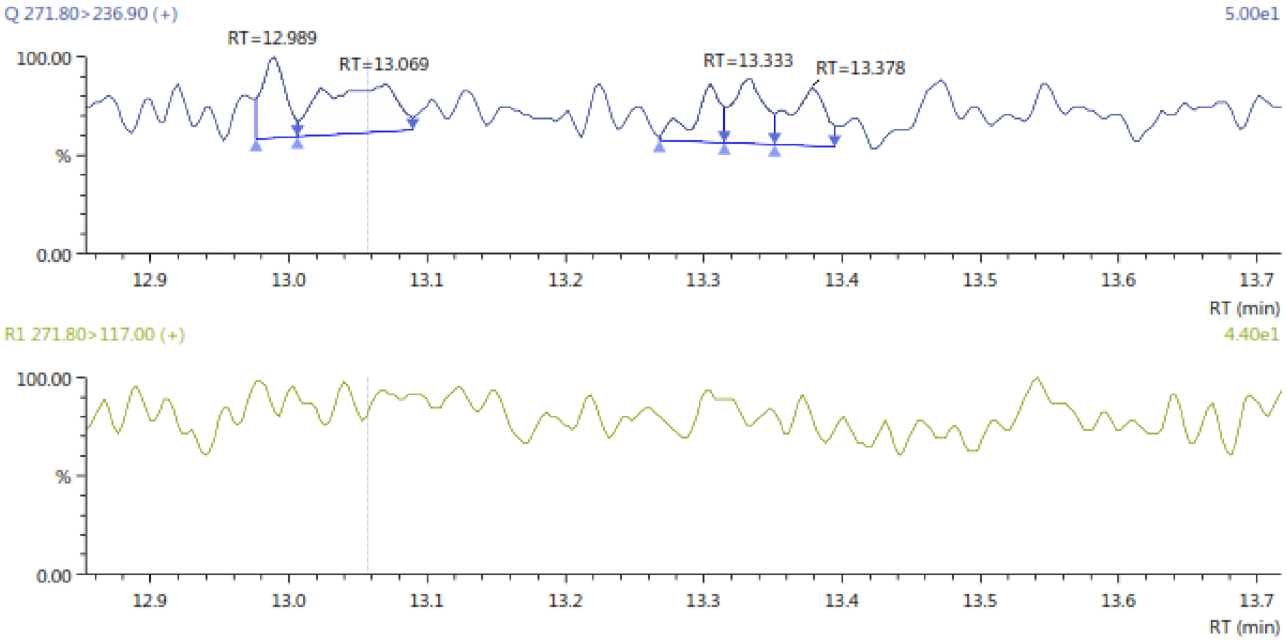
Heptachlor



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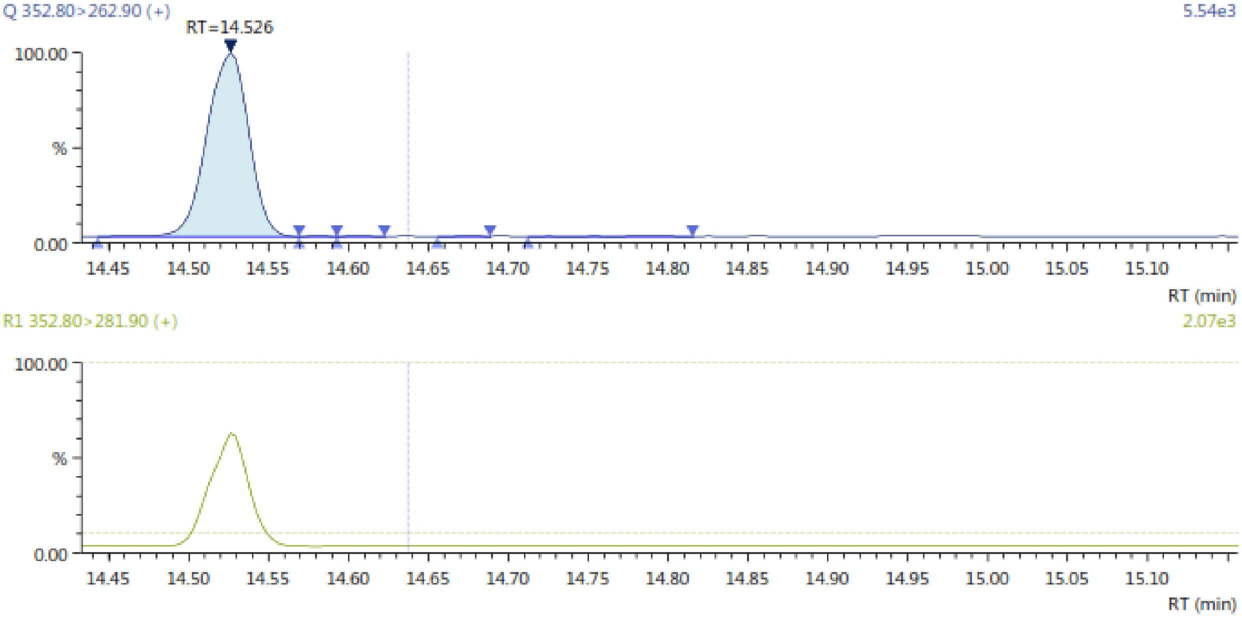
Heptachlor-exo-epoxide



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Date 28-Apr-22
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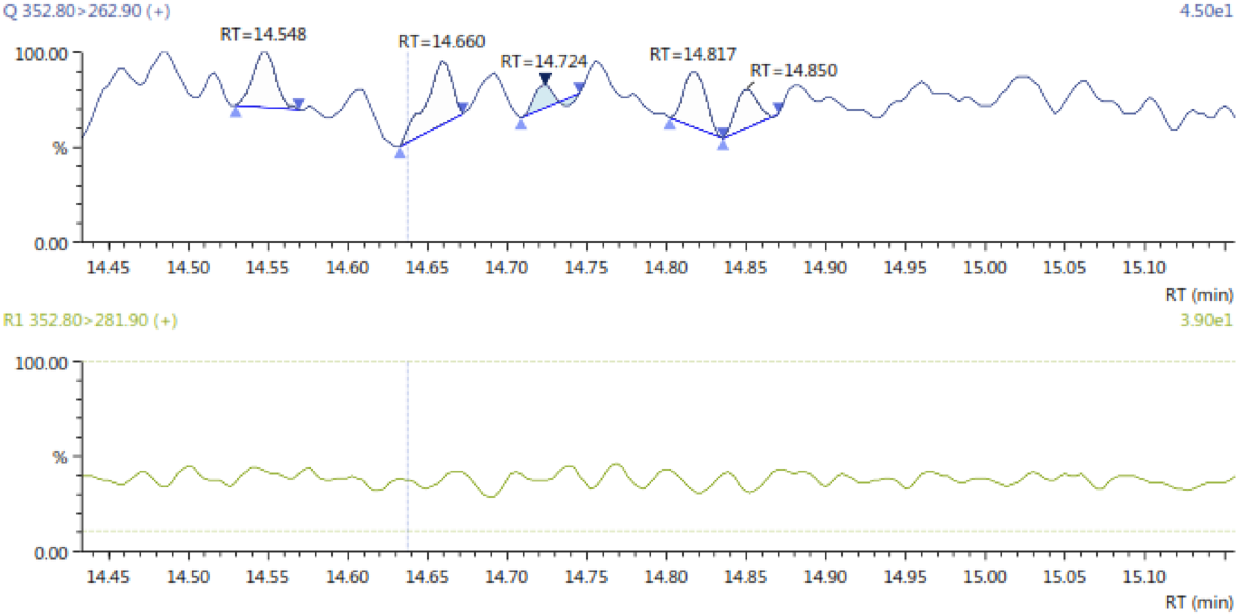
Heptachlor-exo-epoxide



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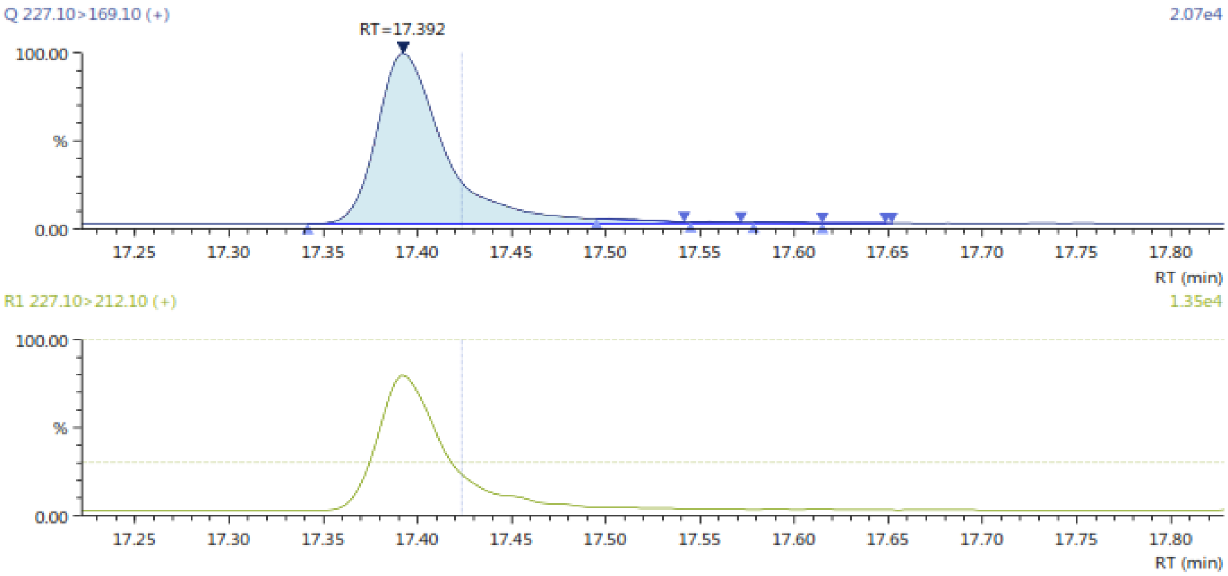
Methoxychlor



Project Version 3.5.137.0 **Insight Chromatogram Report** **User ID** Admin

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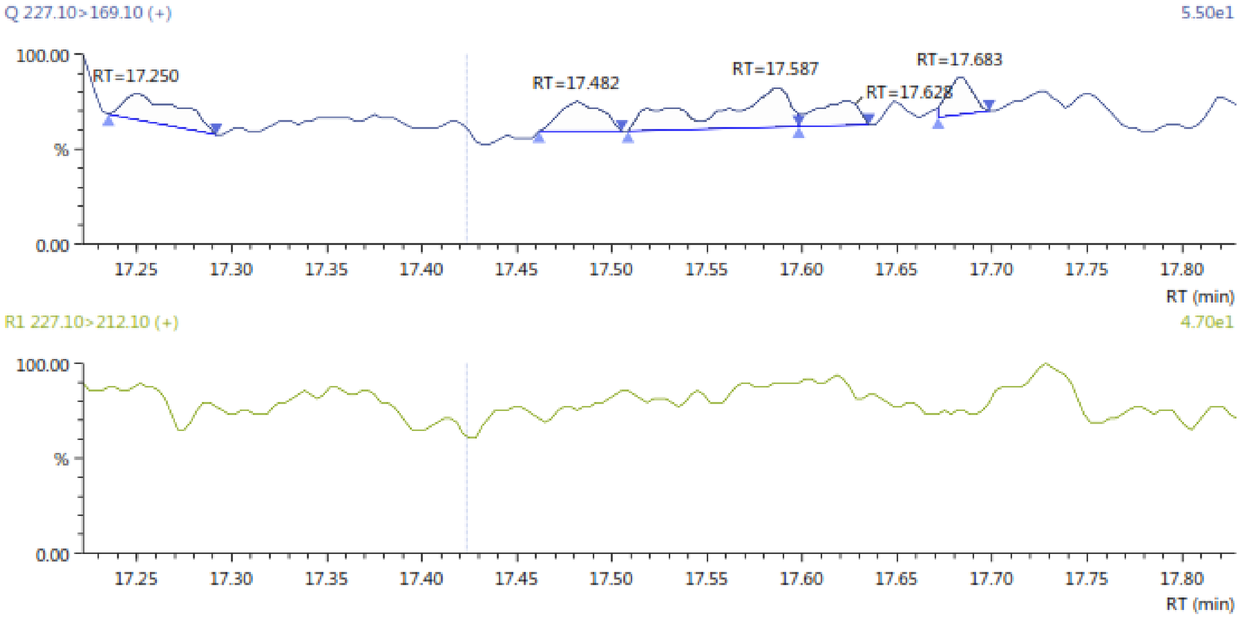
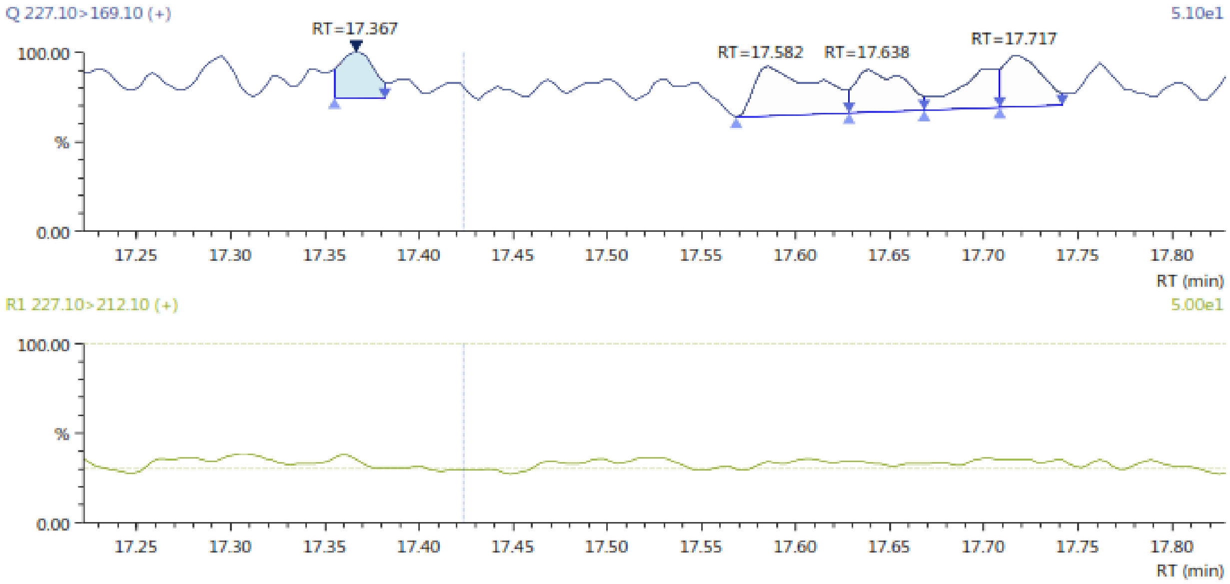
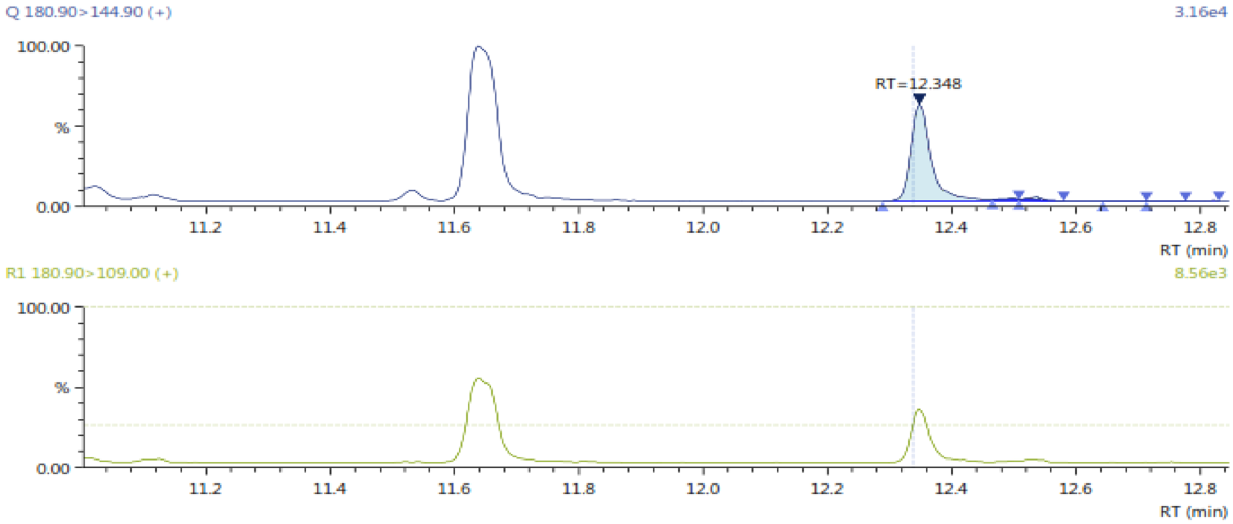
Methoxychlor

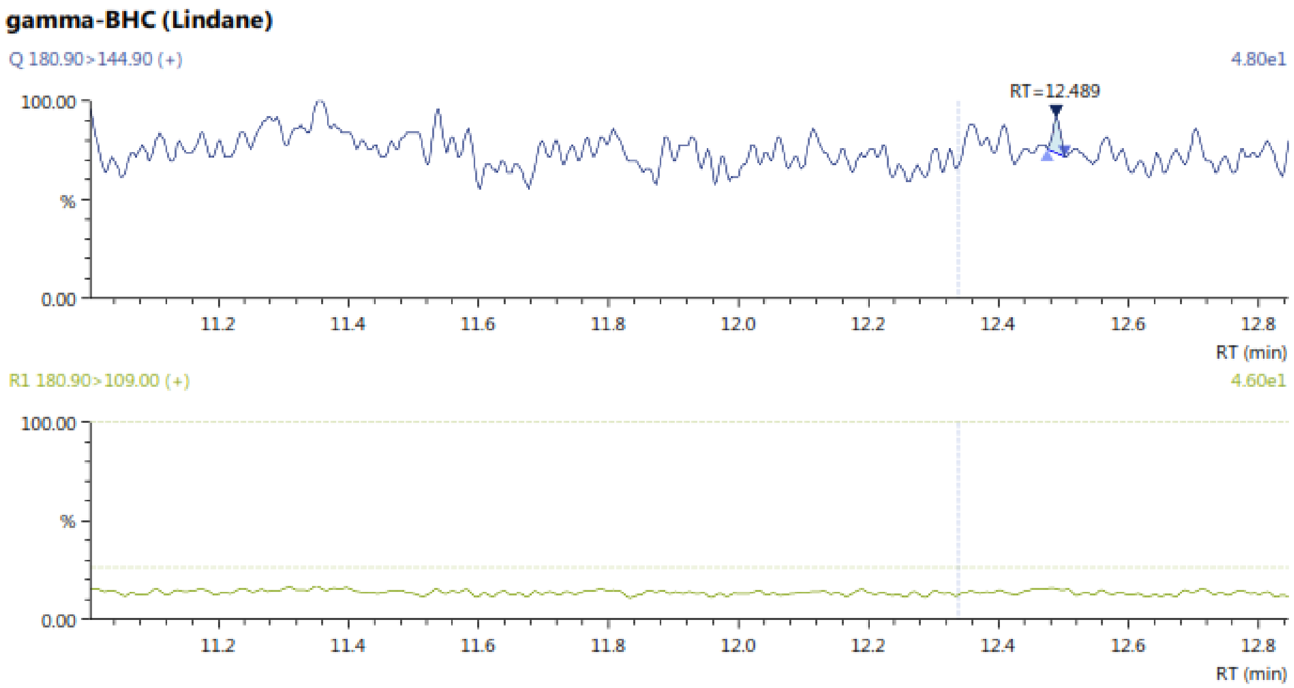


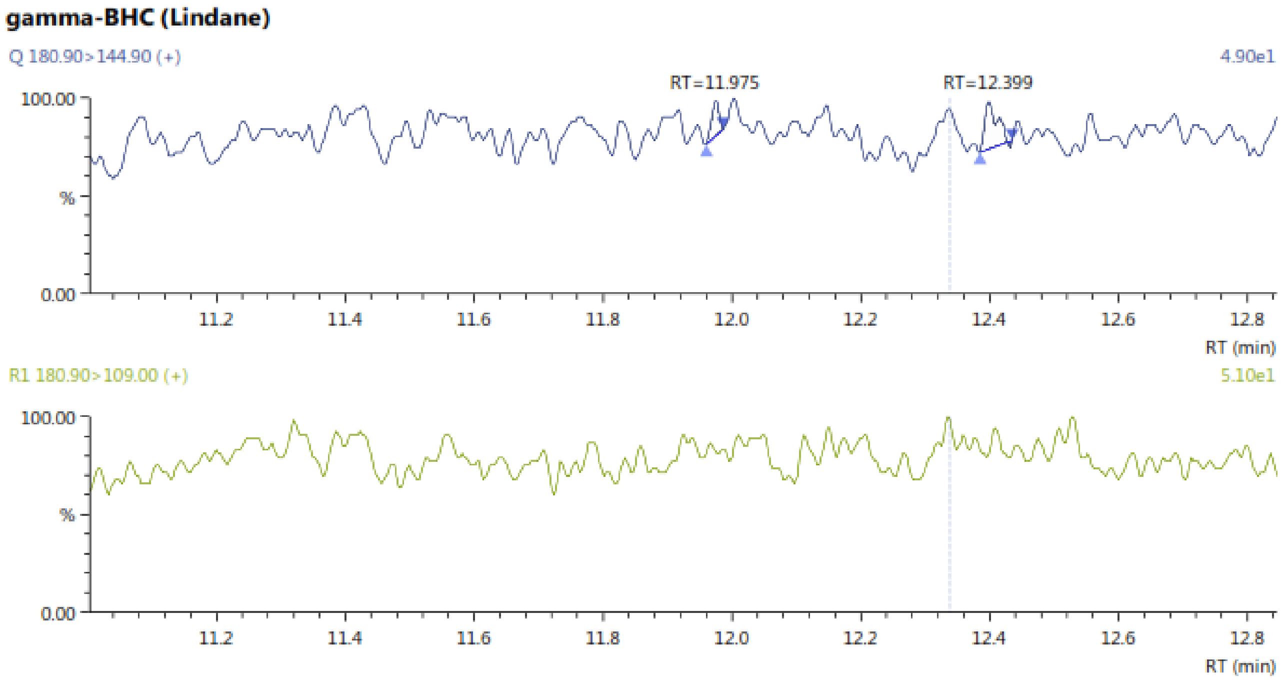
Methoxychlor

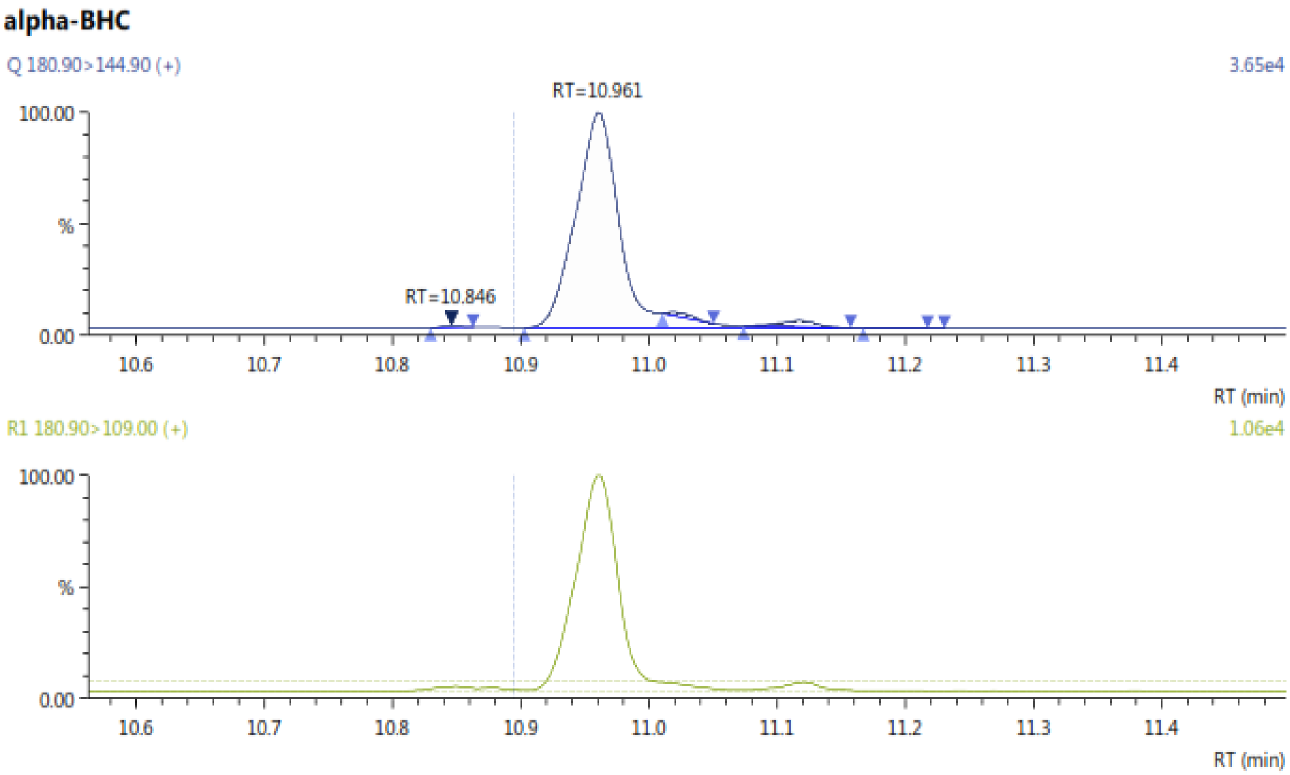


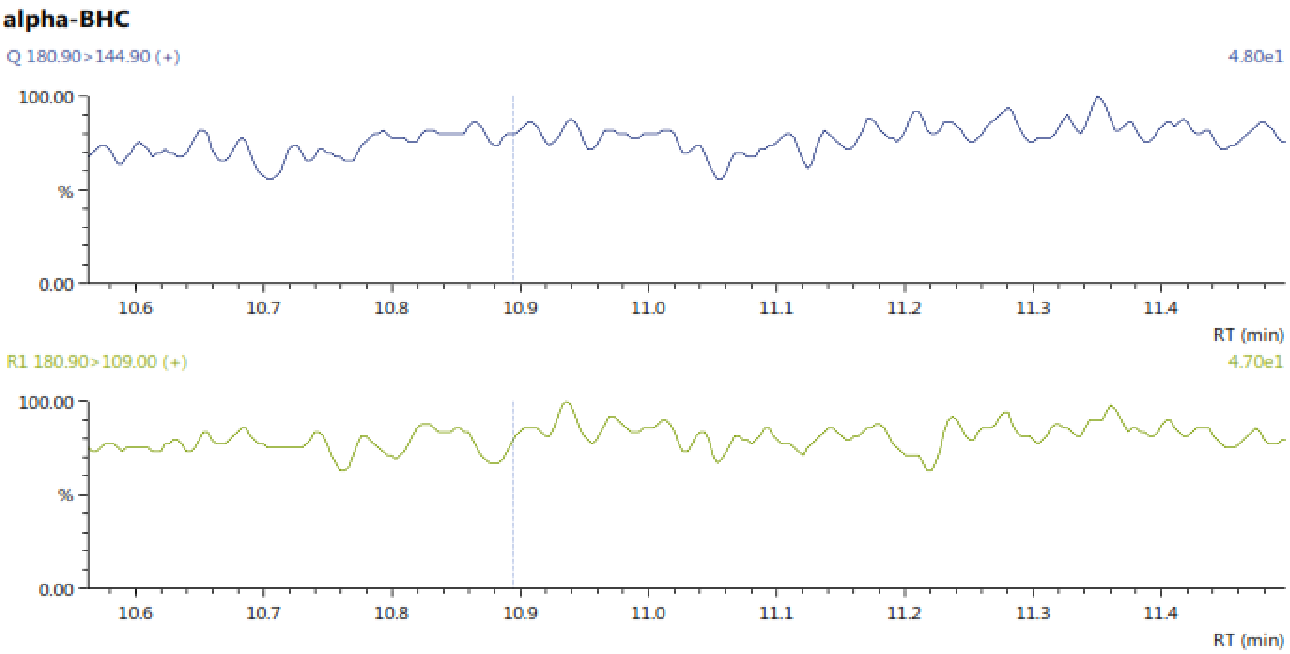
gamma-BHC (Lindane)



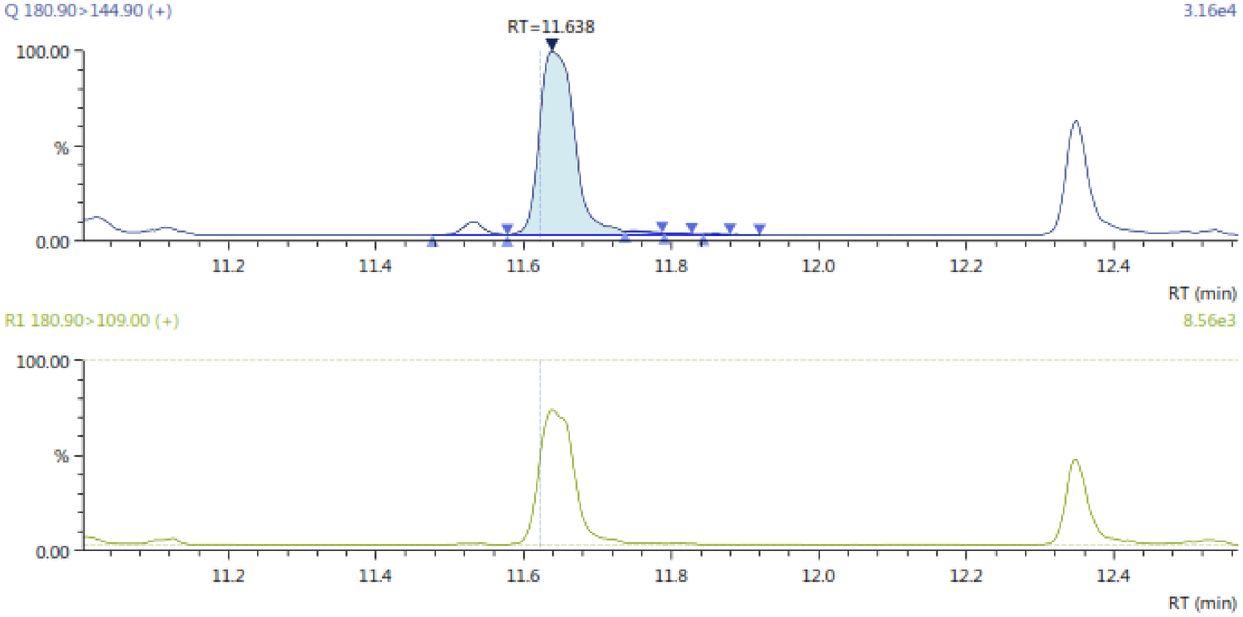

gamma-BHC (Lindane)
Q 180.90>144.90 (+)
4.80e1
RT=12.489
100.00
%
0.00
11.2
11.4
11.6
11.8
12.0
12.2
12.4
12.6
12.8
RT (min)
R1 180.90>109.00 (+)
4.60e1
100.00
%
0.00
11.2
11.4
11.6
11.8
12.0
12.2
12.4
12.6
12.8
RT (min)


gamma-BHC (Lindane)
Q 180.90>144.90 (+)
4.90e1
RT=11.975
RT=12.399
100.00
%
0.00
11.2
11.4
11.6
11.8
12.0
12.2
12.4
12.6
12.8
RT (min)
R1 180.90>109.00 (+)
5.10e1
100.00
%
0.00
11.2
11.4
11.6
11.8
12.0
12.2
12.4
12.6
12.8
RT (min)

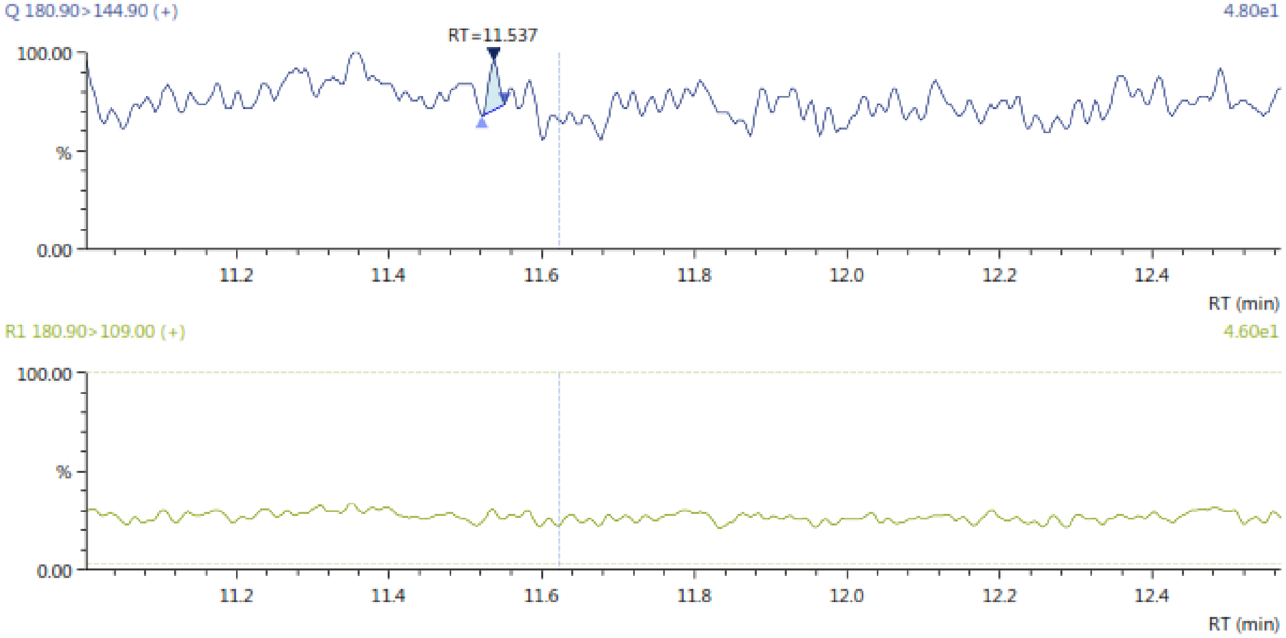

alpha-BHC
Q 180.90>144.90 (+)
3.65e4
RT=10.961
RT=10.846
100.00
%
0.00
10.6
10.7
10.8
10.9
11.0
11.1
11.2
11.3
11.4
RT (min)
R1 180.90>109.00 (+)
1.06e4
100.00
%
0.00
10.6
10.7
10.8
10.9
11.0
11.1
11.2
11.3
11.4
RT (min)


alpha-BHC
Q 180.90>144.90 (+)
4.80e1
100.00
%
0.00
10.6
10.7
10.8
10.9
11.0
11.1
11.2
11.3
11.4
RT (min)
R1 180.90>109.00 (+)
4.70e1
100.00
%
0.00
10.6
10.7
10.8
10.9
11.0
11.1
11.2
11.3
11.4
RT (min)

beta-BHC



beta-BHC



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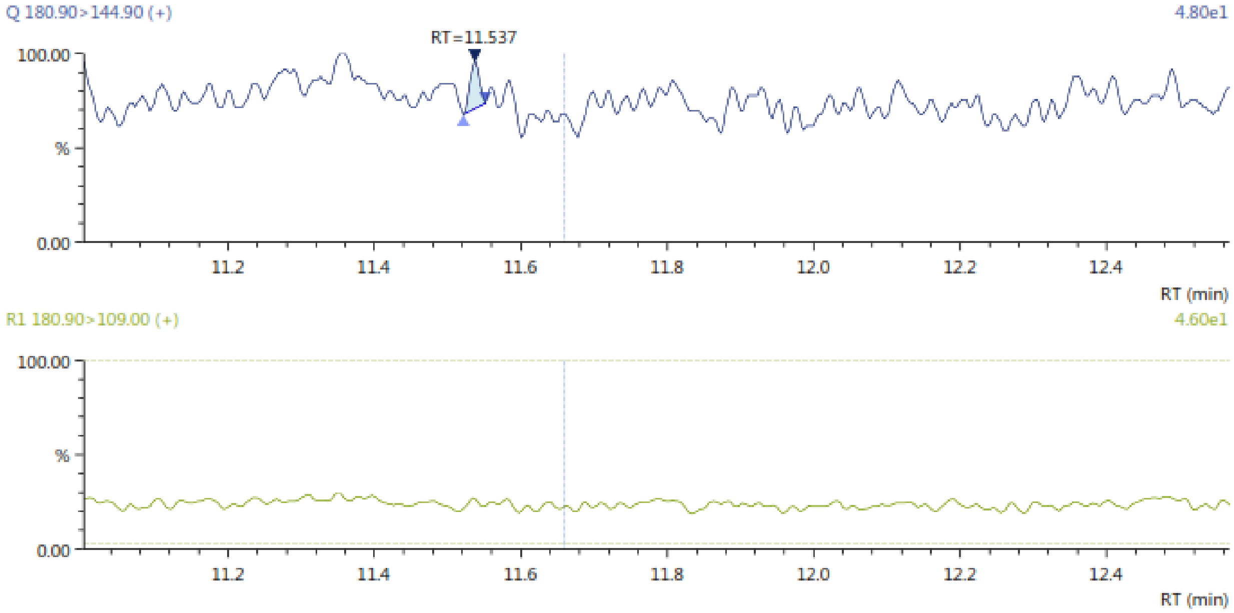
delta-BHC



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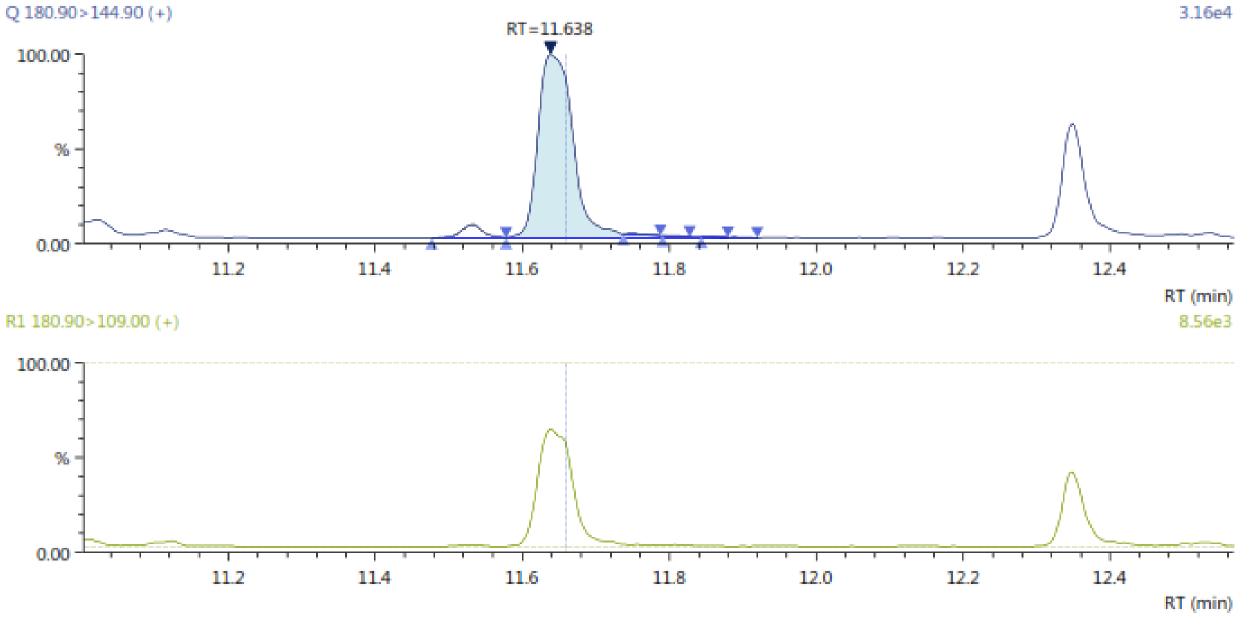
delta-BHC



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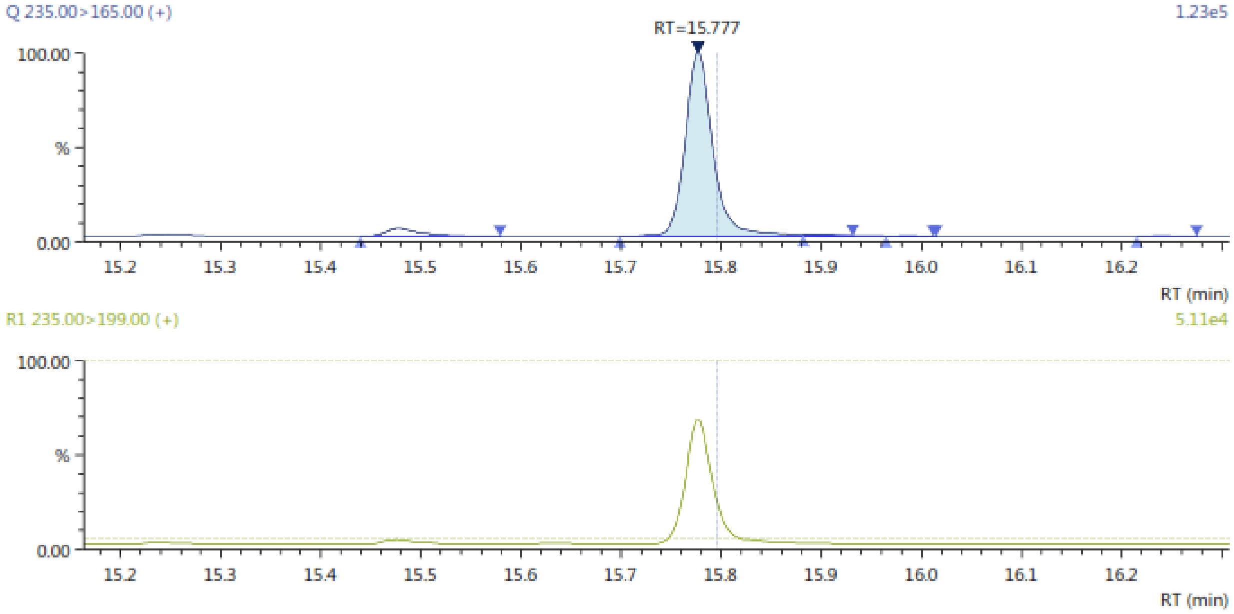
p,p'-DDT



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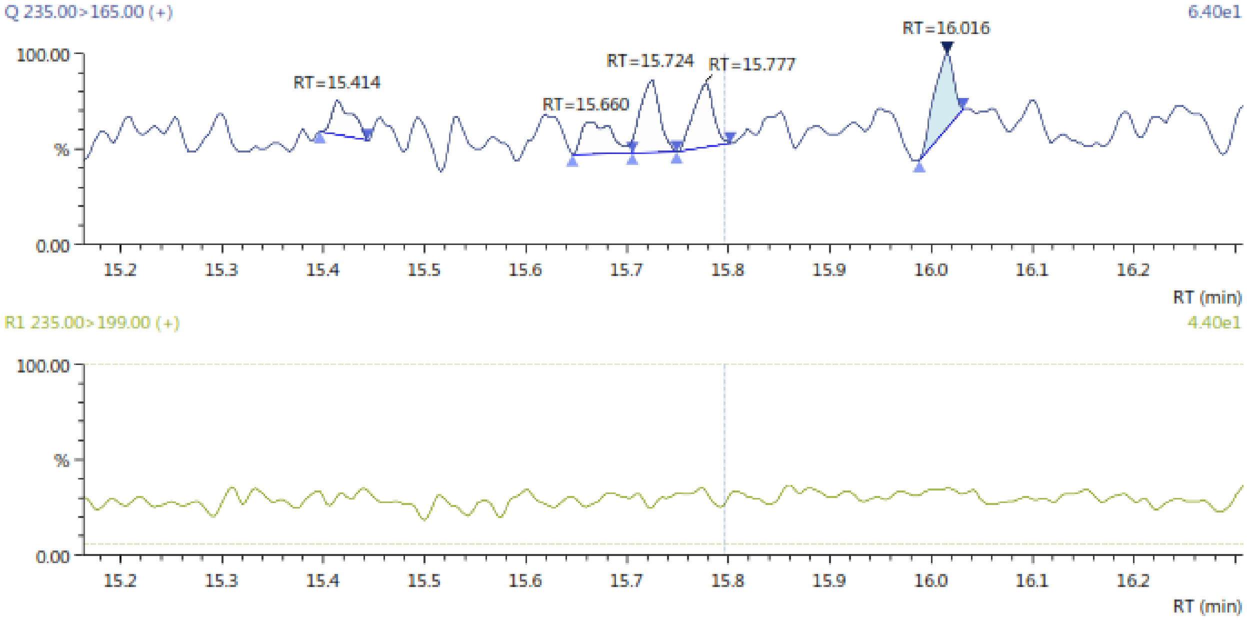
p,p'-DDT



Project Version 3.5.137.0 **Insight Chromatogram Report** **User ID** Admin
Date 28-Apr-22
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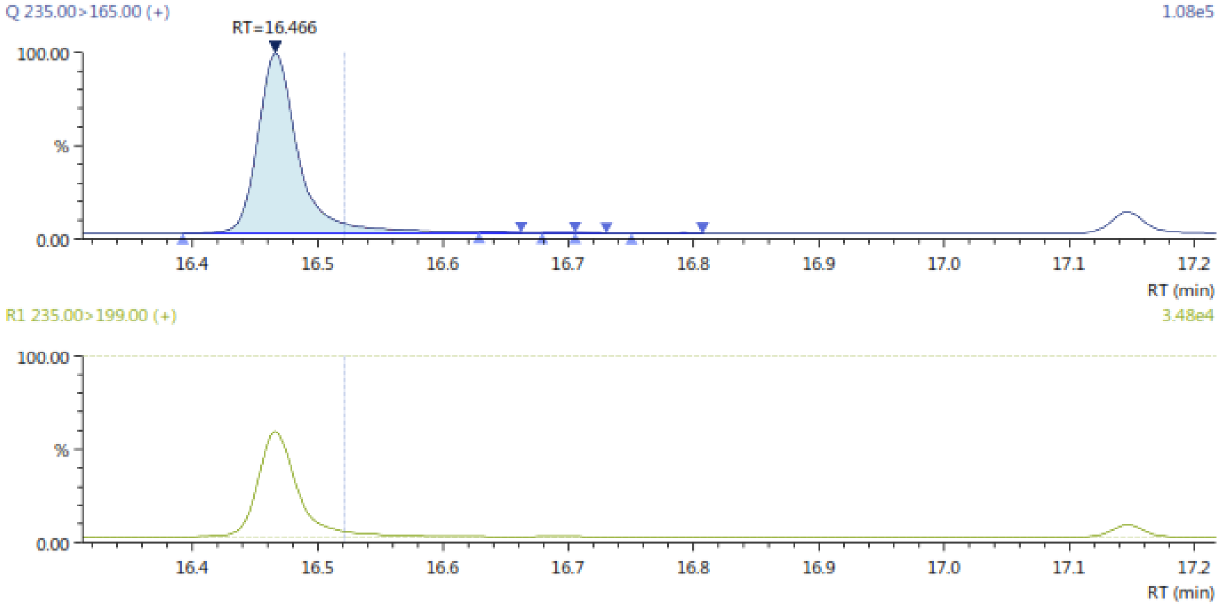
o,p'-DDD



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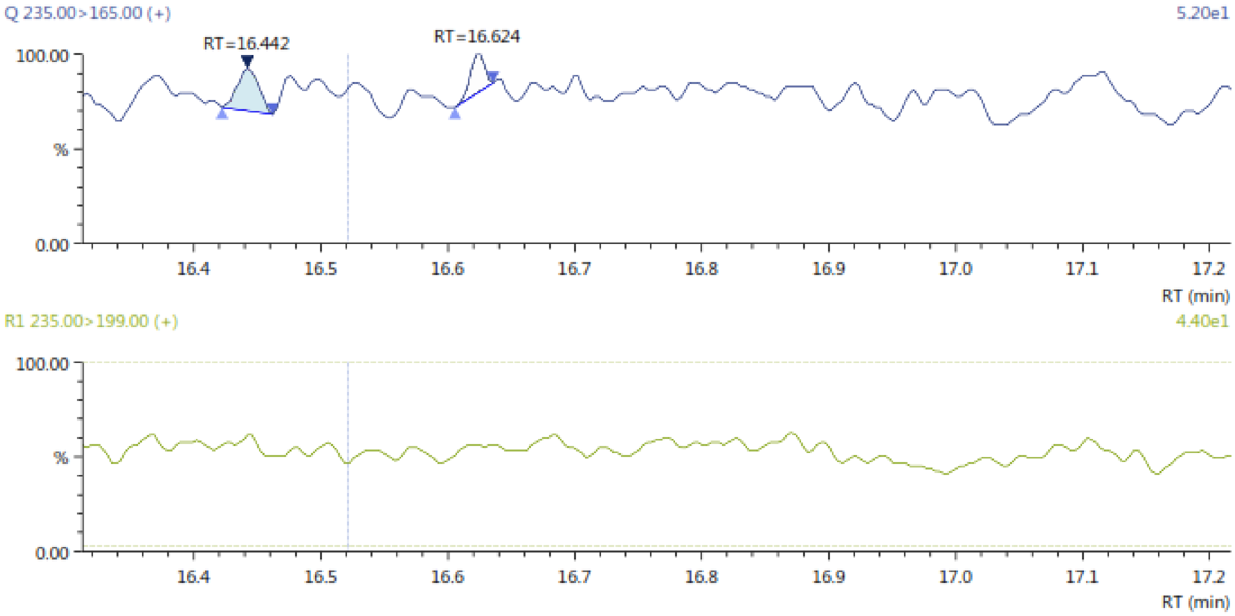
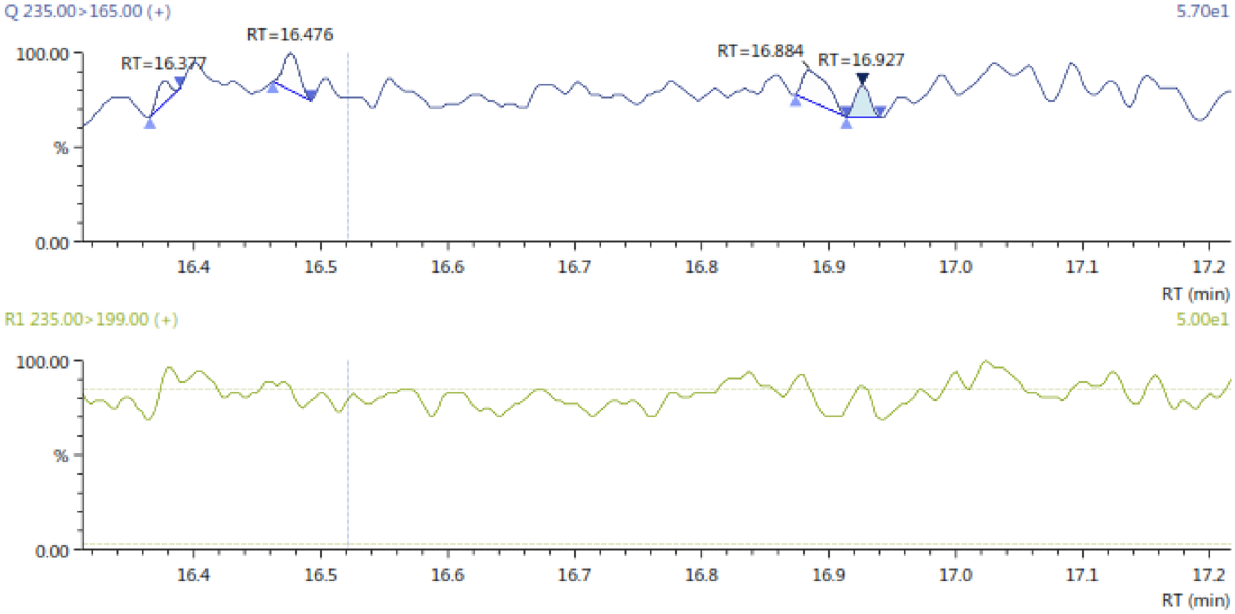
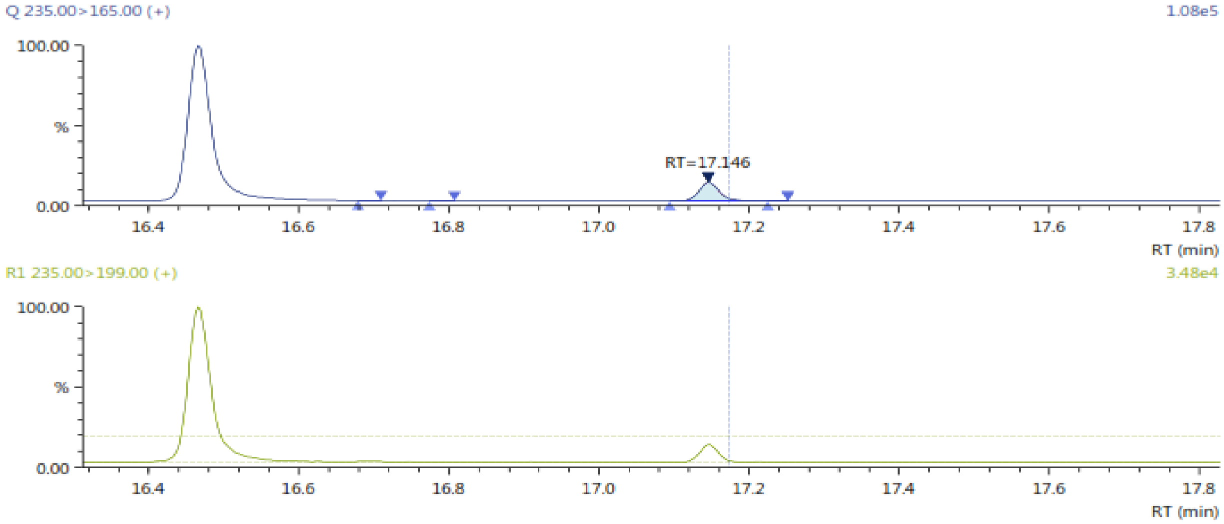
o,p'-DDD



o,p'-DDD


Q 235.00>165.00 (+)
5.70e1
RT=16.377
RT=16.476
RT=16.884
RT=16.927
100.00
%
0.00
16.4
16.5
16.6
16.7
16.8
16.9
17.0
17.1
17.2
RT (min)
R1 235.00>199.00 (+)
5.00e1
100.00
%
0.00
16.4
16.5
16.6
16.7
16.8
16.9
17.0
17.1
17.2
RT (min)

p,p'-DDD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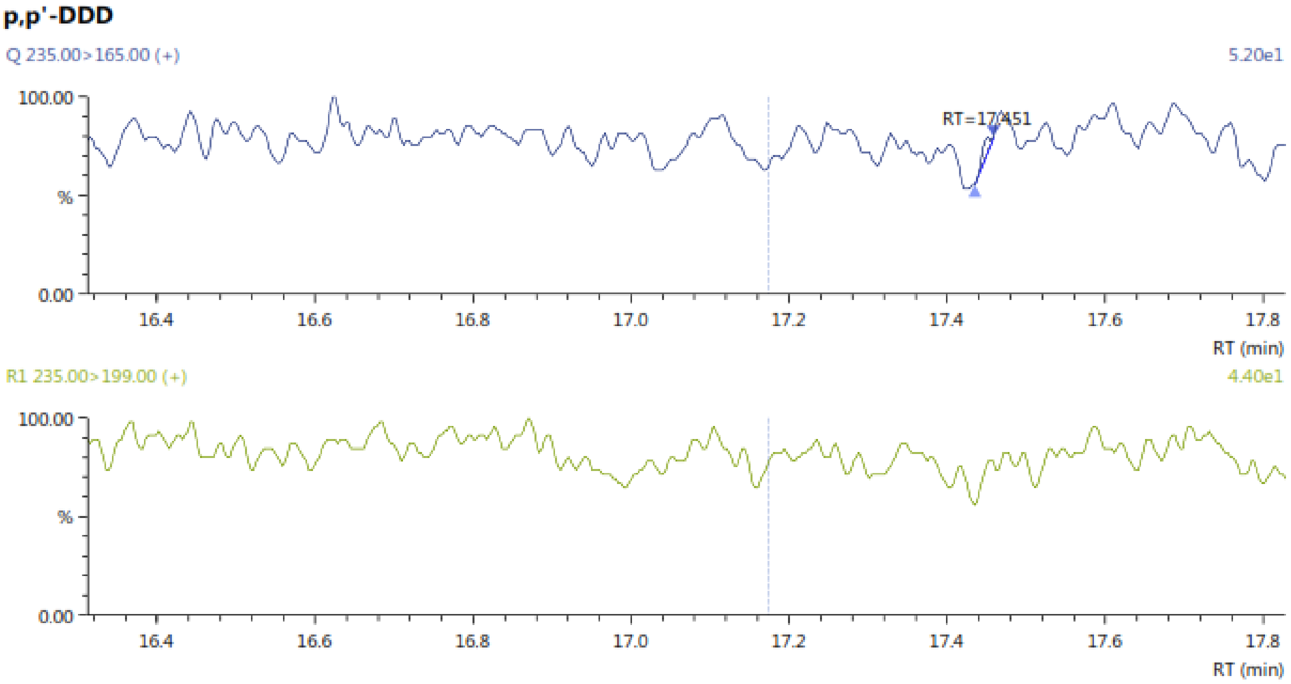
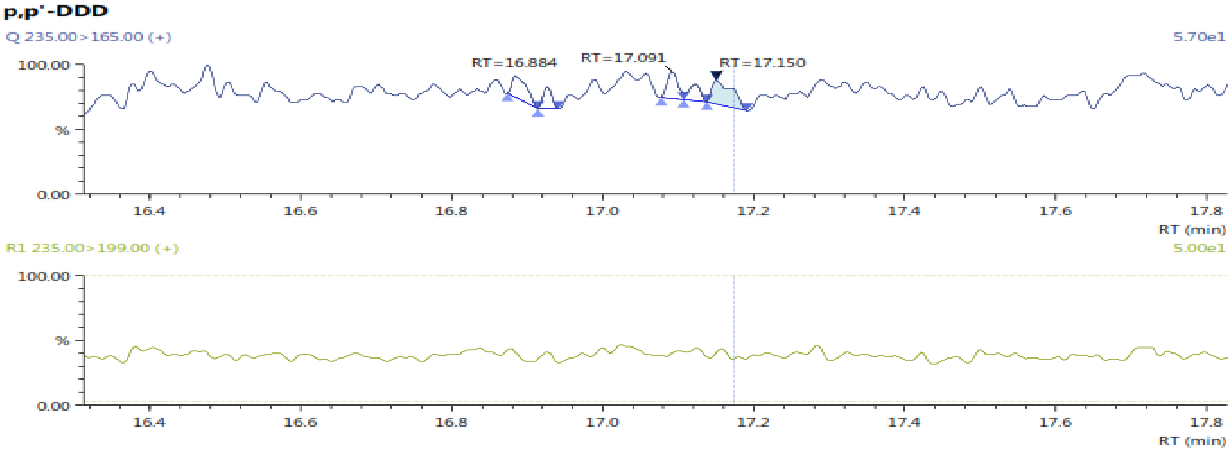
1.08e5
RT=17.146
100.00
%
0.00
16.4
16.6
16.8
17.0
17.2
17.4
17.6
17.8
RT (min)
R1 235.00>199.00 (+)
3.48e4
100.00
%
0.00
16.4
16.6
16.8
17.0
17.2
17.4
17.6
17.8
RT (min)





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Project Version 3.5.137.0 **Insight Chromatogram Report** **User ID** Admin
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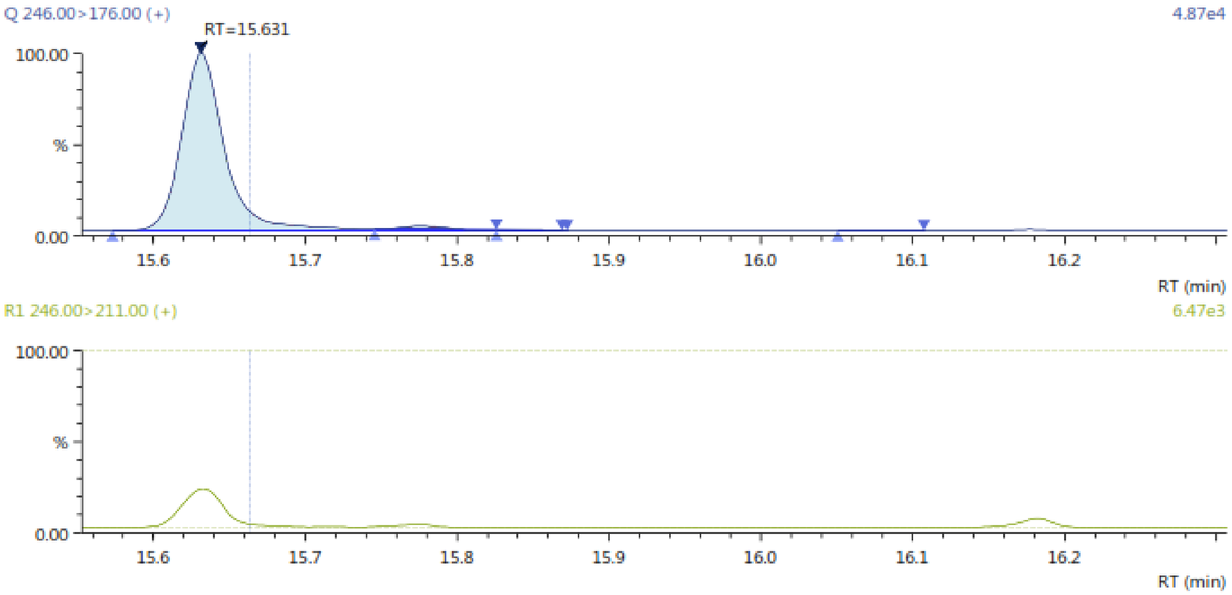
p,p'-DDE



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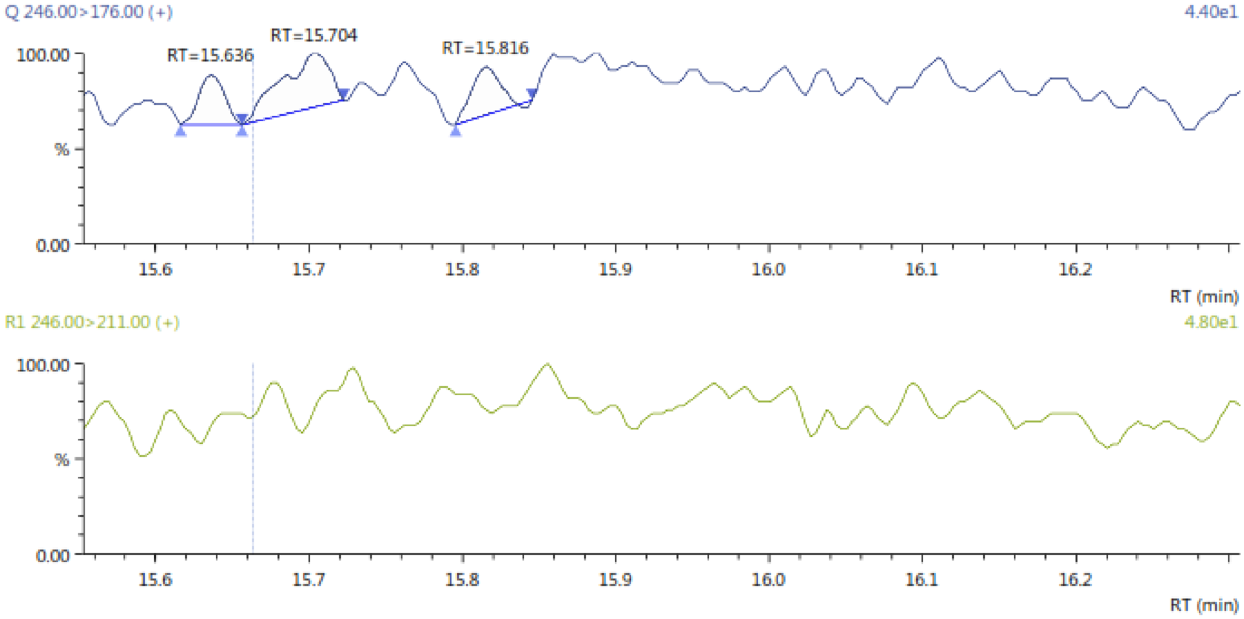
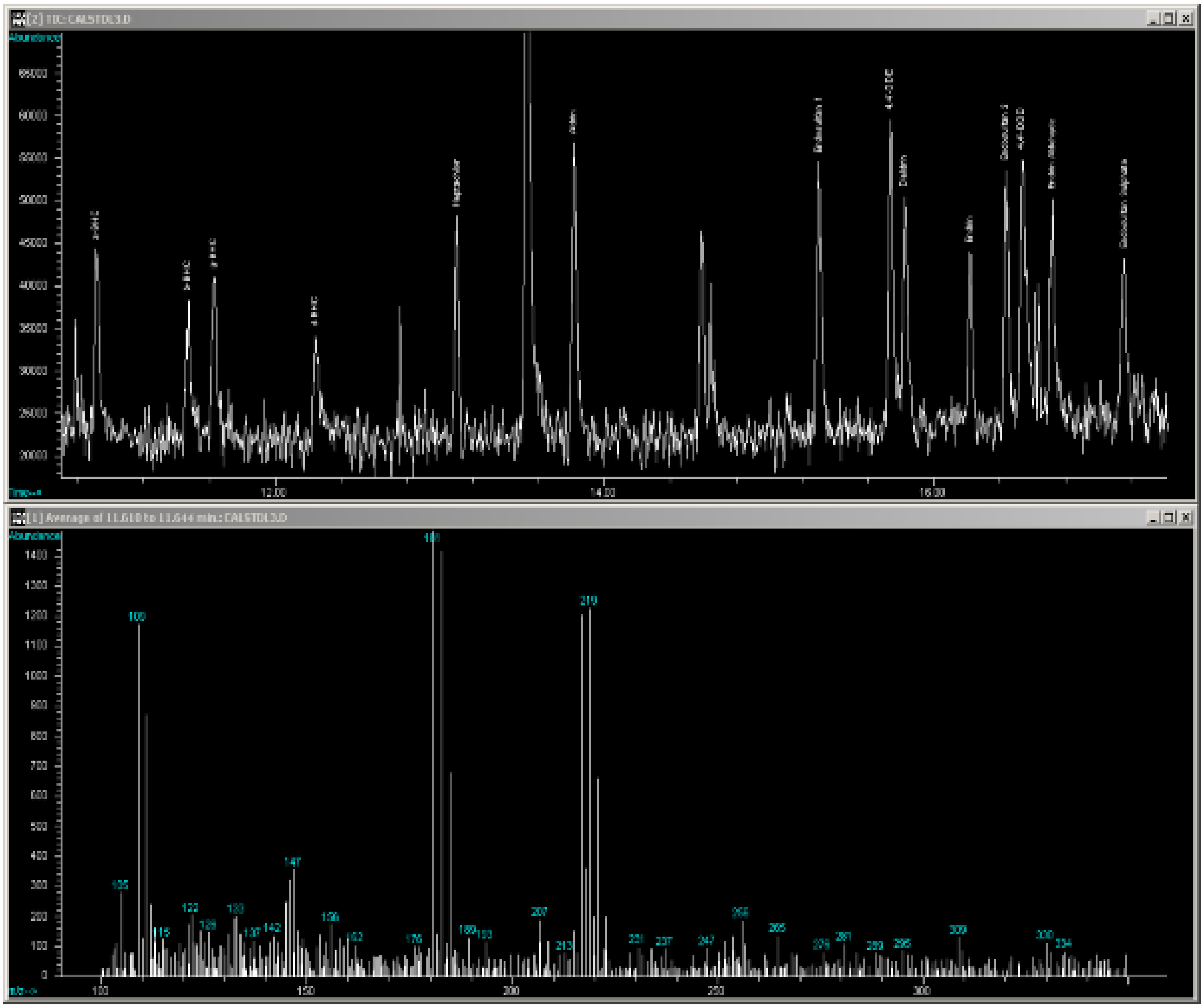
p,p'-DDE

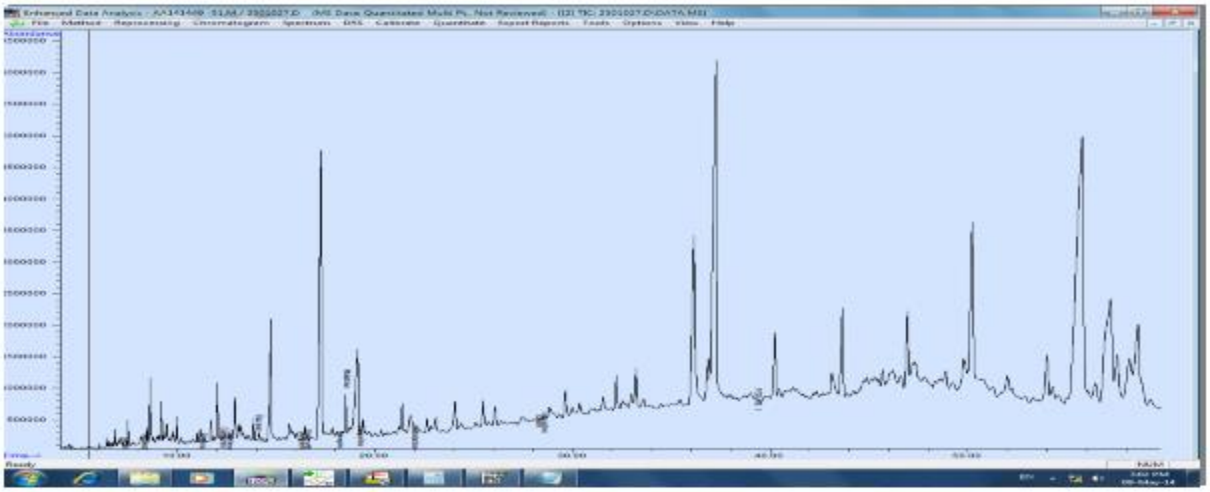


Appendix IV: GC-MS total ion chromatogram for standards showing mass spectra of various OCPs studied



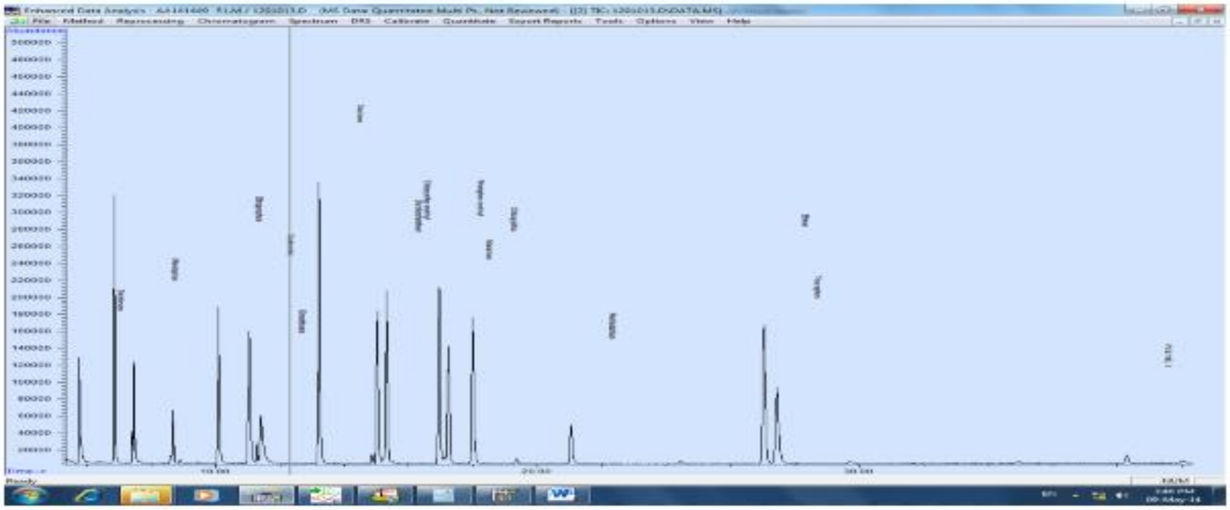
GC-MS total ion chromatogram for standards showing mass spectra of various OCPs studied

Appendix V: Picture of Chromatograms peaks of the organochlorine pesticides in water



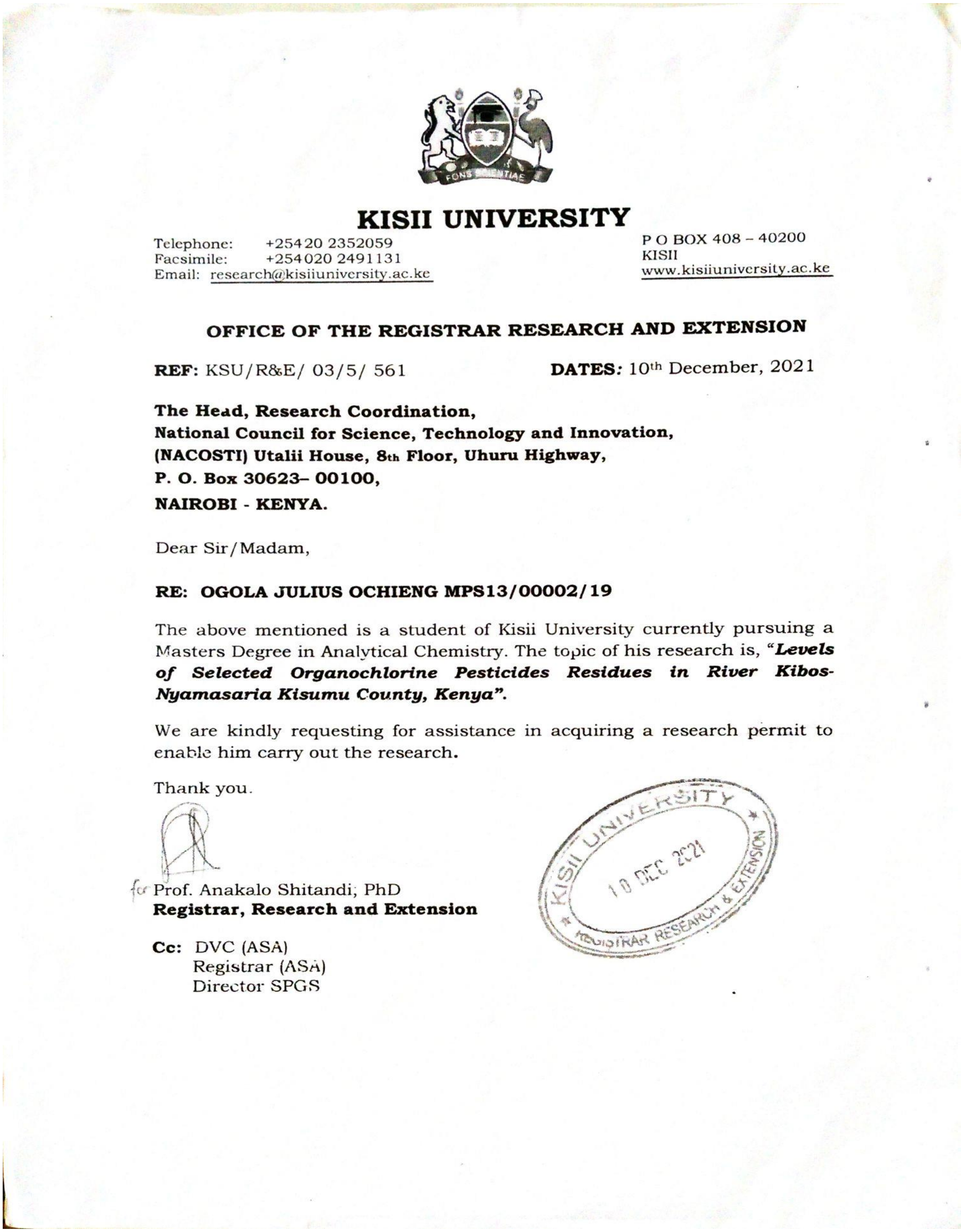
Picture of Chromatograms peaks of the organochlorine pesticides in water samples

Picture of Chromatograms peaks of the organochlorine pesticides in sediment



Chromatograms peaks of the OCPs in sediment samples

Appendix VI: Research Permit Request Letter



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OFFICE OF THE REGISTRAR RESEARCH AND EXTENSION

REF: KSU/R&E/ 03/5/ 561 **DATES:** 10th December, 2021

The Head, Research Coordination,
National Council for Science, Technology and Innovation,
(NACOSTI) Utalii House, 8th Floor, Uhuru Highway,
P. O. Box 30623– 00100,
NAIROBI - KENYA.

Dear Sir/Madam,

RE: OGOLA JULIUS OCHIENG MPS13/00002/19

The above mentioned is a student of Kisii University currently pursuing a Masters Degree in Analytical Chemistry. The topic of his research is, ***"Levels of Selected Organochlorine Pesticides Residues in River Kibos-Nyamasaria Kisumu County, Kenya".***

We are kindly requesting for assistance in acquiring a research permit to enable him carry out the research.

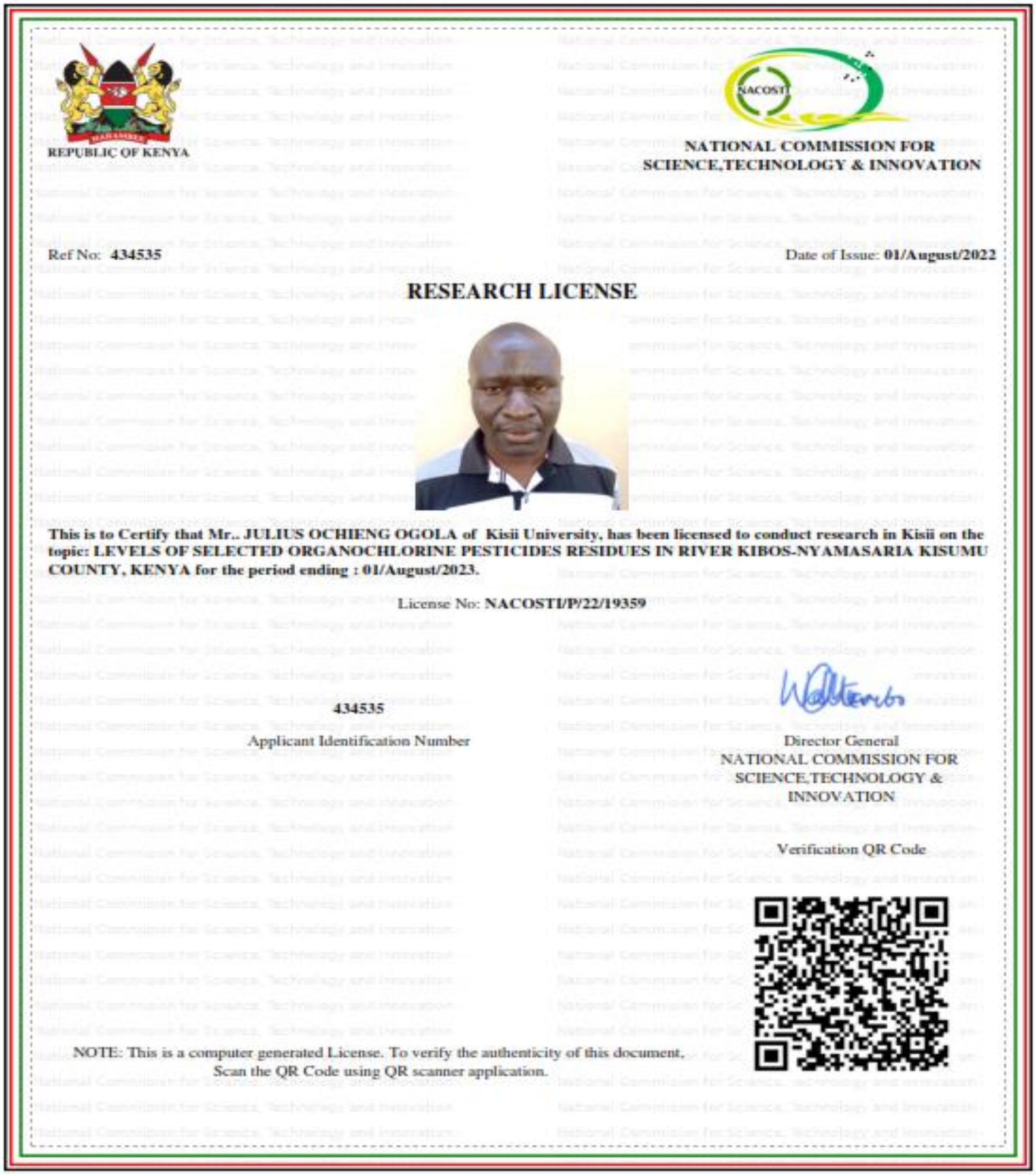
Thank you.

KISII UNIVERSITY
10 DEC 2021
REGISTRAR RESEARCH & EXTENSION

for Prof. Anakalo Shitandi, PhD
Registrar, Research and Extension

Cc: DVC (ASA)
Registrar (ASA)
Director SPGS

Appendix VII: NACOSTI Research Permit or License



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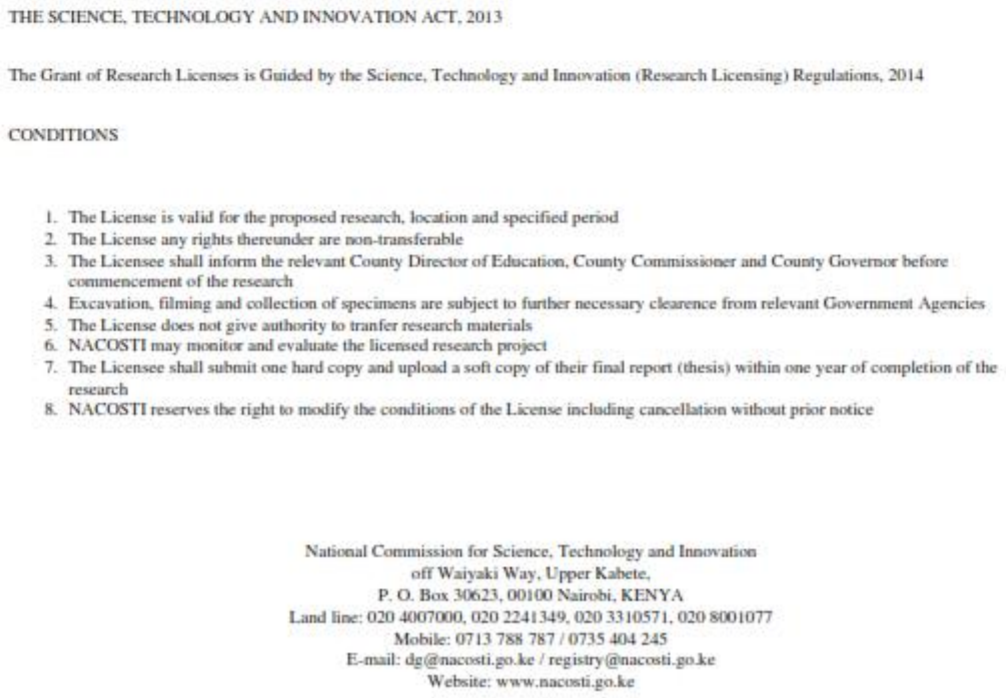

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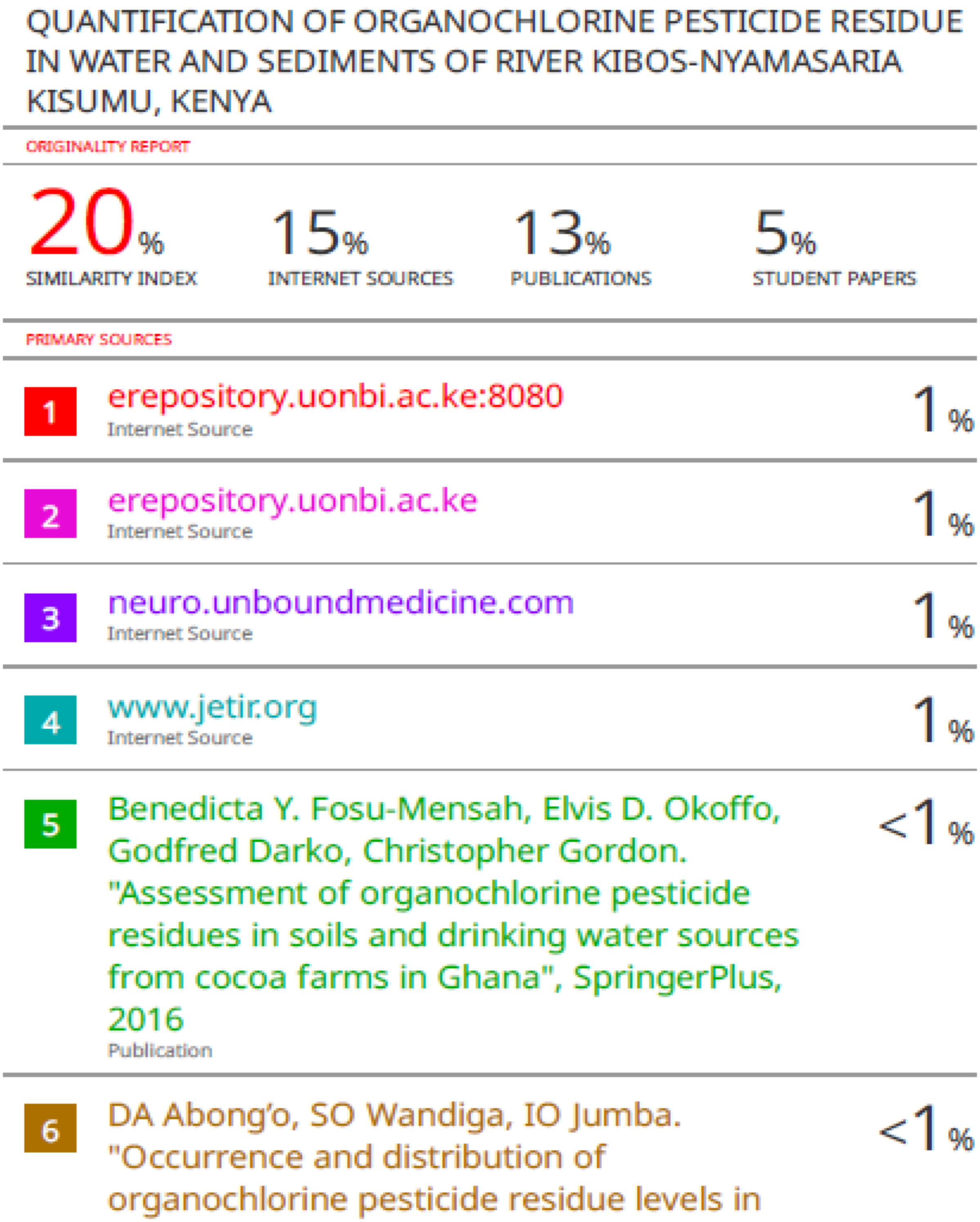
Appendix VIII: Plagiarism Report



QUANTIFICATION OF ORGANOCHLORINE PESTICIDE RESIDUE IN WATER AND SEDIMENTS OF RIVER KIBOS-NYAMASARIA KISUMU, KENYA

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