DISTRIBUTION OF CHLORPYRIFOS AND SOME ORGANOCHLORINE PESTICIDE RESIDUES IN THE UPPER TANA RIVER CATCHMENT.

By:

Joyce G. Njagi-Kithure

A Thesis Submitted in Partial Fulfilment for the Degree of Doctor of Philosophy (PhD) in Environmental Chemistry of the University of Nairobi.

August, 2013

DECLARATIONS

CANDIDATE

I hereby declare that this thesis is my original work and has never before been presented for award of any degree in this or any other university.

Joyce G.Njagi-Kithure

Signature----------

Date----------

We confirm that this thesis has been submitted with our knowledge as University Supervisors.

Prof. Shem. O. Wandiga
Department of Chemistry
University of Nairobi

Signature----------

Date----------

Prof. Isaac Jumba
Department of Chemistry
University of Nairobi

Signature----------

Date----------

Dr. D. Kariuki
Department of Chemistry
University of Nairobi

Signature----------

Date----------

DEDICATION

This work is dedicated to my darling husband Prof. Abraham Kithure Kindiki and to our two lovely daughters Anne Kithure and Peace Kithure, who gave me all the support and inspiration I needed during the study.

ACKNOWLEDGEMENTS

My gratitudes goes to the Almighty GOD for the breakthrough HE bestowed upon me throughout this study. I thank my Supervisors Prof. Shem. O. Wandiga and Prof. Isaac Jumba of the Department of Chemistry for their continual guidance, support and encouragement during the period of the study. I wish to express my profound gratitude to staff members of KEPHIS for allowing me to use their GC-MS for the sample analysis, with special thanks to Mrs. Rosemary Ng'ang'a (Principal Analytical Chemist) and Mr. Robert Koigi (Senior Analytical Chemist) for assisting with the GC-MS analysis.

Further acknowledgment goes to the teaching and non-teaching staff of the Department of Chemistry, University of Nairobi and fellow students who gave me moral support and company in the laboratory during the research.

My deepest gratitude goes to my lovely husband, Prof. Abraham Kithure Kindiki, for his full understanding and financial assistance, and also to our two daughters, Anne Kithure and Peace Kithure of Riara School, for their support and understanding throughout the study.

ABSTRACT

In this study water, sediment and weed samples obtained from Tana River in the upper Tana catchment were screened for chlorpyrifos and organochlorine (OCs) pesticides. The main concern of this study was to investigate the water quality in Tana River in the Upper Tana catchment. This is because of intense crop and livestock farming activities and high rate of industrialization processes taking place in the area. The pesticides residue levels were then correlated with the physico-chemical parameters in water samples. A total of 720 samples of water, sediment and weed were analysed for two years from ten sampling points. The river profile was divided into three sections; upstream, mid-stream and downstream. The extraction of water samples was done by liquid-liquid partitioning method using dichloromethane, while sediment samples were extracted in hexane and acetone solvents by soxhlet extraction method. The extraction of weed samples was done using an orbital shaker in acetone. The analysis of the pesticides was done using Gas chromatography-mass spectrometer and the data analysis conducted using Microsoft excel and Pearson's correlation Statistical Package for Social Scientists. The concentration of the OCs in water samples ranged from <0.00012 to 107.33 µg/L with p,p'-DDT with the highest mean residue level observed at Point 7 (Kiganjo) located at the mid-stream section. Sediments samples had OCs concentration ranging from < 0.00024 to 190.07 µg/kg. These levels were greater than those found in water samples. On the other hand the residue levels of the OCs detected in weed samples ranged from < 0.00012 to 28.82 µg/kg. Generally, there was an increasing trend in levels of individual OCs as well as the total OCs in the mid-stream in all the three matrices. The concentrations were higher during the dry seasons than in the wet seasons. Chlorpyrifos mean residue levels varied between < 0.0001 and 6.80 µg/kg. The highest mean residue level of 6.80 µg/kg was detected at Point 5 (Tetu). On the other hand chlorpyrifos mean residue levels found in sediment samples (< 0.0001 -1.43 µg/kg) were generally lower than those detected in water samples. Mean Chlorpyrifos levels in weed samples ranged between < 0.0001 and 2.57 µg/kg, with the highest concentrations observed at point 7 (Kiganjo) which is situated at the midstream. pH in water samples ranged between 6.71 and 7.54 which falls within the range of 6.5-8.5 levels for natural water bodies recommended by the European Union. Electrical conductivity ranged between 57.02 µS and 373.43 µS, with high mean levels observed at the mid-stream. The correlation of water samples from the upper Tana River showed high positive values for organochlorine pesticides and the physico-chemical parameters. For example a high positive correlation coefficient of 0.925 was observed between OCs and Salinity.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS AND ACRONYMS

ADI	Acceptable daily intake
BDL	Below detection limit
DCM	Dichloromethane
DDD	Dichlorodiphenydichloroethylene
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organization
GC	Gas chromatography
GC-MS	Gas chromatography mass spectrometry
GLC	Gas liquid chromatography
GoK	Government of Kenya
GPS	Geographic Positioning Satellite
GSC	Gas solid chromatography
HCH	Hexachlorocyclohexane
HCL	Hydrochloric acid
HPLC	High performance liquid chromatography
IPEP	International POPs Elimination Project
KEPHIS	Kenya Plant Health Inspectorate Service
IUPAC	International Union of Pure and Applied Chemistry
LC_{50}	The concentration of a

	pesticide in a matrix (sediment, water etc.) that will kill 50% of the test subjects (eg pests) when administered as a single exposure (typically 1 or 4 hours).
LOD	Limit of detection
LOQ	Limit of quantification
MB	Methyl bromide
MRLs	Maximum residue limits
NDP	National Development Plan
NEAP	National Environment Action Plan
NPS	Non-point source
OCs	Organochlorines
OPs	Organophosphates
PACN	Pan African Chemistry Network
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCPB	Pest Control Products Board
PIC	Prior informed consent
POPs	Persistent organic pollutants
SPSS	Statistical Package for Social Scientists
TBT	Trybutyltin
TDS	Total dissolved solids
TEPP	Tetraethyl pyrophosphate

TOMPS	Toxic organic micropollutants
TSS	Total suspended solids
UN	United Nations
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WFB	World Fact Book
WWF	World Wide Fund

CHAPTER ONE

INTRODUCTION AND BACKGROUND OF THE STUDY

1.1 The potential of Agriculture in Kenya

Kenya's physical features are varied; while much of northeastern Kenya is a flat plain, the remainder of the country encompasses the Great Rift Valley and the magnificent Mount Kenya. The land altitude rises from the sea level on the western Indian Ocean shores to 5,500 m on snow-capped Mt. Kenya at the Equator. Kenya covers 581,309 km^2 and has a population of about 38.6 million (KNBS, 2009).The country is named after Mount Kenya, the second highest mountain in Africa (CIA, 2009).

Eighty three percent (83 %) of the Kenya's population in depends on a small fraction of about 15 % of the land area to earn their livelihood through agriculture, wood/timber, tourism and service industries (Ogallo and Mwangi, 1996). This has resulted in an acute competition between land-use for socio-economic activities and water- cycle. The results of this competition are devastating changes on the environment and in the hydrological regime. Flash floods, soil erosion, reduced groundwater recharge and decimated river flows are some of the consequences. The primary source of fresh water in Kenya is rainfall, which is unevenly distributed in the country. Reliability of its occurrence even in areas of high rainfall is low and most of the country suffers from drought. March to May is the long rain season months in most parts of the country, while short rains are experienced from October through December (KMD, 2013). The best time for most outdoor activities (including safari and mountain climbing) is during the low rainfall months of June-September (Ogallo and Mwangi, 1996). Figure 1.1, depicts the long term mean rainfall patterns for March-April-May seasonal rainfall. The figure shows that the highest rainfall

amounts of over 300mm are recorded in Western, Central, the Coastal strip and parts of northern Kenya (Marsabit and Moyale) (KMD, 2013).

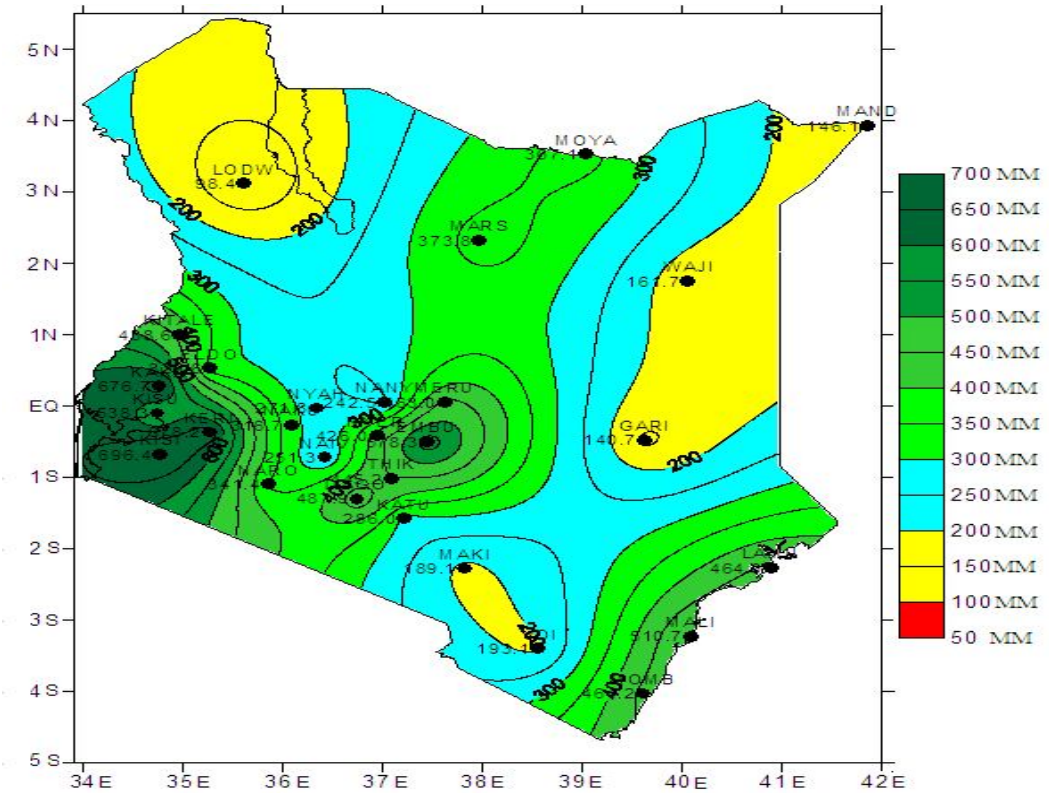


Figure 1.1 March-May seasonal rainfall mean in Kenya

Agriculture remains the most important economic activity in Kenya, although less than 8 % of the land is used for crop and food production (NEAP, 1994). Less than 15 % of the land is suitable for cultivation, of which only 12 % is classified as high potential (adequate rainfall) agricultural land and about 8 % is medium potential land (NEAP, 1994). About 80 % of the work force engages in agriculture or food processing (NEAP, 1994). Kenya is a leading producer of tea and coffee, as well as the third-leading exporter of fresh horticultural produce, such as cabbages, onions and mangoes. Small-scale farmers grow most of the corn and also produce potatoes, bananas, beans and peas (Jones, 1995). White and red sweet potatoes are the most common varieties grown by Kenyan farmers. There has been a steady increase in the area

planted with sweet potato from about 55,000 hectares in 1988 to about 65,000 hectares in 1996 (FAO, 1997). Average yields are about 10 tons per hectare.

Coffee in Kenya has been grown for over a century now, since 1893. The total area under coffee is estimated at 160,000 hectares, about one third of which is the large scale and the rest under small holder with an average of 700,000 growers (Nyandiko, 2001). The total annual production has been fluctuating widely due to climate as well as socio-economic factors. At the moment, production stands at about one million bags (approximately 50 kg each) per year. Tea was introduced into Kenya from India by a European settler G.W.L. Caine in 1903 (Nyandiko, 2001). Over the years Kenya has grown into a formidable world tea producer, with an annual production of about 300 million kilogrammes and is rated as the fourth largest tea producer and the second biggest exporter in the world. This formidable growth has seen the tea industry grow into the most important agricultural sub-sector and the leading foreign exchange earner in Kenya (Nyandiko, 2001).

There are different types of livestock farming practiced in Kenya: beef farming, sheep farming, goat farming, pig farming and poultry farming. The market for livestock supplies is increasingly expanding both locally and regionally. Nearly all the cattle from Moyale and some of the cattle and goats from Mandera market originate from the Borana and Somali regions of Ethiopia (Leete, 2001). Kenya's livestock population is estimated at 12 million herds of cattle; of which 3.2 million are in dairy herds, close to 20 million are goats and 1 million camels (Leete, 2001). The use of pesticides in their various agricultural sectors therefore, plays a major role in maintaining high levels of agricultural production in Kenya (Mwaisaka, 1999). Pesticides are defined as any agent intended for preventing, destroying, repelling, or mitigating any pest (U.S. EPA, 2007). They are classified into groups, such as insecticides, acaricides, nematocides,

herbicides, avicides, rodenticides and molluscicides depending upon the species of the pest (Farrely *et al.,* 1984).

1.2 Importation and Regulation of Pesticides in Kenya

Kenya imports approximately 7,000 metric tones of synthetic pesticides annually, valued at KShs. 4 billion (US$ 50 million). Of the total imports, insecticides account for about 40 % (Birech *et. al.,* 2006). The Pest Control Products Act Cap 346, which came into law on 19 May 1983 regulates the importation, exportation, manufacture, and distribution and use of pesticides in Kenya (PCPB, 2005). By mid-2010, the Pest Control Products Board (PCBP) had registered over 1000 pest control products for use in agriculture, animal health and public health **(**PCPB, 2012). In order to ensure that only registered pesticides are brought into the country and in the right quantities, the Board has been controlling importation and exportation of pesticides through processing and issuing of import licences **(**PCPB, 2012).

It was established under an act of parliament, the Pest Control Products Act, Cap 346, laws of Kenya of 1982. Through its pesticide registration process, the Board ensures that only products that have been assessed for safety, quality, efficacy and economic value are authorized for use in the country. PCPB is also charged with the responsibility of informing the industry, extension agencies and the Ministry of Agriculture, of the authorized use of crop protection products (PCPB, 2008).

As a predominantly agricultural country, Kenya's demand for pesticides is high. Domestic as well as demand for exports to neighboring countries continue to grow. The further development of the industry based on the locally available pyrethrum and the importation of products are likely to continue to get government encouragement as a means of increasing food production and tackling public health concerns. A major issue with the pesticide industry, which has in the

past slowed investment in this area, is the duty paid on raw materials used in the pesticide industries, while most of the finished products are imported duty free (Wandiga, 2001).

According to PCPB statistics, a total of 119 applications were considered for registration in the year, 2007/2008. Seventy one Pest Control Products were registered which, was lower compared with 177 products granted registration in 2006/2007 (PCPB, 2008). The high figure in 2006/2007 was attributed to mass promotion of products under provisional registration status to full registration (PCPB, 2008). Approximately 12,983 metric tons of pesticides valued at Kshs 10.7 billion were imported into the country in 2011/2012 (PCPB, 2012). In that year more insecticides were imported in comparison to the other pesticide groups. The approximate quantities (in tonnes) and values (in million Kenya Shillings) of the various categories of pest control products imported between 2003/2004 and 2011/2012 are shown in Figure 1.2 below and Table 1.1, respectively.

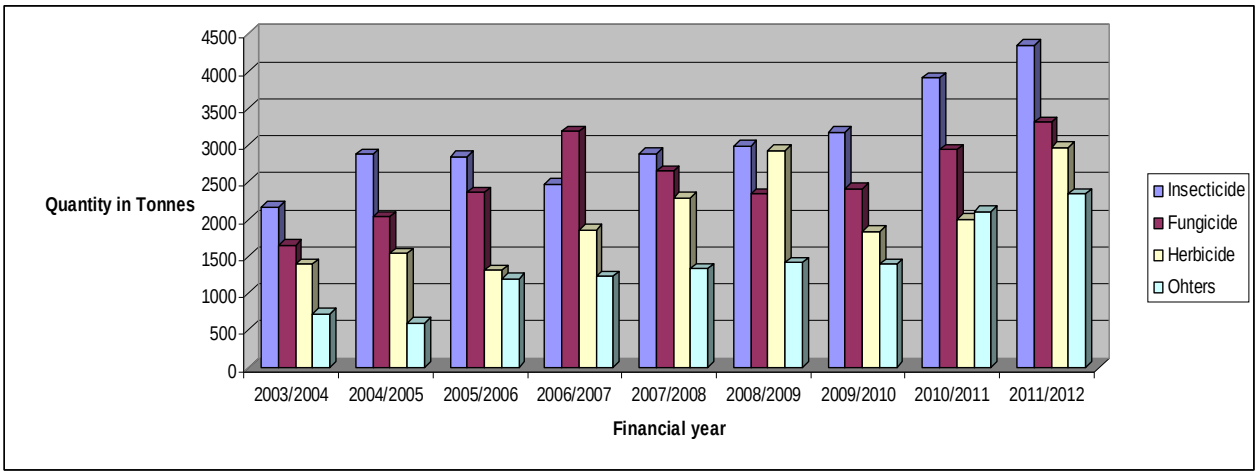


Figure 1.2: Quantities of pesticides imported into Kenya in 2003/04 – 2011/2012

Source: (PCPB, 2012).

Table 1.1: Value of Pesticides Imported from 2003/2004 – 2011/2012 in million Kshs

Financial Year / Category	2003/2004	2004/2005	2005/2006	2006/2007	2007/2008	2008/2009	2009/2010	2010/2011	2011/2012
Insecticide	2165	2881	2844	2475	2887	2995	3181	3913	2897
Fungicide	1657	2031	2361	3190	2651	2340	2415	2940	4827
Herbicide	1396	1538	1311	1859	2289	2933	1840	2000	1537
***Others**	723	597	1192	1225	1330	1413	1396	3913	1482
Total	5941	7047	7708	8749	9157	9681	8832	12766	10743

* Others include Acaricides, Fumigants, Plant Growth regulators, mitigants etc.

Source: (PCPB, 2012).

The pesticides industries in Kenya consist mainly of firms formulating pesticide materials. There are more than eleven firms manufacturing and selling various pesticide products in the country (PCBP, 2008). Other types of pesticides formulated and marketed in Kenya include, herbicides, miticides, plant growth regulators and insect repellents (PCBP, 2008).

1.3 Pesticides usage in Kenya

There are different types of insecticides, which include, organochlorines (OCs), organophosphates (OPs), carbamates and pyrethroids. As in most tropical countries in Africa, pesticides are extensively used in the public health sector in Kenya to control vectors such as trypanosomiasis (IPEP, 2006). DDT is also known to reduce malaria cases drastically, a disease that kills approximately 700 Kenyans a day (WHO, 1989). DDT is the common name approved by the International Standards Organization for the technical product in which 1,1,1,-trichloro-2,2-di(chlorophenyl)ethane (p,p'-DDT) is the predominant component. Technical DDT is a mixture of isomers containing 65-80 % p,p'-DDT and several other components, including: o,p'-DDT (up to 15-21 %), p,p'-DDD (up 4 %), 1-(p-chlorophenyl)-2,2,2-trichloroethanol (up to 1.5 %) and traces of o,o'-DDT and bis(p-chlorophenyl) sulfate, with up to 1 % m,p'-DDT present in some samples of technical DDT (WHO, 1989).

Aldrin and dieldrin which were banned in Kenya in 1992 (IPEP, 2006), were initially used for seed dressing. The organochlorine pesticides still officially in use in Kenya are endosulfan, alpha and gamma-BHC, and alachlor (IPEP, 2006). Herbicides can be used to kill invasive weeds that may cause environmental damage. Herbicides are commonly applied in ponds and lakes to control algae and plants such as water grasses that can interfere with activities like swimming and fishing and cause the water to look or smell unpleasant (Helfrich *et al*, 1996). In Kenya most herbicides are used to con troll weeds in agriculture. There has been concern on the

possible effects that the use of pesticides has on tropical environments, including tropical marine and fresh water ecosystems. The situation in Kenya is aggravated when cases of pesticide misuse occur due to farmers' ignorance and illiteracy. Kenyan farmers, especially those from pastoral communities have lost herds of cattle after spraying with insecticides instead of acaricides. Sale of fake, expired or banned pesticides is also common (PCPB, 2005).

The effects of pesticides depend on several factors such as climate (in particular temperature and rainfall), soil type and nature of the vegetative cover, biotic activity, light intensity, agricultural practices, and mode of introduction of the pesticide into a particular environmental compartment (Mark, 2003). These factors determine the persistence of a pesticide in a specific environment.

1.4 The Tana River

Tana River with length of some 1000 km, originates from Mount Kenya running through the arid and semi-arid lands in the eastern part of the country to Indian Ocean. It is the only permanent river in the arid and semi-arid region, and constitutes a vital water resource for all sectors of the human population. Five hydroelectric power stations built along its course which include, Kindaruma, Kamburu, Gitaru, Masinga and Kiambere now, generate 480 megawatts of electricity. Table 1.2 shows the reservoirs within the Tana River drainage area (WRMA, 2008).

Table 1.2: Reservoirs within the Tana River Drainage Area (by WRMA)

Name of the Dam	Year constructed	River	Catchment Area km²	Gross Storage (Mm^3)	Remarks
Sasumua	1956	Chania	65	16	Water Supply to Nairobi City
Ndakaini	1993	Thika	71	70	Water Supply to Nairobi City
Masinga	1981	Tana	7,335	1,560	Hydro-power 40 MW
Kamburu	1975	Tana	9,520	150	Hydro-power 94.4 MW
Gitaru	1978	Tana	9,525	20	Hydro-power 147 MW
Kindaruma	1968	Tana	9,807	16	Hydro-power 44 MW
Kiambere	1988	Tana	11,975	585	Hydro-power 144 MW

The upper basin comprises the Mount Kenya mountain ranges in the eastern part of the catchment, from where the watershed's gradient gradually declines till it reaches the Indian Ocean towards the southeast (WRMA, 2012). The highest rainfall (annual average of 1050 mm) is observed in the upper Tana basin, while the lowest rainfall (annual average 500 mm) is in the lower basin (WRMA, 2012). During the long rains the rains there are storms, winds and splashes, which probably lead to pollution of Tana River with pesticide residues and other contaminants from the farming areas along the river.

1.5 Problem statement

A large variety of pesticides is still used both in agriculture and public health in Kenya and are imported in large quantities. Due to lack of relevant data, equipment, and qualified personnel, these pesticides are normally applied following specifications set in the countries of manufacture (Lalah, 1993).

The various activities in the upper Tana River Basin are currently causing stress to the Tana River waters. These activities include: Livestock farming and crop farming. The crops produced in the area are coffee, maize, beans, tea, potatoes, carrots and vegetables. There is intense farming at the mid stream than in the upstream and downstream of the river. There are also

industry and factory activities going on in the area which include: Murang'a Chalk industry, near Kahuhia, Coca cola industry in Nyeri, Kihara Timber industry near Karatina and Cereal Board near Sagana. There is a coffee factory in Kirinyaga and Marua coffee factory at Marua, with Kiganjo fisheries which is stuated in Kiganjo area. Pesticides that are commonly used in the area under the study include: Chlorpyrifos (Dursban), dimethoate lambda-cyhalothrin (Karate), DDT, Aldrin, Dieldrin, Diazinon and Malathion (they are mostly used on vegetables, maize, beans and on fruit trees like bananas and oranges to kill aphids and on livestock to kill ticks). These pesticides are toxic to non-target organisms such as man and domestics animals. The current study therefore involves the analysis of chlorpyrifos and some organochlorine pesticides in water, sediment and weed samples collected from the upper Tana River. The weed analysed in the study include: *Pennisetum Purpureum* (Napier grass), *Cyperus Rotundus* (Nut grass) and *Elymus Elymoides* (squirreltail grass). Chlorpyrifos and organochlorine pesticides were analysed in this study since they are on rampant use on domestics animals and food crops in the area.

1.6 Justification

Pesticides being toxic compounds to the target material may have a detrimental effect on non-target organisms. It is therefore expected that the Tana River in the upper Tana catchment may be receiving and accumulating considerable levels of pest control products that may be detrimental to ecosystem health. It would therefore be important to assess these levels in order to determine the extent of the health risk to non-target organisms in the basin. Although there is available data by Munga (1985), on the analysis of DDT and Endosulfan residue in fish from Hola there is no such data, on the analysis of pesticides in the Tana River in the upper Tana

catchment area. The concern for the quality of the water used from Tana River has therefore contributed to the interest in the current study.

1.7 General objective

To assess the impact of Chlorpyrifos and organochlorine residue levels in water, sediments and weed samples from Tana River in the upper Tana catchment.

1.7.1 Specific objectives

a) To identify and quantify the organochlorines (which includes: *α-HCH, β -HCH, γ-HCH, δ-HCH, Heptachlor, Adrin, Heptachlor epoxide, Endosulphan I, ,p'p-DDE, Dieldrin, Endrin, Endosulphan II, p,p'-DDD, Endrin aldehyde, p,p'-DDT, Endosulphan sulphate, Methoxychlor*) residue levels present in: water, sediment and some selected weed samples from Tana River in the upper Tana catchment.

b) To determine the chlorpyrifos residue concentration levels present in: water, sediment and some selected weed samples from Tana River in the upper Tana catchment.

c) To determine selected physico-chemical parameters in the upper Tana River water samples

CHAPTER TWO

LITERATURE REVIEW

2.1 Water quality

Water plays an important role in the world economy. It functions as a solvent for a wide variety of chemical substances and facilitates industrial cooling. Approximately 70% of freshwater is consumed by agriculture (Baron *et al.*, 2007).

Water quality depends on the natural processes, such as seasonal trends, underlying geology and hydrology, weather and climate, and human activities, including domestic discharge, agriculture, industry and environmental degradation. Seventy five percentage (75 %), of Africa's drinking water comes from groundwater and is often used with little or no purification. Water contaminated by microbiological pollutants spreads diseases such as dysentery, cholera and typhoid (UNWA, 2011)

2.2 Pollution of water

Pollution of water bodies (lakes, rivers, oceans and ground water) affects plants and organisms living in them. The effect is damaging not only to individual species and populations, but also to the natural biological communities. Water pollution occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds. There are two types of water pollution sources: point source pollution and non-point source water pollution. Point source water pollution refers to contaminants that enter a waterway through a discrete conveyance, such as a pipe. Examples of sources in this category include discharges from a sewage treatment plant, a factory, or a city storm drain. Non-point source (NPS) pollution refers to diffuse contamination that does not originate from a single discrete source. NPS pollution is often the cumulative effect of small amounts of contaminants gathered

from a large area. The leaching out of nitrogen compounds from agricultural land which has been fertilized is a typical example. Nutrient runoff in storm water from "sheet flow" over an agricultural field or a forest is also cited as an example of NPS pollution (EPA, 2009). The specific contaminants in water include a wide spectrum of chemicals like persistent organic pollutant (POPs) (EPA, 2008).

The temperature of water also has extremely important ecological and quality consequences. Temperature exerts a major influence on aquatic organisms with respect to selection, occurrence and level of activity of the organisms. In general, increasing water temperature results in greater biological activity and more rapid growth. All aquatic organisms have preferred temperature in which they can survive and reproduce optimally. For example, trout typically needs cold water which may not be available in shallow waters during the summer. Temperature is also an important influence on water chemistry. Rates of chemical reactions generally increase with increasing temperature. The solubility of important gases, such as oxygen and carbon dioxide increases as temperature decreases. For example, warm water contains less dissolved oxygen (DO) than cold water. The solubility of most minerals increases with increasing temperature. Dissolved oxygen is probably the single most important factor affecting water quality (Mark, 2010).

Total organic carbon (TOC) is the amount of carbon bound in an organic compound and is often used as a non-specific indicator of water quality. Since the early 1970s, TOC has been recognized as an analytical parameter to measure water quality during the drinking water purification process. TOC in source waters comes from decaying Natural Organic Matter (NOM) and from synthetic sources. Humic acid, fulvic acid, amines, and urea are types of NOM. Detergents, pesticides, fertilizers, herbicides, industrial chemicals and chlorinated

organics, are examples of synthetic sources of water pollution (Hendricks, 2007). Before source water is treated for disinfection, TOC provides an important role in quantifying the amount of NOM in the water source. Calcium, zinc, manganese, phosphate, and sodium compounds may be added directly to water as a result of treatment processes such as pH adjustment or corrosion control. Other mineral nutrients such as copper and zinc can leach from plumbing materials; chromium and selenium can be present as impurities in paints, sands and other water contact materials (EPA, 2009).

2.3 Persistent Organic Pollutants

Persistent organic pollutants (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes. Because of this, they have been observed to persist in the environment, bioaccumulate in human and animal tissue, biomagnify, and can bio-concentrate up to 70,000 times their original concentrations in food chains (Ritter *et al.,* 2007). They have been found to have potential significant impacts on human health and the environment (Ritter *et al.,* 2007). UNEP (1999) also describes POPs as organic compounds of anthropogenic origin with a particular combination of physical and chemical properties such that, once released into the environment, they remain intact for exceptionally long period of time because of their resistance to photolytic, chemical and biological degradation. For example the half-life of most organochlorine insecticides can exceed 10 years (Ritter, *et al.,* 2007). POPs have the ability to volatilize and travel long distances through the atmosphere to become deposited in remote regions (Wandiga, 2001). In addition, POPs are both hydrophobic and lipophilic. In aquatic environments POPs partition and adsorb strongly to organic rich solids avoiding the aqueous phase and accumulates in the lipid rich tissues in animals where they solubilise and persist for extended period of time (Wania and Mackay,

1996). Due to their lipophilic nature, POPs biomagnify in the food chains along the tropic levels. POPs are also semi-volatile, and as a result they are distributed globally through the cycle of volatilization and deposition, known as the grass-hopper effect (Wania and Mackay, 1996). Groups of compounds that make up POPs include: Polychlorinated biphenyls (PCBs), Organochlorines and dioxins. These groups are also classified as Persistent, Bioaccumulative and Toxic (PBTs) or Toxic Organic Micro Pollutants (TOMPs) (Ritter *et al.* 2007). POPs may continue to poison non-target organisms in the environment and increase risk to humans by disruption of the endocrine, reproductive, and immune systems (Wandiga, 2001). They can be passed from mother to child and are known to have significant negative teratogenic, immunological, neurological and reproductive health effects (ASTDR, 2000). The Stockholm Convention, which was adopted in 2001 and became effective in 2004, requires Parties to take measures to eliminate or reduce the release of POPs into the environment. Organochlorines are among the persistent organic pollutants (POPs) for they resist breakdown, store easily in fat, and bioaccumulate through the food chain. The Stockholm Convention of 2004 and the EPA regulations have banned the use and manufacture of many organochlorines (e.g. aldrin, endrin, mirex, chlordane, heptachlor, toxaphene, dieldrin, hexachlorobenzene, lindane, α and β-hexachlorocyclohexane, chlordecone and polychlorinated biphenyls (PCBs). DDT was however allowed only for use in indoor house spraying against mosquitoes. Lindane, a pesticide commonly used in head lice treatments in the U.S. and whose use has already been banned in many countries, was added recently to the list for phase out (UNEP/GEF, 2010).

2.4 The organochlorine insecticides

The half-life of most organochlorine insecticides can exceed 10 years (Ritter, *et al.,* 2007). Even though the usage of most organochlorine insecticides is prohibited, a number of studies on rivers

and sediments throughout Malaysia have demonstrated that most of these compounds are present in the aquatic environment (Cheah and Lum, 1994). DDT, whose import was banned in Kenya in 1986 and is now banned in the United States because of its harm to the health of wildlife and people, is a notable example of an organochlorine pesticide. The half-life of DDT in humans is approximately 4 years (PCPB, 2008). Appendix IV (Table IV A and Table IV B) shows the list of all the banned and the restricted pesticides in Kenya respectively, while the structures, molecular formulae and half-lives of the organochlorine compounds analysed in this study are shown in Appendix 1 (Table 1 A).

2.4.1 Organochlorines mode of action

Organochlorine pesticides control pests by disrupting nerve-impulse transmission through interference with Na^+/Ka^+ ion flow at the axon/synapse level. They are generally persistent in soil, food, human and animal bodies and can thus accumulate in fatty tissue. Traditionally, they were used for insect and mite control, but many are no longer used due to their ability to remain in the environment for a long time. Examples of organochlorines include: Aldrin, Dieldrin, Chlordane, Endrin and Lindane (Freedman, 1995).

2.4.2 Health effects of organochlorines

In varying degrees, organochlorines are absorbed from the gut and also by the lung and across the skin. The efficiency of dermal absorption is variable. Lindane has a documented 9.3 % dermal absorption rate (Feldmann and Maibach, 1974), and is absorbed even more efficiently in abraded skin. Many organochlorine pesticides are endocrine disrupting chemicals, meaning they have subtle toxic effects on the body's developmental systems (Lemaire *et al.*, 2004). Endocrine

disrupting chemicals often mimic the body's natural hormones, disrupting normal functions and contributing to adverse health effects.

2.4.3 Ecological effects of organochlorines

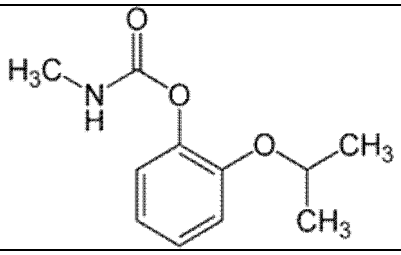
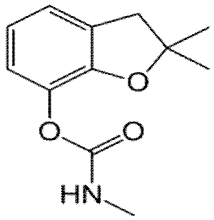
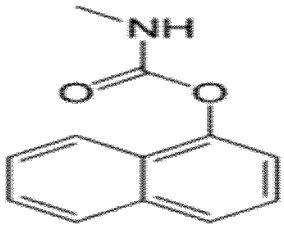
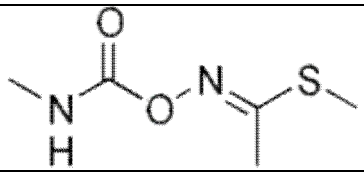
The presence of high concentrations of organochlorine pesticides and Polychlorinated biphenyls (PCBs) or their residues in marine mammals have been suggested as the cause of pathological changes and reproductive failures in whales (Wagner, 1989) and immunity suppression. To achieve snail control in flowing waters, such as irrigation canals, a concentration of niclosamide at 0.3 to 1 mg/L for 24 hours is recommended. This concentration would be toxic to fish in the same waters. DDT and trifenmorph can accumulate in fish tissues (Munga, 1985), which can be of great risk to the humans who consume the fish. This is one reason the use of the two pesticides at the Mwea Tebere settlements scheme was discontinued. Benthic organisms samples from the Kenyan coast were analysed for PCBs and cyclic pesticides by Everaarts *et al.,* (1997). They found that PCB congeners and cyclic pesticides concentrations were higher at the mouth of Sabaki River than in Tana River. They also found that bivalve molluscs from the mouth of the Sabaki River and Kiwaya Bay had the highest levels of PCBs (30 and 65 ng/g of lipid for congener 153) and 40 ng/g of lipid for congener 153. All samples were found to have *p,p'*-DDE, at levels ranging from 15 to 48 ng /g of lipid in both bivalve and gastropod mollusks. The above study by Everaats *et al*.,(1997), observed the presence of some groups of POPs compounds: organochlorines (p,p'-DDE) and PCBs, implying that these compounds could still be in use regardless of their ban in Kenya.

2.5 Carbamates

These pesticides are made from carbamic acid and control pests by acting on the nervous system through interference with nerve-impulse transmission by disrupting the enzyme cholinesterase

that regulates acetylcholine, a neurotransmitter. They are generally less persistent in the environment unlike the organochlorine pesticides. They can serve as insecticides, herbicides and fungicides and their health hazard to humans and animals is mild. Examples include: Carbaryl, Propoxur, Methomyl and Carbofuran 15 (Freedman, 1995) as shown in Table 2.1 below:

Table 2.1: Structures, molecular formula and half-lives of carbamate pesticides

Carbamate	**Structure**	**Molecular formula**	**Half-life**
Propoxur		$C_{11}H_{15}NO_3$	It has a field half-life of 14 to 50 days
Carbofuran		$C_{12}H_{15}NO_3$	22 days in 25 °C, pH 5.7, sandy-loam, 2.1 % organic carbon and 21 % moisture
Carbaryl		$C_{12}H_{11}NO_2$	4-17 days in (sandy loam soil) 21-27 days in (clay loam soil)
Methomyl		$C_5H_{10}N_2O_2S$.	a field 4-5 day

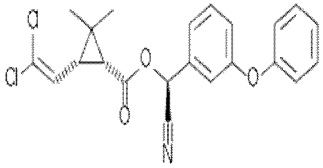
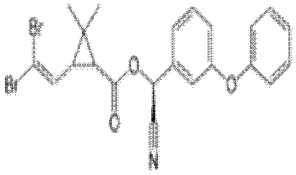
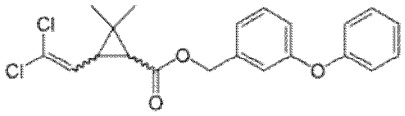
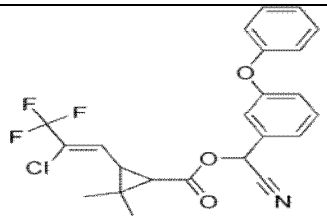
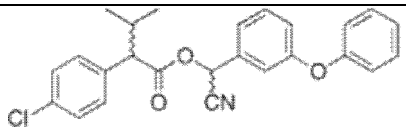
Source: Freedman, 1995

2.6 Pyrethroids

A pyrethroid is a synthetic organic compound which is similar to one of the natural pyrethrins molecule extracted from the flowers of pyrethrums. Pyrethroids now constitute

the majority of commercial household insecticides (Robert, 2002). Pyrethroids were introduced in the late 1900s by a team of Rothamsted Research scientists. They presented a major advancement in insecticidal activity with relatively low mammalian toxicity and usually fast biodegradation unlike the organochlorines (Robert, 2002). Pyrethroids control pests by disrupting nerve-impulse transmission, which stimulate nerve cells and eventually causes paralysis. They are much stable in sunlight. Examples include Cyhalothrin, Cypermethrin, Deltamethrin, Esfenvalerate and Permethrin (Freedman, 1995). Some examples of pyrethroids, their structures and half-lives are shown in Table 2.2 below:

Table 2.2 Structures, molecular formula and half-lives of pyrethroids pesticides

Pyrethroid	**Structure**	**Molecular formula**	**Half-life**
Cypermethrin		$C_{22}H_{19}Cl_2NO_3$.	30 days in soil and 9 days in water
Deltamethrin		$C_{22}H_{19}Br_2NO_3$	31-35 days
Cyhalothrin		$C_{25}H_{19}ClF_3NO_3$	In soil is 4 to 12 weeks and on plant surfaces is 5 days
Permethrin		$C_{25}H_{19}ClF_3NO_3$	In soil is 38 days. 51-71 days At pH=5 and at 25°C
Esfenvalerate		$C_{25}H_{22}ClNO_3$	17 days in soil 21 days in Water

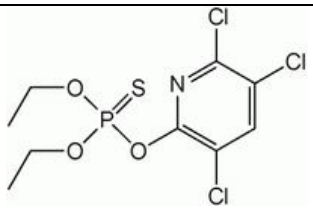
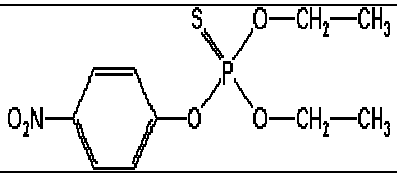
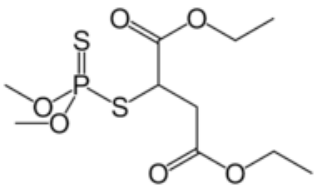
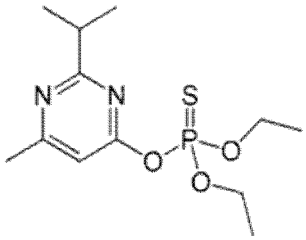
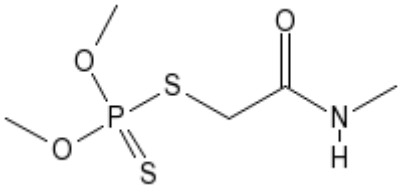
Source: Freedman, 1995

2.7 Organophosphate pesticides

Organophosphate pesticides (OPs) are usually made from phosphoric acid and most are insecticides controlling pests. OPs act on the nervous system through interference with nerve impulse transmissions by disrupting the enzyme cholinesterase that regulates acetylcholine, a neurotransmitter. With a few exceptions, most are highly toxic but are less persistent in soil, food

or animal feeds unlike organochlorine pesticides. Examples include Parathion, Chlorpyrifos, Diazinon, Dimethoate, Fenthion, Malathion, Naled, Phorate, Temephos and Trichlorfo (Freedman, 1995). Table 2.3 below shows some organophosphate pesticides and their structures.

Table 2.3 Structures of some organophosphate pesticides

Organophosphate Pesticides	**Structure**	**Molecular formula**	**Half-life**
Chlorpyrifos		$C_9H_{11}Cl_3NO_3PS$	1 day in blood, 62 hours in fat and 30 days in soil
Parathion		$C_{10}H_{14}NO_5PS$	3-6months in soil and 2 weeks to 1 Month in water
Malathion		$C_{10}H_{19}O_6PS_2$	1.65 days at pH 8.16 and 17.4 days at pH 6.0 in water 17 days in soil
Diazinon		$C_{12}H_{21}N_2O_3PS$	39 days in soil 185 days in neutral waters at pH 7.4, 0.5 days at pH 3.14 and 6 days at pH 10.9
Dimethoate		$C_5H_{12}NO_3PS_2$	21 day in soil 4 Months in water

Source: Freedman, 1995

2.8 Chlopyrifos

Chlorpyrifos is an organophosphate insecticide used to control infestation of variety of insects such as aphids. It was introduced in Kenya in 1965 and marketed by Dow Chemical Company under the trade names Dursban, Lorsban and Renoban. It is available in emulsifiable concentrate, dust, flowable, pellet, spray, granular and wettable powder formulations (Meister, 1992). While originally used to control mosquitoes in the immature, larval stage of development, chlorpyrifos is no longer registered for this use. Chlorpyrifos is used to control various species of fever ticks (*Boophilus sp*.), ear ticks, lice and horn flies on beef cattle and non-lactating dairy cattle, by use of emulsifiable liquid formulations in water with concentrations varying from 0.025 to 0.125 % applied as a spray or dip (Meister, 1992). Chlorpyrifos is also used in industries and factories during the construction of the buildings to prevent termite infestation. This is done by applying it as an under slab treatment combined with a circum-foundation soil barrier treatment during contruction (Meister, 1992).

Treatment for all ear ticks is limited to six applications at 21-day intervals, and not within two weeks of slaughter. Sheep dipped or sprayed with wettable powder or emulsifiable formulations of chlorpyrifos are protected from blowfly, ticks, body lice and sheep keds. A minimum interval of seven days is required between treatment and slaughter (U.S. EPA, 1991).

Chlorpyrifos is also effective in controlling cutworms, corn rootworms, cockroaches, grubs, flea beetles, flies, termites and fire ants (U.S. EPA, 1988). It is used as an insecticide on grain, cotton, field, fruit, nut and vegetable crops, as well as on lawns and ornamental plants (U.S. EPA, 1988). It is registered in U.S. for direct use on sheep and turkeys, horse site treatment, dog kennels, domestic dwellings, farm buildings and storage bins. Considerable work on the analysis of cattle tissues for residues of chlorpyrifos as well as its oxygen analogue and pyridinol metabolite has been documented (U.S. EPA, 2003). Cattle dipped in a 0.025 % chlorpyrifos emulsion, at an

interval of 21 days showed the first-phase half-life of chlorpyrifos to be 22 days (U.S. EPA, 2003).

Amjad *et al.,* (2010) analysed chlorpyrifos in wild plants (*Melilotus Indica*), in Lahore area, Pakistan, using HPLC. They found that the chlorpyrifos residue levels in the wild plant ranged between 20 and 710 µg/kg. Maximum limit of chlorpyrifos residue in these plants established by WHO and European Union (EU) are 50 and 500 µg/kg, respectively. Their highest level of 710 µg/kg was therefore above the limits set by the two bodies, while the lowest level of 50 µg/kg was below them. This study set out to determine the chlorpyrifos concentration residue levels in some selected samples from the upper Tana River, to confirm their state of contamination.

2.9 Physico-Chemical Parameters

2.9.1 Total Dissolved Solids (TDS)

Total dissolved solids (TDS) is the term used to describe the inorganic salts and some organic matter present dissolved in water. The principal constituents are usually calcium, magnesium, sodium, and potassium cations and carbonate, fluoride, chloride, sulfate, and nitrate anions. The presence of dissolved solids in water may affect its taste (WHO, 1996). The palatability of drinking water has been rated in relation to its TDS level as follows: excellent, less than 300 mg/L; good, between 300 and 600 mg/L; fair, between 600 and 900 mg/L; poor, between 900 and 1200 mg/L; and unacceptable, greater than 1200 mg/L (WHO, 1996). Higher concentrations of suspended solids can serve as carriers of toxics, which readily cling to suspended particles. This is particularly a concern where pesticides are being used. Where solids are high, pesticide concentrations may increase well beyond those of the original application. This is because more exotic and harmful elements of TDS are pesticides arising from surface runoff (APHA, 1992).

Higher levels of solids can also clog irrigation devices and might become so high that irrigated plant roots will lose water rather than gain it.

TDS in water supplies originate from natural sources like: sewage, urban and agricultural run-off, and industrial wastewater. Salts used for road de-icing in temperate climates can also contribute to high TDS loading in water. Concentrations of TDS from natural sources have been found to vary from less than 30 mg/L to as much as 6000 mg/L (WHO/UNEP, 1989), depending on the solubility of minerals in different geological regions. Different surveys have revealed different levels of TDS. In Canada, levels were found to be 500 mg/L in 36 of 41 rivers monitored (WHO, 1996), while, in the Great Lakes, levels ranged from 65 to 227 mg/L (Upper Lakes Reference Group, 1977). The levels of TDS in all of the Great Lakes except Lake Superior have been on the rise in the last 70 years, by up to 50–60 mg/L in Lakes Erie and Ontario (WHO/UNEP, 1990).

2.9.2 Total Suspended Solids (TSS)

The suspended or colloidal particles, commonly referred to as total suspended solids (TSS), are the extremely small suspended solids in water which will not settle out by gravity. They are basically those particles which will not pass through a two micrometers filter. Suspended solids are present in sanitary wastewater and many types of industrial wastewater. There are also non point sources of suspended solids, such as soil erosion from agricultural and construction sites. Runoff-related input usually leads to an increase of water level, nutrients and total suspended solids (TSS) in the water bodies; pesticides may enter the surface water as either water-dissolved or particle-associated chemicals, (Michaud, 1994). OCs tends to adsorb to the organic particles in water hence their positive correlation with TSS.

2.9.3 Water pH

Water is generally considered safe to drink as long as its pH is between 6.5 and 8.5 and therefore the human body operates well within this normal, “safe” pH range (Victoria, 2009). When pH is at the acidic end of the safe range, the human body becomes more inviting to viruses and bacteria, as well as more vulnerable to mucus secretion, congestion, and other chronic or “mysterious” recurring health issues such as sore throat, persistent headaches, cold and flu, fatigue, gout, chronic pain and itchiness or arthritis (Victoria, 2009).

Some pesticides, particularly carbamate and organophosphate insecticides, undergo an hydrolysis reaction in the presence of alkaline water (at pH value greater than 7), which reduces the effectiveness of the pesticide's active ingredient (Fred, 2002). Water with a lower pH also contains a higher number of suspended solids and dissolved minerals. This is because the suspended material typically has high salt concentrations. These substances also affect the performance of pesticides. The degradation and breakdown of the pesticides depend on the specific chemical properties of the pesticide, the pH of the mix water and the length of time that the pesticide is in contact with the water. Spray-mix water with a pH value between 8 and 9 can cause a rapid hydrolysis to the point that the degree of pest control is greatly diminished or lost (Fred, 2002).

Most aquatic animals and plants have adapted to life in water with a specific pH and may suffer from a slight change. Moderately acidic waters (low pH) may reduce the hatching success of fish eggs, irritate fish and aquatic insect gills and damage membranes. Water with extremely high or low pH is deadly. A pH below 4 or above 10 will kill most fish and very few animals can tolerate waters with a pH below 3 or above 11. Amphibians are particularly vulnerable to low pH, probably because of the high sensitivity of their skins to pollutants. Some scientists believe the

recent drop in amphibian numbers around the world is due to low pH levels caused by acid rain (Gregory *et al.,* 2005).

2.9.4 Electrical Conductivity

Conductivity is a measure of the ability of water to pass an electrical current. The Standard International unit of conductivity (SI) is siemens per (S) cm. Conductivity measurements are used routinely in many industrial and environmental applications as a fast, inexpensive and reliable way of measuring the ionic content in a solution For example, the measurement of product conductivity is a typical way to monitor and continuously trend the performance of the water purification systems. Conductivity is also affected by temperature; the warmer the water, the higher the conductivity. It is also linked directly to the total dissolved solids (TDS).

2.9.5. Salinity of water

Salinity is the saltiness or dissolved salt content in a body of water (Lewis, 1982). Salinity is part of total dissolved solids. The amount of dissolved material in the water is often used to estimate salinity, but because it usually includes dissolved organic matter it will overestimate the amount of salt present. Salinity is a general term used to describe the levels of different salts such as sodium, calcium sulfates, and bicarbonates. It is related to conductivity in that; different salts in water have a different ability to conduct electricity. This is because of the differences in charge and size of the different ions (Lewis, 1982).

2.10 Pesticides and Ecosystem Health

Freshwater systems are created by water that enters the terrestrial environment as precipitation, and flows both above and below the ground towards the sea (Chapman, 1998). These systems encompass a wide range of habitats, including rivers, lakes, and wetlands, and the riparian zones

associated with them. Their boundaries are constantly changing with the seasonality of the hydrological cycle. Their environmental benefits and costs are distributed widely across time and space, through the complex interactions between climate, surface and groundwater, and coastal marine areas. Freshwater ecosystems in rivers, lakes and wetlands contain only a small fraction (0.01 %) of the Earth's water and occupy less than 1 percent of the Earth's surface (Chapman, 1998). The different types of pesticides used globally could potentially reach to the groundwater. Although, the application of pesticides has decreased within the last decade (Damalas and Ilias, 2011), this does not necessarily indicate a decrease in environmental impact, as new pesticides continue to be released into the market.

Munga (1985) conducted a study in the Hola irrigation scheme, which demonstrated a strong correlation between DDT and endosulfan tissue residue and the level of fat in fish. The study that involved four species had the highest DDT residue levels of 423 µg/kg. Sediments serve as a habitat for benthic biota (such as insects, which are commonly consumed by fish). They also serve as both a source and a removal mechanism for some contaminants to and from the stream, and as a vehicle for contaminant transport downstream. Aquatic biota such as fish is also important in the food web of terrestrial animals such as humans and wildlife. Analyzing contaminants in sediment and aquatic biota provides an efficient way to test the presence of hydrophobic contaminants and their implications for ecosystem health (Abhik, 1996).

Madadi (2005) examined organochlorine and organophosphorus compounds residues levels in water, soil, weeds and fish samples from Lake Victoria. In general, the residue levels ranged from BDL-0.44 µg/L in water, BDL-65.48 g/kg in soils, BDL-10.07 g/kg in weeds and BDL-481.18 g/kg in fish samples. Dieldrin, p,p'-DDD, aldrin, p,p'-DDT, heptachlor, heptachlor

epoxide, endosulfan sulfate and lindane, (which are all organochlorines) had the highest concentrations.

2.11 Analysis of PCB, OCs and OPs

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCs) are some of the persistent organic pollutants (POPs) in the environment. The analytical methods for the analysis of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCs) are available, which are as a result of a vast amount of environmental analytical method development and research on persistent organic pollutants (POPs) over the past 30–40 years (UNEP, 2001). Critical to the successful application of this methodology is the collection, preparation and storage of samples, as well as specific quality control and reporting criteria. The current trend to use isotope-labeled analytical standards and high-resolution mass spectrometry for routine POPs analysis is particularly expensive (UNEP, 2001). These costs limit participation of scientists in developing countries and this is clear from the relative lack of publications and information on POPs from countries in Africa, South Asia and South/Central America. Access to modern capillary gas chromatography (GC) equipment with either electron capture or low-resolution mass spectrometry (MS) detection to separate and quantify OCP/PCBs is essential.

PCBs and OCs can be considered together because they are extracted and analyzed together in most cases. In practice, most laboratories determine about 30 or more individual PCB congeners, and 10–20 individual OCs and their metabolites, regardless of the sample matrix. Ongoing POPs monitoring programs vary in their analyte lists. For example, the Integrated Atmospheric Deposition Network (IADN) in the Great Lakes region of North America includes over 100 PCB congeners (IADN, 1994), while the UNEP/World Bank/GEF project on Persistent Organic Pollutants, Food Security, and Indigenous Peoples in Arctic Russia included 15 PCB congeners

(GEF, 2001). The Arctic Monitoring and Assessment Program recommended 30 ortho-substituted PCBs (AMAP, 2000).

Organophosphates and organochlorines have similar methods of analysis because they are both organic compounds which can be extracted from their media only by the use of organic solvents.

2.12 Gas Chromatopraphy Mass Spectrometry (GC-MS)

Gas chromatography–mass spectrometry (GC-MS) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. The use of a mass spectrometer as the detector in gas chromatography was developed during the 1950s after being discovered by James and Martin in 1952 (Robert and Adams, 2007). The development of affordable and miniaturized computers has helped in the simplification of the use of this instrument, as well as allowed great improvements in the amount of time it takes to analyze a sample. The Figure 2.1 shows a schematic diagram of a GC-MS

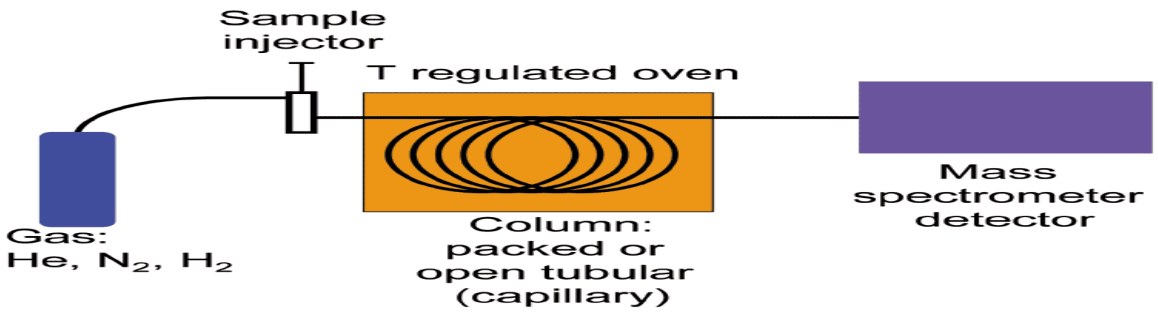


Figure 2.1: Schematic diagram of a GC-MS

An Agilent GC-system 6890N, Inert Selective Mass Detector (MS) –system 5975, and an Agilent split/splitless injector 7683 B series were used for qualification and quantification of organochlorines and chlorpyrifos in the sample extracts in the current study. The GC-MS was run using Helium as the carrier gas while injections were made on the splitless mode.

CHAPTER THREE

METHODOLOGY

3.1 Upper Tana River Catchments

The Upper Tana basin is located 50 km northeast of Nairobi and covers an area of approximately 16,000 km^2 with a population of about 3.1 million people (World Bank, 2007). Moreover, high population densities and intense agriculture in these areas are a cause of over abstraction of surface water and conflicts are common (WRMA, 2012). The high number of agro-based factories and urbanization contribute to pollution to the water resource. In this zone, water quality is affected by pollution from tea factories and sanitation from tea zone dwellers (there is a lack of sanitation facilities in tea zones) (WRMA, 2012). Potential evapotranspiration ranges from around 1700 mm in the low elevation savannah zone to less than 500 mm in the summit region. All areas below the forest zone have a rain-fall evapotranspiration deficit. As a consequence, the high elevation forest and moorland zones provide most of the discharge of the rivers in the dry periods (Notter et *al.,* 2007). The main river in the catchment is the Tana River, which supplies water to 17 million people, which was about 50 % of the country's population in 2004 (IFAD/UNEP/GEF, 2004). Tana River receives its water from the higher elevation regions, in particular from the Aberdares range and Mount Kenya. Other rivers originating from Mount Kenya are: the Thingithu, Rutugi, Ena, Rupingazi, Nyandi, Ragati, Nyamidi and Thiba. Mathioya, Maragua and Sagana drain from the Aberdares. The water resources of the Upper Tana basin provide water for 1 million hectares of rain fed agriculture and 68,700 hectares of irrigated land (Hoff and Noel, 2007).

The Tana River basin is divided into two distinct ecosystems. The Upper Tana basin, in the central part of Kenya, receives more rainfall and is the source of most of the water. Then there is

the lower, drier and flatter Lower Tana. Tana River is used to produce hydroelectricity and it supplies irrigation water to some of the largest public agricultural schemes in Kenya. However, the reservoirs in the middle part of the river are threatened by sediments generated from the intensively farmed areas in the upper Tana catchment. Ecosystem degradation has resulted in unpredictable flows of water amidst rising demand. The degradation is caused by deforestation, and the expansion of commercial and subsistence farming activities especially in the upper Tana catchment area. This study focuses on the Tana River in the Upper Tana catchment, where ecosystem degradation has the highest impact on the river's life supporting functions. There is increasing demand for irrigation water on the slopes of Mount Kenya, particularly to support horticulture production. Water usage in the upstream areas affects water availability in the lower drier areas (Mogako *et al.,* 2006).

Ten sampling sites were selected, which include: Makuyu, Sagana, Murang'a, Kirinyaga, Tetu, Karatina, Marua, Kiganjo, Hombe and Ndathi and their distribution is shown in Figure 3.1; while their local names and their Geographic Positioning Satellite (GPS) locations are also given in Table 3.1.

Table 3.1: GPS and local names of the selected ten sampling points

Sample No.	Sampling site	Name of the exact place of sampling on the river	GPS location
1	Makuyu	Mananja	00° 47’ 17S 037°16’06E 1058m
2	Sagana	Sagana Bridge or Kambi Moto	00° 39’ 59S 037°12’11E 1197m
3	Murang’a	Murang’a	00° 40’ 08S 037°10’10E 1206m
4	Kirinyaga	Kirinyaga	00° 40’ 29S 037°12’18E 1187m
5	Tetu	Aguthi	00° 31’ 07S 037°04’57E 1559m
6	Karatina	Katiki	00° 31’ 21S 037°05’06E 1549m
7	Marua	Marua	00° 27’ 11S 037°02’47E 1631m
8	Kiganjo	Kirumuga	00° 26’ 45S 037°02’34E 1634m
9	Hombe	State Lodge	00° 31’ 07S 037°4’57E 1756m
10	Ndathi	Kabaru	00° 19’ 44S 037°06’06E 1879m

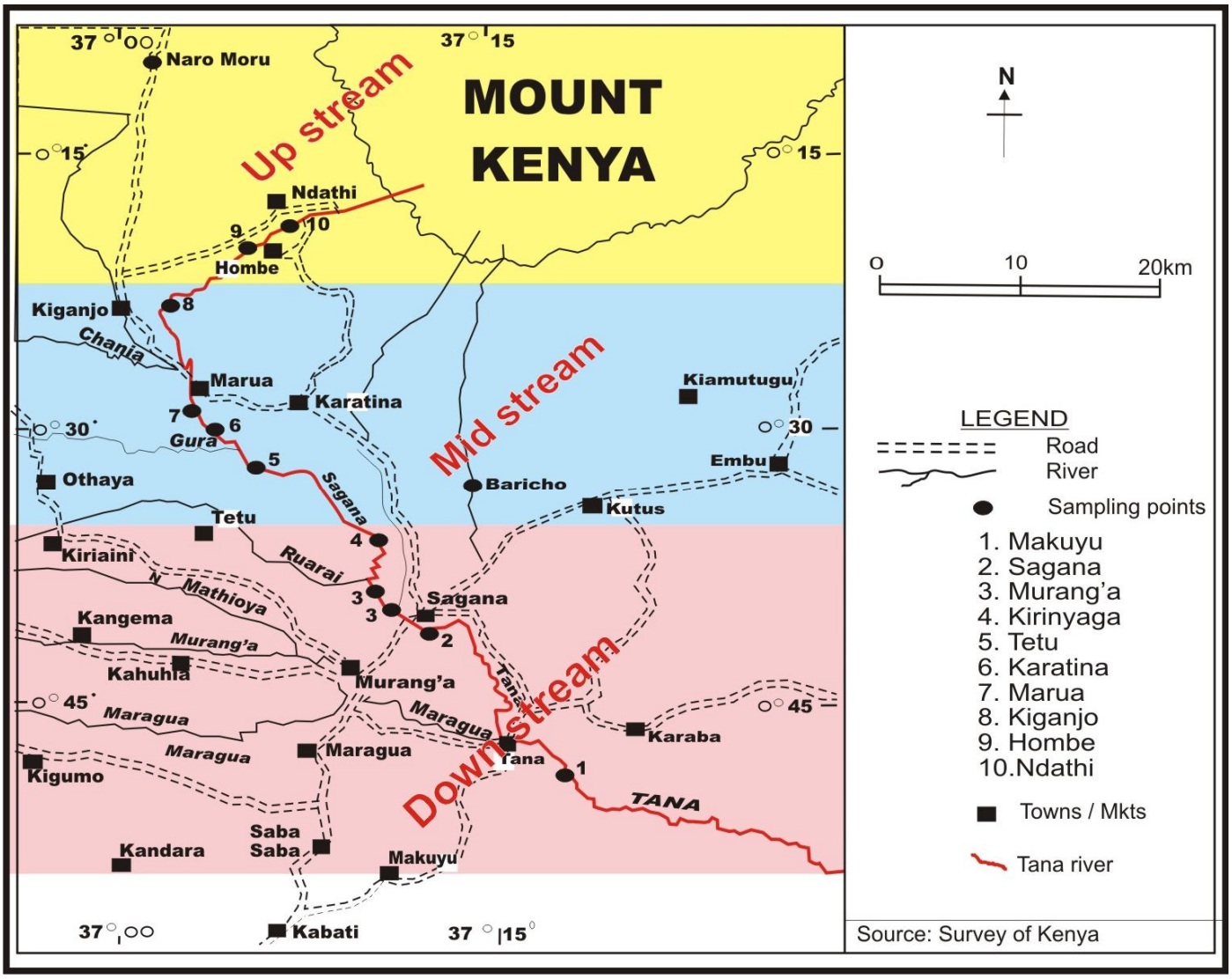


Figure 3.1: A map showing the sampling points of the study area

The selection of sampling points in the area of study (in Tana River in the upper Tana catchment), was based on the existing human and industrial activities along the upper Tana River and the River's profile, which was classified into upstream, midstream, and downstream.

3.1.1 The upstream section

The upstream comprises of Hombe and Ndathi with GPS positioning of 00^{o} 31' 07S 037^{o}4'57E 1756m and 00^{o} 19' 44S 037^{o}06'06E 1879m respectively, which can be observed in Table 3.1.

The Hombe area also locally referred as State Lodge, is mostly covered with forest with low population. The forest is normally preserved as a game park and for rain catchment. Nevertheless, ranching is going on in the area with little farming. Pesticides use is not common because of limited crop and livestock farming. Charcoal burning is also practiced deep in the forest, a possible source of pollution to the environs. Ndathi area is at the source of Tana River in Mount Kenya ranges, where by zero grazing and farming practices are also practiced. There is very rare crop farming activities in the area, with cabbage, carrots and potatoes dominating the area.

3.1.2. Midstream section

The sampling points in the midstream section are Tetu, Karatina, Marua and Kiganjo, with GPS positioning as 00^{o} 31' 07S 037^{o}04'57E 1559m, 00^{o} 31' 21S 037^{o}05'06E 1549m, 00^{o} 27' 11S 037^{o}02'47E 1631m and 00^{o} 26' 45S 037^{o}02'34E 1634m respectively as shown in Table 3.1. The waste from the Marua coffe factory in Marua, Mtu Athi coffee factory in Tetu and Nguguru coffee factory in Karatina, all of them situated in the mid-stream may be contributing to upper Tana River pollution especially during the rainy seasons due to flooding effect. The mid stream area is dominated with heavy crop and livestock farming than the upstream area. Tea, coffee, beans and maize are the main produced crops in the area. Some organochlorine pesticides like, DDT, aldrin and dieldrin are still on use in the midstream area.

3.1.3 Down stream section

The down stream section was represented by Makuyu, Sagana, Murang'a and Kirinyaga points. Farming activities take place in the area although not as much as in the mid stream areas. Zero grazing is practiced in the down stream especially in Makuyu. French beans, bananas and

potatoes are the main crops produced in the area. The wastes from KENGE in Makuyu, Cereal Board in Sagana and Kirinyaga coffee factory in Kirinyaga could be a possible source of pollution to Tana River waters.

The GPS positioning of the ten sampling points are 00^{o} 47' 17S 037^{o}16'06E 1058m, 00^{o} 39' 59S 037^{o}12'11E 1197m, 00^{o} 40' 08S 037^{o}10'10E 1206m and 00^{o} 40' 29S 037^{o}12'18E 1187m, respectively, as shown in Table 3.1. Some of the ten sampling sites selected in this study have their local names at the exact points of sampling on the river as shown in Table 3.1. The names of the towns near the samplings points have been used since the local names may not be very familiar to most Kenyans and globally. This assumption was made when it was realized that most of the residents in the areas were unaware of those names (especially the youth).

3.2 Sampling

The sampling was done per point from down stream to upstream of the river. The time of sampling during each sampling period are shown in Table 3.2.

Table 3.2: The time of sampling at each point during the study period

Points/Time	**Dec., 08**	**Feb., 09**	**June, 09**	**Sept., 09**	**Dec., 09**	**Feb., 10**	**April, 10**	**Sept., 10**
Makuyu	7.50 am *(Tuesday, 16/12/08)*	7.10 am *(Thursday, 12/02/09)*	7.40 am *(Tuesday, 16/06/0902)*	7.30 am *(Monday, 14/09/09)*	7.05 am *(Thursday, 17/12/09)*	8.08 am *(Tuesday, 16/02/10*	7.50 am *(Tuesday, 6/04/10)*	7.10 am *(Wednesday, 15/09/10)*
Sagana	9.30 am *(Tuesday, 16/12/08)*	10.13 am *(Thursday, 12/02/09)*	10.10 am *(Tuesday, 16/06/09)*	9.37 am *(Monday, 14/09/09)*	9.34 am *(Thursday, 17/12/09)*	10.30 am *(Tuesday, 16//10*	10.05 am *(Tuesday, 6/04/10)*	9.30 am *(Wednesday, 15/09/10)*
Murang'a	12.54 pm *(Tuesday, 16/12/08)*	12.04 pm *(Thursday, 12/02/09)*	1.34 am *(Tuesday, 16/06/09)*	1.54 am *(Monday, 14/0,9/09)*	11.54 am *(Thursday, 17/12/09)*	1.54 pm *(Tuesday, 16/02/10*	1.54 pm *(Tuesday, 6/04/10)*	11.35 am *(Wednesday, 15/09/10)*
Kirinyaga	3.52 pm *(Tuesday, 16/12/08)*	2.14 pm *(Thursday, 12/02/09)*	3.22 pm *(Tuesday, 16/06/09)*	3.52 pm *(Monday, 14/09/09)*	1.52 pm *(Thursday, 17/12/09)*	4.52 pm *(Tuesday, 16/02/10*	5.32 pm *(Tuesday, 6/04/10)*	2.52 pm *(Wednesday, 15/09/10)*
Tetu	8.21 am *(Wednesday, 17/12/08)*	5.00 pm *(Thursday, 12/02/09)*	5.41 pm *(Tuesday, 16/06/09)*	6.21 pm *(Monday, 14/09/09)*	4.21 pm *(Thursday, 17/12/09)*	8.21 am *(Wednesday, 17/02/10)*	7.21 am *(Wednesday, 07/04/10)*	5.21 pm *(Wednesday, 15/09/10)*
Karatina	11.55 am *(Wednesday, 17/12/08)*	7.51 am *(Friday, 13/02/09)*	8.52 am *(Wednesday, 17/06/09)*	9.55 am *(Tuesday, 15/09/09)*	8.55 am *(Friday, 18/12/09)*	11.55 am *(Wednesday, 17/02/10)*	9.45 am *(Wednesday, 07/04/10)*	8.55 am *(Thursday, 16/09/10)*
Marua	2.00 pm *(Wednesday, 17/12/08)*	10.21 am *(Friday, 13/02/09)*	11.09 am *(Wednesday, 17/06/09)*	1.00 pm *(Tuesday, 15/09/09)*	11.00 am *(Friday, 18/12/09)*	2.00 pm *(Wednesday, 17/02/10)*	12.20 pm *(Wednesday, 07/04/10)*	11.30 am *(Thursday, 16/09/10)*
Kiganjo	4.12 pm *(Wednesday, 17/12/08)*	3.23 pm *(Friday, 13/02/09)*	2.11 pm *(Wednesday, 17/06/09)*	3.12 pm *(Tuesday, 15/09/09)*	4.12 pm *(Friday, 18/12/09)*	5.12 pm *(Wednesday, 17/02/10)*	3.12 pm *(Wednesday, 07/04/10)*	2.12 pm *(Thursday, 16/09/10)*
Hombe	8.23 am (Thursday, 18/12/08)	5.33 pm *(Friday, 13/02/09)*	5.28 pm *(Wednesday, 17/06/09)*	6.23 pm *(Tuesday, 15/09/09)*	7.23 am *(Saturday, 19/12/09)*	7.16 am *(Thursday, 18/02/10)*	8.43 am *(Thursday, 08/04/10)*	5.23 pm *(Thursday, 16/09/10)*
Ndathi	11.23 am (Thursday, 18/12/08)	8.11 am *(Saturday, 14/02/09)*	7.21 am *(Thursday, 18/06/09)*	7.23 am *(Wednesday, 16/09/09)*	10.32 am *(Saturday, 19/12/09)*	10.42 am *(Thursday, 18/02/10)*	11.23 am *(Thursday, 08/04/10)*	7.23 am *(Friday, 17/09/10)*

Samples of water, sediments and weed [*Pennisetum Purpureum* (Napier grass), *Cyperus Rotundus* (Nut grass) and *Elymus Elymoides* (squirreltail grass)], were collected in triplicate from each of the ten identified sampling points during each sampling for two years, covering the dry and wet seasons.

Eight samplings were made to make a total of 720 samples, which means 240 samples of each matrix was collected for analysis. Each sampling site covered approximately 2,500 square meters. Within each site at least 3 samples were collected at each of three points but within 50 m and homogenized to form a representative sample.

Water samples were taken from the surface of water using amber bottles (two and half litres). The amber bottles were cleaned with laboratory detergent, rinsed with sufficient amount of tap water followed by distilled water, and then dried. The bottles were rinsed further with an organic solvent (acetone), and then dried. The water samples were collected at the center of the flow but against the wave current. Care was taken to avoid the foreign objects or oil films floating on the surface from being gathered into the sample as they could contaminate the water samples. The contaminants can cause matrix interferences during the analysis process. In chemical analysis, matrix refers to the components of a sample other than the analyte (Nick, 2006). The matrix can have a considerable effect on the way the analysis is conducted and the quality of the results obtained; such effects are called matrix effects or matrix interferences (Fifield, 2000).

Sediment samples were collected at 10 cm depth under the surveillance water using a shovel. Foreign matter, such as pebbles, pieces of shell or animal or plant body parts were removed from the sample before wrapping with an aluminium foil. The samples were labeled and put in an ice box. The weed samples were plucked by hands while the hard ones were cut using a clean stain

less steel knife and then placed in polythene bags. All samples were preserved using ice in a ice box.

3.3 Equipment and Chemicals

Table 3.3 shows the list of the Equipment, chemicals and solvents used in this study, along side with their manufacturers and their purity details.

Table 3.3: A list of Equipment and Chemicals used in the study

Item No.	Equipment/ Chemical/ Solvent	Manufacturer	Purity	Vendor
1.	Dichloromethane (DCM)	New Delhi-b110 020 India	GPR	Fisher, Kenya
2.	Mercuric chloride	New Delhi - b110 020 India	99.8 %	Fisher, Kenya
3.	Copper powder	New Delhi - b110 020 India	99.6 %	Fisher, Kenya
4.	An hydrous sodium sulphate	New Delhi- b110 020 India	99.7 %	Fisher, Kenya
5.	Sodium chloride	New Delhi - b110 020 India	99.9 %	Fisher, Kenya
6.	Aluminium oxide	New Delhi - b110 020 India	99.7 %	Fisher, Kenya
7.	Hydrochloric acid (HCL)	New Delhi - b110 020 India	99.8 %	Fisher, Kenya
8.	Disodium hydrogen phosphate	New Delhi - b110 020 India	99.7 %	Fisher, Kenya
9.	Methanol	New Delhi - b110 020 India	99.6 %	Fisher, Kenya
10.	Isooctane	New Delhi- b110 020 India	99.7 %	Fisher, Kenya
11.	Chlorpyrifos standard	New Delhi- b110 020 India	99.8 %	Fisher, Kenya
12.	PCB 155 standard	A-3 Okhla Industrial area, Phase -1	99.5 %	New Delhi-110 020 (India)

Table 3.3 contd. A list of Equipment and Chemicals used in the study contd.,

Item No.	Equipment/ Chemical/ Solvent	Manufacturer	Purity	Vendor
13.	PCB 198 standard	A-3 Okhla Industrial area, Phase -1	99.5 %	New Delhi-110 020 (India)
14.	OCs standard mix	A-3 Okhla Industrial area, Phase -1	99.5 %	New Delhi-110 020 (India)
15.	GC-MS		-	Chemetris pty. Ltd. S.A.
16.	Rotary evaporator	Made in UK Stuart Scientiufic	-	Fisher, Kenya
17.	Moisture content determination oven	D-78532 Tuttlingen/ Germany	-	Fisher, Kenya
18.	Soxhlet extractors	Made in UK Stuart Scientiufic	-	Fisher, Kenya
19.	pH meter	Extech Instruments Corporation Company, USA- A Flir Company	-	Fisher, Kenya
20.	Hexane	New Delhi-b110 020 India	GPR	Fisher, Kenya
21.	Acetone	New Delhi-b110 020 India	GPR	Fisher, Kenya

Key: GPR- General Purpose Reagent

3.4 Reagents preparation

Anhydrous sodium sulphate, Na_2SO_4 was prepared by heating for 16 hours at 150 ^oC in the oven to remove all the impurities. Aluminum oxide (Al_2O_3) was activated by heating at 150 ^oC for 16 hours. To deactivate the Al_2O_3, 8 ml of HPLC grade water was added to every 100 g of the activated portion and used where appropriate. For laboratory work, the commercial acetone, hexane and dichloromethane were each triple distilled before use.

3.5 Quality Assurance and Quality Control

Quality assurance and quality control were checked by spiking each matrix and blanks with a surrogate standard of each pesticide. For water samples, the blanks contained 1 L of double distilled water, while for sediment and weed samples, the blanks contained 20 g and 5 g of anhydrous Na_2SO_4 respectively. After extraction and clean-up, the extracts were subjected to GC-MS analysis. Recoveries were determined to ascertain the level of quality assurance and experimental quality control. For all analysis, PCB 198 was used as an internal standard for monitoring detector sensitivity. The experimental limit of detection (LOD) was determined using the formula:

$$LOD = \frac{3NC}{R}$$

Where N is the noise peak area for the lowest calibrating standard, C is the concentration of the standard injected and R is the analyte response in the lowest point. All concentrations found to be lower than LOD were reported as below detection limit (BDL).

3.5 Sample Extraction

3.5.1 Water samples

Water samples were extracted by liquid-liquid partitioning using dichloromethane as follows: One litre of the sample was transferred into a 2.0 litre separatory funnel. 50 ml of the buffer was

added to each sample to neutralize the solution to pH 7. The buffer was prepared by mixing 0.1 M of Hydrochloric acid and 0.1 M of disodium hydrogen phosphate in the ratio of 1:2. The mixture was shaken with 100 g of sodium chloride to salt out the pesticides from the aqueous phase. Sixty ml of triple distilled dichloromethane was added and the mixture shaken for two minutes and allowed to settle for 30 minutes. The organic layer was separated and filtered using glass wool. The extract was then concentrated using a rotary evaporator at 60 ^{o}C, and reconstituted in 5 ml HPLC isooctane before transferring into the vials for GC-MS analysis.

3.5.2 Sediment samples

The frozen sediment samples were allowed to thaw out for at least 5 hours in the laboratory. A 20 g portion of each sample was weighed in triplicate and mixed with 5 g anhydrous Na_2SO_4 and ground using mortar and pestle to form an homogenous powder. The dried samples were placed in a thimble and spiked with 100 µl of PCB 155 as a recovery standard, then transferred into a Soxhlet extractor. The mixture was extracted with 130 ml of hexane: acetone (3:1 v/v) for a minimum of 16 hrs. 2 ml of isooctane was then added as a keeper and the extract concentrated to 1 ml using rotary evaporator and stored awaiting the clean-up and the GC-MS analysis processes.

3.5.3 Weed samples

The weed samples were air dried prior to extraction. They were then ground using a blender in order to increase the surface area for thorough interaction with the acetone solvent during extraction. 10 g of each sample was weighed in triplicate into 150 ml Erlenmeyer flask and extracted for 16 hours with 50 ml of triple distilled acetone on an orbital shaker. The extract was filtered through Buchner funnel fitted with filter papers No.1. Two (2) ml of isooctane was then added to the extract as a keeper prior to concentration process, which was done using a rotary

evaporator. The 1 ml extract obtained after the concentration process was then stored in a refrigerator at 4 ^{o}C, awaiting clean up and analysis processes.

3.6 Sulphur removal from sediment extracts

Sulphur removal from sediment extracts was done using activated copper powder. The copper powder was activated by shaking 10 g of the powder with 30 ml dilute HCl. The content was then centrifuged for one minute at 300 revolutions per minute. The liquid was discarded and copper powder rinsed with methanol which was then followed by re-centrifuging. The process of rinsing and re-centrifuging was repeated thrice and the copper powder dried at 30 ^{o}C in a water bath under a stream flow of white spot nitrogen gas. Portions of the activated copper powder (1 g) were added to the sediment extracts and the contents mixed and let to stand for 20 minutes to allow for sulphur removal.

3.7 Clean-up of the extracts

Each sample extract was purified by passing through a 60 cm long glass column of 2 cm internal diameter packed with a slurry of 10 g alumina and topped with 2 g anhydrous sodium sulphate. The pesticide residues were eluted with 80 ml of hexane. The eluent was then concentrated to 2 ml on a rotary evaporator at 60 ^{o}C, and then further reduced to 0.5 ml under white spot nitrogen. 100 µL of the standard (PCB 198) was added, and the contents mixed before injecting 1 µl into the GC-MS for analysis.

3.8 Preparation of the calibration curves

Stock standard solution (a mixture of organochlorines and chlorpyrifos) was prepared using isooctane. Working standards for GC-MS calibration were prepared by serial dilution of the stock standard solutions using isooctane. The series consisted of eight calibration levels each with different concentration as shown in Table 3.4 below:

Table 3.4: Serial dilutions of the stock standard

Vial	**Concentration of OC mix standards in µg/L**	**Concentration of chlorpyrifos standard in µg/L**
1.	0.83	0.88
2.	0.62	0.72
3.	0.42	0.53
4.	0.34	0.39
5.	0.12	0.24
6.	0.09	0.12
7.	0.03	0.04
8.	0.01	0.01

The purpose of the calibration was to ascertain the relationship between the amount of standard injected and peak area at the specific retention time for each pesticide.

The Ionic Mass Spectra for different organochlorine compounds and chlorpyrifos were used to ascertain the compound, identified by virtue of their different abundance and mass to charge ratios. A spectrum in this case refers to a fragment unique to a certain molecule; while the fragments represent various masses which are unique to a particular compound. In this case a library with specific spectra for pesticides was used, which has about 600 pesticides.

3.9 Moisture Content determination in sediment and weed samples

Moisture content in sediment and weed samples was determined by first drying them (10 g of sediment and 5 g of weed sample) to constant weight in an oven (Binder, E28 LB04-71528, Germany) at 105 ^{o}C for 24 hours in triplicate. The weight differences were used in calculating the moisture contents of the samples at the time of extraction (UNEP, 1984).

3.10 Determination of pH of water samples.

The pH of the water samples was determined at the sampling site using a combined scientific pH/Conductivity/TDS meter. The meter was calibrated using buffers of pH 10.0, 7.0, and 4.0 before use.

3.11 Conductivity of the water samples

The conductivity was also done using the combined scientific pH/Conductivity/TDS Meter previously calibrated. The calibration was done by dipping the electrode in 20 ml buffer solutions of 84 µS/cm, 1,413 µS/cm and 12,880 µS/cm.

3.12 Total Dissolved Solids in water

The TDS was obtained by multiplying the electrical conductivity value of the same sample by a known factor (0.7). The meter used allows a selection of a conversion ratio in the range of 0.4 to 1.0. The ratio varies with the application, but is typically set between 0.5 and 0.7. The TDS values were therefore presented in mg/L.

3.13 Total Suspended Solids

TSS was determined by filtering a 100 ml of a thoroughly mixed water sample through a pre-weighed standard Whatman filter paper No. 1 under vacuum. The residue was dried to constant weight in an oven at 105 ^{o}C. The increase in weight of the filter represents the total suspended solids calculated by the following formula:

$$\text{Total suspended solids} = \frac{(A-B) \text{ X } 1000}{\text{Sample volume, mL}}$$

Where:

A = weight of filter paper + dried residue, (mg) and

B = weight of filter paper (mg).

3.14 Statistical analysis of Data

The statistical analysis and the drawing of calibration curves was done using Microsoft excel and ANOVA, while the relationship between pesticides concentration and the physico- chemical

parameters were done using Pearsons' correlation Statistical Package for Social Scientists (SPSS 10).

CHAPTER FOUR

RESULTS AND DISCUSSION

The results of the identification and quantification of OCs and Chlorpyrifos at each of the ten sampling points including their seasonal variations, determination of other physico-chemicals parameters in the matrices and the correlation of those physico-chemical parameters with the OCs and chlorpyrifos over the two years of sampling and analyses, are presented in this chapter.

The recoveries were determined in all the samples (water, sediment and weed) analysed in this study by spiking with 100 µL of surrogate standard, PCB 155 prior to extraction. The average recoveries of PCB 155 were 83 %, 89 % and 83 % in water, sediment and weed samples respectively, which were all within the recommended range of between 70 % and 120 % (UNEP, 2007), and therefore the method of extraction and analysis that was carried out in this study is recommendable.

According to the Kenya Meteorological Department, at Nyeri, Sagana and Mt. Kenya stations the average monthly rainfall recorded in the upper Tana catchment across the sampling period were as shown in Table 4.2. Some of the standards and samples chromatograms and their spectra realized in this study during the GC-MS analysis are shown in Appendix VI of this text. The BDL for each of OC compounds and chlorpyrifos are as listed in Table 4.1.

Table 4.1 The LOD for each OC compounds and Chlorpyrifos (µg/kg)

Analyte	LOD	Analyte	LOD	Analyte	LOD
a-HCH	0.00051	Endosulphan I	0.00108	Heptachlor epoxide	0.00052
b-HCH	0.00092	pp-DDT	0.00015	Endosulphan sulphate	0.00023
g-HCH	0.00032	Dieldrin	0.00021	Methoxychlor	0.00012
d-HCH	0.00214	Endrin	0.00201	Chlorpyrifos	0.000102
Heptachlor	0.00023	Endosulphan II	0.00024		
Adrin	0.00044	pp-DDD	0.00032		
pp-DDE	0.00191	Endrin aldehyde	0.00021		

Table 4.2: Average rainfall recorded in the sampling area

Sampling period	**Average rainfall recorded in mm**
December- 2008	137.9
February-2009	9.1
June-2009	68.2
September-2010	10.5
December-2009	120.3
February-2010	9.1
April-2010	121.23
September-2010	3.5

4.1 Levels of organochlorines (OCs) in water samples

The specific objective in this subsection was to identify the concentration of organochlorine pesticides in water samples

4.1.1 Spatial distribution of OCs in water

Table 4.4 below shows the overall mean concentration of each OC compound during the two years of sampling from the ten sampling points. The OC compounds detected in the water samples ranged from < 0.00021 to 107.33 µg/L with the p,p'-DDT showing the highest level of 107.33 µg/L, which was observed in water samples from Point 7 (Marua) in the mid-stream section. The lowest OC levels on the other hand were detected at Point 10 (Ndathi) located up stream section with the lowest concentration of 0.14 µg/L.

National governments introduced residue limits and guideline levels for pesticide residues in water when policies were implemented to minimize the contamination of ground and surface waters. Initially, the main attention was given to drinking water (IUPAC, 2003). The basis for limits and guideline values issued by WHO, Australia, the United States, New Zealand, Japan, Canada, European Union, and Taiwan is described, and examples of the limits are provided in Table 4.3. Only 10 % of the DDT and its isomers residue levels detected were below the WHO, Australia, the United States, New Zealand, Japan and Canada limit guidelines for drinking water,

whereas 90 % were above the recommended values in Table 4.3. 95 % of the other OCs compounds residue levels were below the WHO, Australia, the United States, New Zealand, Japan and Canada with only 5 % above the same levels.

Table 4.3: Health-based guideline values for pesticide residues in drinking water in µg/L

Pesticides	**WHO**	**EPA**	**Australia**	**US**	**New Zealand**	**Canadian**
Aldrin	0.03	-	0.3	0.3	0.03	0.7
DDT & its derivatives	2	0.2	2		2	
Methoxychlor	20	40	0.02	50	20	
Chlorpyrifos	40				70	
Dieldrin	0.03	-	0.01	0.5	0.03	0.7
Endrin	-	2	-	20		
Heptachlor	0.08	0.4	0.05	10	0.04	
Heptachlor epoxide	0.03	0.2	0.05	10	0.04	
Lindane	2	0.2	0.06	10		

In comparison a study done on the analysis of OCs residues in the Marine Environment along the Coastal Region of Kenya by Yugi (2000), reviewed a high concentration residue levels of DDT of 3,284 µg/L in water samples. This level was above the WHO, Australia, the United States, New Zealand, Japan and Canada limit guidelines for drinking water. Similarly p,p'-DDT had the

highest concentration residue level of 107.33 µg/L in the current study, which is also above the set guidelines by the same international bodies.

Table 4.4: Mean residue levels of OCs in water samples in µg/L±sd

OCs compounds/sampling points	**Makuyu**	**Sagana**	**Murang'a**	**Kirinyaga**	**Tetu**	**Karatina**	**Marua**	**Kiganjo**	**Hombe**	**Ndathi**
a-HCH	1.59±0.28	0.72±0.39	4.82±0.7	3.42±0.62	5.9±0.82	2.12±0.53	1.23±0.88	1.23±0.88	0.75±0.15	0.26±0.05
b-HCH	1.62±0.34	0.65±0.23	13.90±0.3	26.36±0.3	2.69±0.23	3.06±0.5	12.43±1.2	12.43±1.3	0.35±0.25	1.40±0.29
g-HCH	1.16±1.27	0.46±0.25	43.85±2.9	9.22±0.54	1.23±1.23	1.51±0.14	26.17±0.9	26.17±0.3	2.10±0.25	< 0.00032
d-HCH	2.12±0.53	5.12±0.97	11.54±0.5	10.50±0.83	5.01±0.67	12.43±1.2	9.63±1.08	2.55±0.48	2.07±0.2	51.79±2.05
Heptachlor	1.50±1.32	1.96±0.6	48.4±3.21	12.46±3.1	2.89±1.04	2.29±0.31	1.87±0.29	1.87±0.21	3.33±0.12	1.69±0.34
Adrin	1.38±0.26	5.12±0.5	18.09±2.8	11.54±0.5	1.21±0.05	6.10±0.46	3.31±0.71	3.31±0.3	0.54±0.26	0.14±0.13
Heptachlor epoxide	< 0.00052	0.34±0.03	106.03±6.	12.51±0.6	4.80±0.34	1.45±0.81	2.07±0.21	2.07±0.12	1.73±0.71	1.50± 0.4
Endosulphan I	1.70±0.24	2.13±0.63	17.03±1.3	5.83±0.58	1.33±0.17	1.45±0.07	13.23±0.3	13.23±0.1	2.41±0.17	0.39±0.2
pp-DDE	7.87±0.96	3.85±4.19	38.39±4.5	10.62±0.2	4.60±0.59	7.05±0.66	26.76±7.6	26.76±7.4	12.26±5.3	6.18±0.31
Dieldrin	1.22±0.96	4.19±0.08	6.07±0.94	1.67±0.15	0.72±0.11	3.87±0.26	1.54±0.13	1.54±0.21	1.97±0.17	0.46±0.28
Endrin	1.03±0.55	4.32±0.03	21.07±4.3	13.12±2.7	5.40±1.13	4.08±0.33	49.31±7.6	49.31±4.3	6.13±1.22	1.51±1.32
Endosulphan II	4.35±0.65	0.63±0.02	1.07±4.3	1.12±2.7	5.20±1.13	5.01±0.67	12.20±0.4	12.20±0.4	8.78±0.21	0.42±0.28
pp-DDD	3.85±1.19	5.0±1.5	1.51±4.8	21.0±3.58	1.20±0.45	107.33±2.	11.03±3.13	26.36±0.3	2.41±0.16	< 0.00032
Endrin aldehyde	7.96±2.19	< 0.00021	46.46±4.3	5.12±0.97	0.95±0.26	9.63±1.06	11.03±1.0	11.03±3.1	9.03±1.62	4.13±0.25
pp-DDT	5.19±1.91	1.36±0.09	8.67±1.25	8.61±2.64	3.69±1.06	105.10±4.	107.33±2.	102.33±3.	65.71±1.2	51.79±1.0
Endosulphan sulphate	3.40±0.25	3.58±0.5	2.24±0.23	3.34±0.88	1.20±0.45	20.61±0.5	2.55±0.8	2.55±0.2	< 0.00023	11.65±2.0
Methoxychlor	6.72±0.13	1.5±0.12	11.94±0.2	4.76±0.09	0.78±1.5	14.55±0.1	63.32±0.0	63.32±0.3	3.38±1.79	0.68±2.04

Key: sd- standard deviation

The mean concentration of each OC compounds in water samples from all the sites over the two years of sampling are as shown in Table 4.4. p,p'-DDT was observed to have the highest total levels of 384.04 µg/L and dieldrin had the lowest levels of 25.1 µg/L. The first column in Table 4.4 above shows the OC compounds that were analysed, while the first row shows the names of the sampling sites.

Some of the mean had equal or higher value of the standard deviation. This occurs where the replica sample concentrations are not consistent; which is due to systematic error incurred in analytical produres.

Figure 4.1 below shows the distribution of the total of the means of the OC compounds in every sampling point. Kiganjo had the highest value of 334.32 µg/L while Murang'a had the lowest value of 39.60 µg/L. Kiganjo area, which is located in the mid-stream had the highest total of the mean of OCs probably because of the intense crop and cattle farming activities going on in the area.

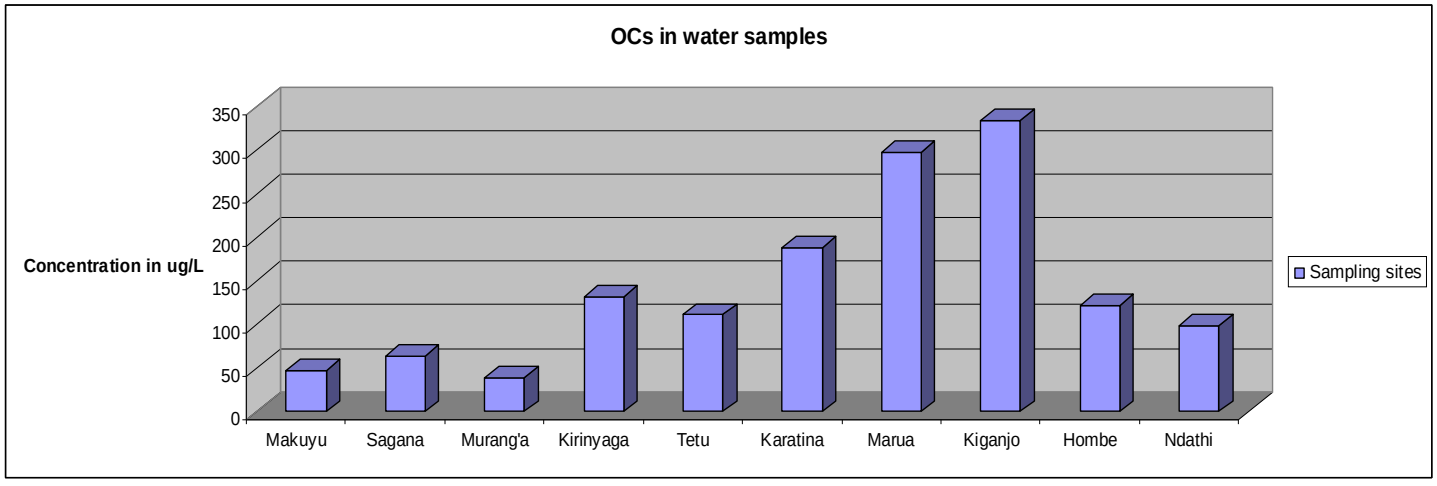


Figure 4.1: Total organochlorine residue levels in water samples per site

The mid-stream had higher total mean concentration residue level of OCs (of 728.63 µg/L) than those on the downstream (283.1µg/L) and up stream (219.93µg/L) as shown in Figure 4.2 below.

Mtu Athi coffee factory in Tetu and Nguguru coffee factory in Karatina are situated very close to the sampling point, a possible sources of contaminants due to the discharges. Farming activities are much carried out at the midstream than at the down and up stream of the upper Tana River. It was also found that the farming activities have an older history at the midstream than at the downstream.

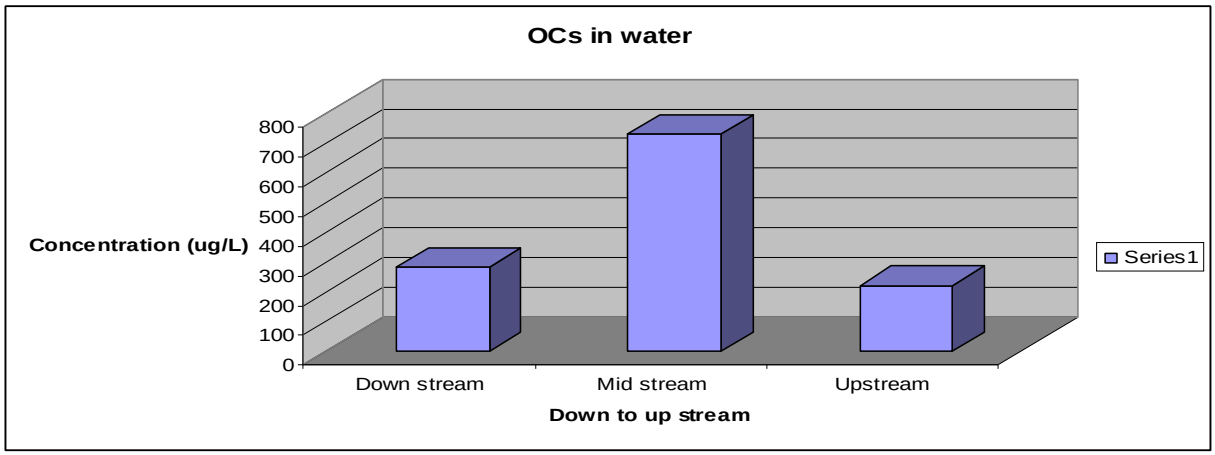


Figure 4.2: The total organochlorine residue levels in water samples

4.1.2 Temporal distribution of organochlorines in water

OC compounds were detected in all the water samples across the sampling period. Low concentrations of OC residue levels were detected in the water samples that were collected during the wet seasons than those sampled during the dry seasons as indicated in Figure 4.3. For example high total OC concentration residue level was recorded from the samples collected in February, 2009 (dry season) of 874.23 µg/L while the lowest total concentration of 326.32 µg/L was observed on samples that were sampled in December, 2008 (wet season) as shown in Figure 4.3. This is expected because during the wet seasons there occurs a high run-off into the rivers which therefore increases the water volume hence the dilution of the contaminants. The other

possible reason behind the low concentrations during the wet season could the nature of the organic compounds adsorbing the organic matter.

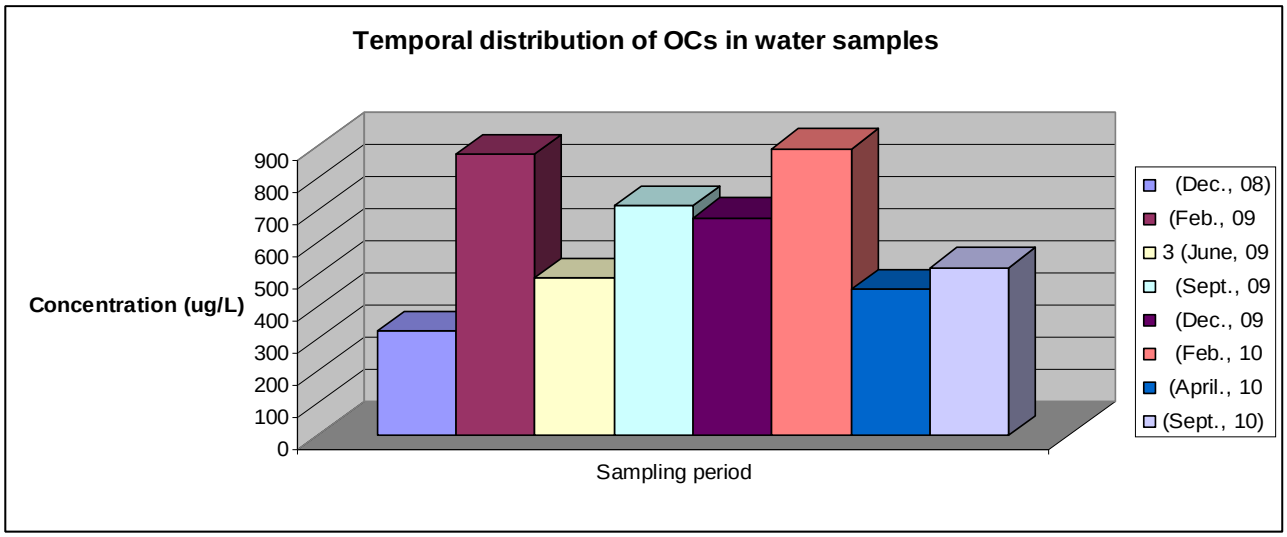


Figure 4.3: Temporal distribution of organochlorine compounds levels in water samples

4.1.3 Seasonal variation of the organochlorines levels in water samples

The seasonal changes were observed to influence the concentrations of OCs in the area of study. The OCs residue levels in water samples depicted a general trend of decreasing mean total concentration levels: dry season > short rains > long rains as can be observed from Figure 4.4.

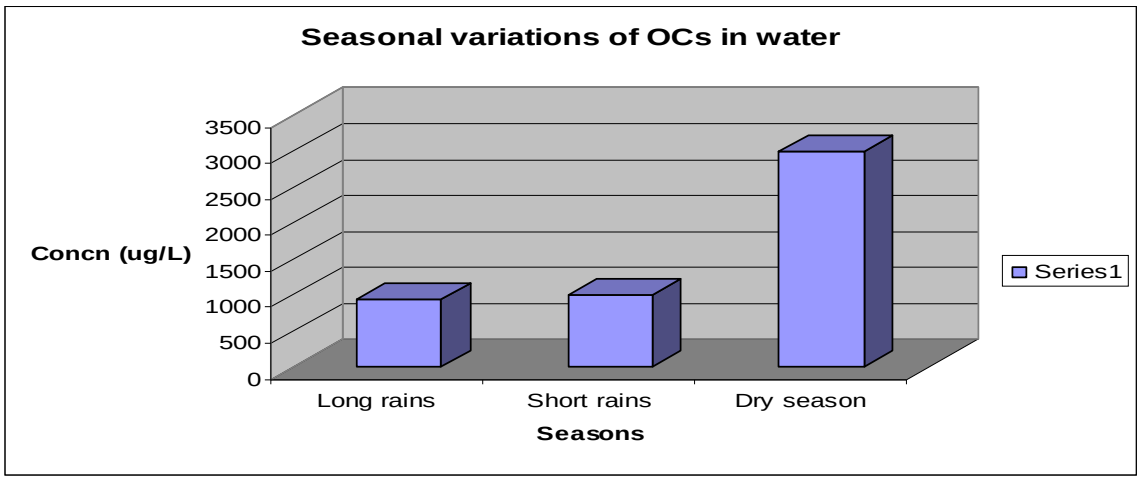


Figure 4.4: Seasonal variations of organochlorine residue levels in water samples

4.2 Distribution of organochlorines in sediment samples

The main aim in this sub-section was to determine the OCs in sediment samples. Table 4.5 shows the means and total concentration of the OC residue levels in sediment samples during the two years of sampling from the ten points. The mean residue levels of OC compounds detected in sediments samples ranged between < 0.00024 and 190.07 µg/kg based on dry weight. The individual OC compounds analysed in this study are located on the first column of the same Table 4.5 while the sampling points are shown on the first row. Generally, the OC compounds residue levels were higher in sediment samples than in water samples. A probable reason for this could be; OCs are found in higher concentrations in the sediments of aquatic systems due to their chemical and physical properties which cause high sorption interactions. Chloride substituents modify the physical properties of organic compounds; they are typically denser than water due to the presence of high atomic weight of chlorine. The chlorine-carbon bonds are very strong which means that they do not break down easily. Sorption increases with chlorine content, surface area and with the organic content of the sorbent. Therefore, OCs adsorb onto falling sediments that eventually end up as bottom sediments (U.S.EPA, 1988).

Table 4.5: Mean and total concentrations of OC levels in sediment in µg/kg±sd (based on dry weight)

OCs compounds/sampling points	Makuyu	Sagana	Murang'a	Kirinyaga	Tetu	Karatina	Marua	Kiganjo	Hombe	Ndathi
a-HCH	11.01±0.1	10.05±1.32	16.59±2.21	2.02±1.52	13.36±1.4	9.11±0.45	3.31±0.13	6.53±0.13	31.14±0.41	< 0.00051
b-HCH	1.08±0.03	2.15±0.18	13.26±0.39	8.76±0.15	13.28±0.29	20.03±2.03	4.78±0.16	3.34±0.18	10.17±0.86	1.18±0.02
g-HCH	45.5±0.43	7.69±0.23	4.32±0.08	4.37±0.26	9.83±0.08	6.12±0.39	5.67±0.14	3.29±0.03	4.01±0.11	3.35±0.1
d-HCH	8.01±0.18	10.05±0.1	8.76±0.2	13.36±0.22	34.35±0.03	4.51±0.01	6.54±0.1	12.1±0.04	8.01±0.11	4.22±0.31
Heptachlor	3.27±0.08	2.78±0.12	4.34±0.2	5.68±0.3	4.43±0.22	98.8±0.21	4.75±0.2	2.11±0.02	7.75±0.21	1.06±0.07
Adrin	3.17±0.07	2.23±0.08	3.22±0.09	4.32±0.18	3.32±0.06	7.56±0.07	9.01±0.03	1.11±0.03	4.01±0.11	< 0.00044
Heptachlor epoxide	44.09±0.32	22.17±0.31	8.89±0.34	8.72±0.32	10.23±0.21	11.15±0.65	4.89±0.3	< 0.00052	2.336±0.43	4.56±0.21
Endosulphan I	10.23±0.15	< 0.00108	98.66±0.44	10.02±0.22	21.26±0.54	23.36±0.4	10.08±0.3	17.82±0.58	19.17±0.37	< 0.00108
pp-DDE	< 0.00191	26.54±0.65	59.82±1.7	83.23±2.97	47.79±048	93.39±3.21	34.37±0.7	29.81±0.46	15.13±2.33	9.89±0.27
Dieldrin	4.67±0.06	13.37±1.67	9.91±0.34	51.11±0.37	8.71±0L1	3.12±0.01	6.07±0.19	4.49±0.04	7.07±0.03	2.35±0.1
Endrin	5.41±0.10	7.79±0.03	2.67±0.1	21.14±1.43	14.23±0.22	3.21±0.01	3.08±0.18	3.01±0.09	6.01±0.24	< 0.00201
Endosulphan II	53.28±0.92	25.45±0.73	2.515±0.86	110.02±0.32	< 0.00024	59.32±0.03	70.81±1.7	50.07±0.06	5.07±0.13	2.77±0.03
pp-DDD	13.27±0.18	2.15±0.12	80.03±0.1	29.87±0.23	1.13±0.01	4.51±0.02	9.93±0.21	5.07±0.05	35.05±0.43	3.35±0.21
Endrin aldehyde	127.67±3.21	125.47±4.04	73.45±1.58	80.03±1.77	59.97±1.37	43.42±0.81	34.23±1.02	77.66±1.09	29.99±0.03	5.01±0.02
pp-DDT	64.37±1.01	24.34±1.1	39.23±1.05	190.07±1.4	91.88±0.21	35.65±0.21	58.43±1.23	35.45±0.68	46.57±1.6	7.65±0.02
Endosulphan sulphate	5.43±0.1	11.13±0.62	12.2±1.3	1.012±0.25	20.09±0.02	10.34±0.31	4.44±0.27	3.32±0.09	6.04±0.22	2.09±0.21
Methoxychlor	9.81±0.22	8.78±0.16	5.45±0.12	5.49±0.11	17.34±0.32	15.46±0.09	6.02±0.13	4.42±0.08	7.65±0.25	2.05±0.05

Key: sd- standard deviation

4.2.1 Spatial distribution of organochlorines in sediments

p,p'-DDT had the highest total mean concentration of 616.51 µg/kg followed closely by endrin aldehyde with the concentration of 613.31 µg/kg in sediment samples, while adrin had the lowest concentration of 45.85 µg/kg as indicated in Figure 4.5 below. Madadi (2005) examined OC residues in soil samples from Lake Victoria, where by the p,p'-DDT gave the highest concentration of 65.48 g/kg. His study showed high levels of p,p'-DDT in soil samples, similar to the current study. The two studies therefore, are comparable, since p,p'-DDT has the highest levels in both cases.

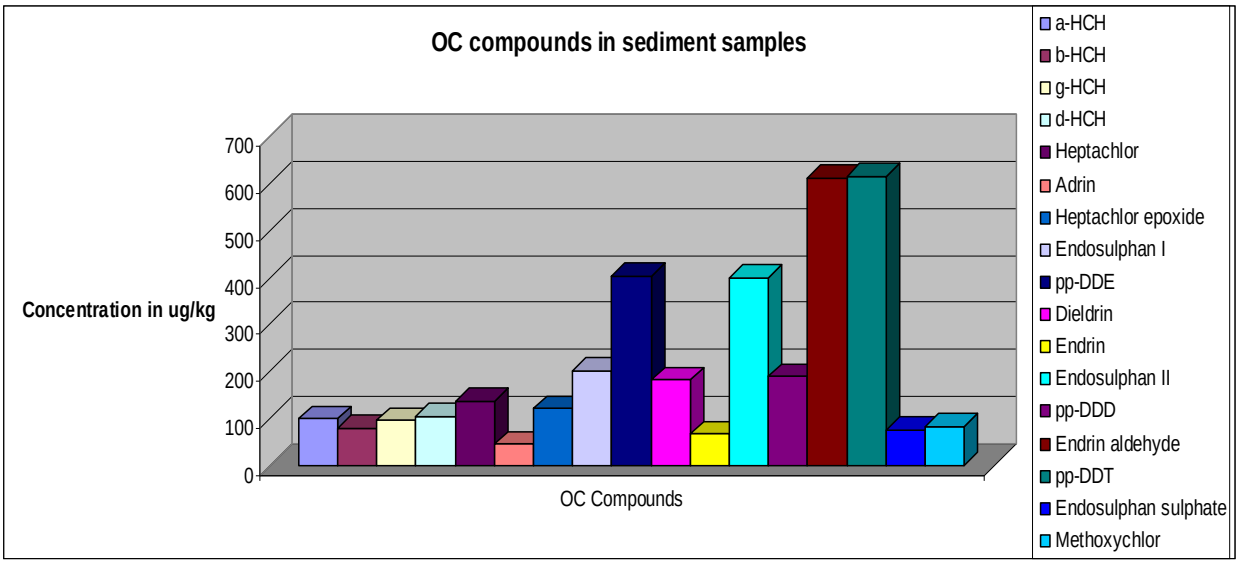


Figure 4.5: Total concentrations of each OC compound in sediment samples

High levels of OCs residue levels in sediments were detected in the midstream than in the upstream and downstream as it was in the water samples, which can be observed from Figure 4.6 below. Karatina had the highest total OC concentration of 472.92 µg/kg while Ndathi site had the lowest level of 168.19 µg/kg. Karatina is situated at the midstream area with intense farming and factories (e.g Nguguru coffee factory), which could probably be reason for high levels of OC residue levels. Ndathi is at the source of the river and therefore the levels were the lowest as

there is rare settlement and farming activities in the area, hence less anthropogenic activities in the area.

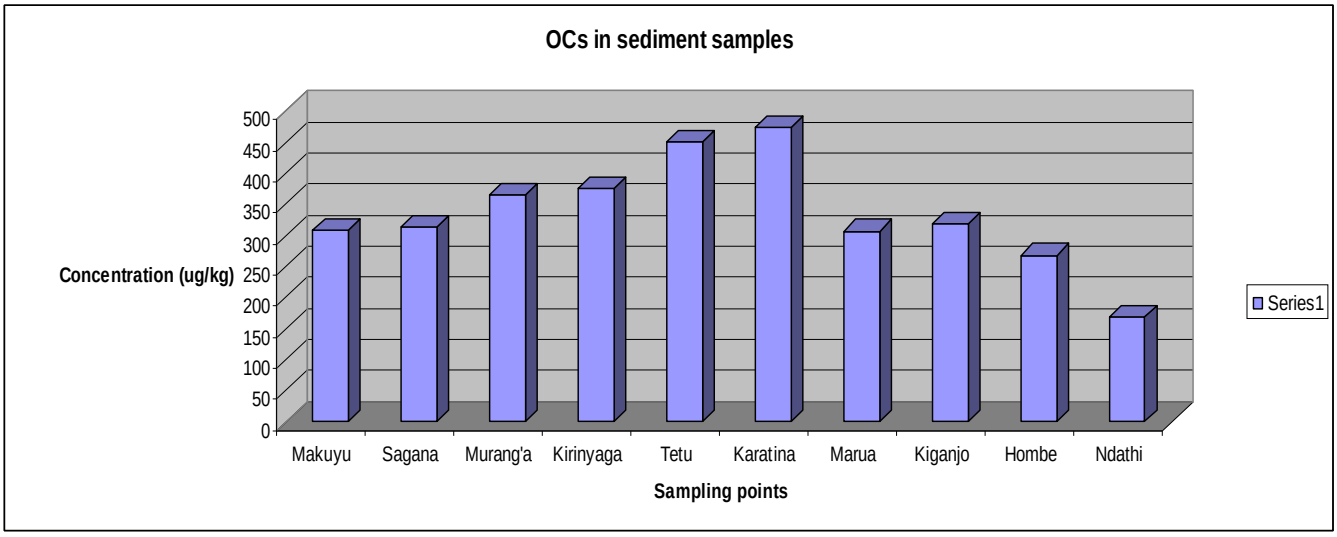


Figure 4.6: Mean of the total organochlorine residue levels in sediment samples

4.2.2 Temporal distribution of organochlorines in sediment samples

Higher OC residue levels were observed from sediment samples that were collected during the dry season than during the wet seasons as can be observed from Figure 4.7 below. For instance, the sediment samples that were sampled from Makuyu in September, 2009 had higher total OC residue levels (123.76 µg/kg) than those sampled in June, 2009 (76.45 µg/kg) (Figure 4.7). This could be attributed to the effect of contaminants dilution that take place in the rivers due to floods and wash off of contaminants from the farms into the water body during the rain seasons. There is also limited usage of pesticides during the wet seasons as the pests tend to be more during the dry season than during the wet season. More pests and insects are destroyed at their larvae stage by rain water which lead to their almost non-existence during the rainy seasons.

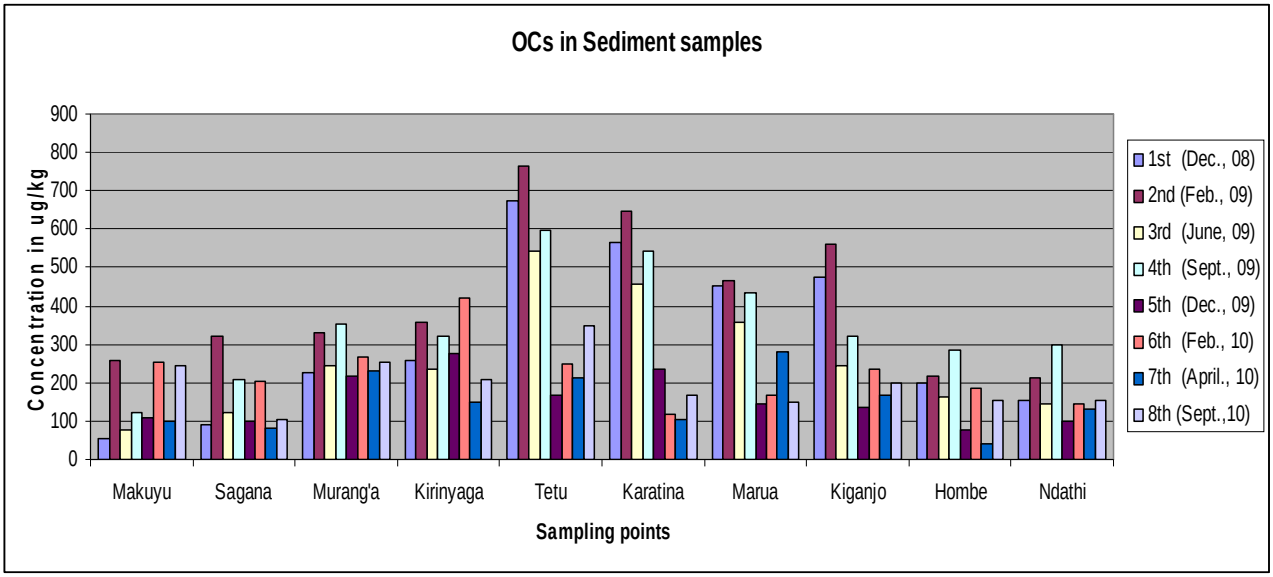


Figure 4.7: Temporal distributions of total organochlorine residue levels in sediment samples

4.2.3 Seasonal variation of OCs residue levels in sediment samples

The seasonal changes were observed to influence the concentrations of OCs in sediment samples from the area of study just like in the water samples. The OCs residue levels in sediment samples depicted a general trend of total mean concentration levels as dry season > short rains > long rains as is indicated in Figure 4.8. Most OC residues in sediment samples were diluted during the long rains than during the short rains due to high tides as was observed in the water samples hence higher OCs concentration during the short rains than during the long rains.

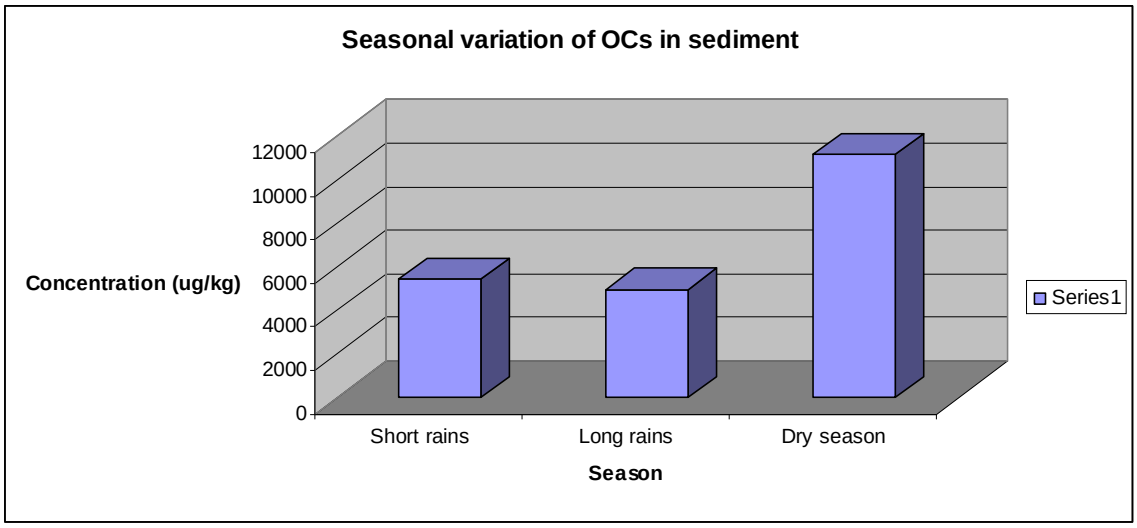


Figure 4.8: Seasonal variation of the organochlorine residues in sediment samples

4.3 Distribution of organochlorines in weed samples

The main aim here was to assess the amount of OC pesticides present in the weed samples derived from the Tana River in the upper Tana catchment. All the weed samples were therefore found to be contaminated with OC pesticides after the analysis, with the extent of contaminations reported in Figure 4.9.

4.3.1 Spatial distribution of OCs in weed samples

Figure 4.9 shows the overall mean concentration of each OC compound in weed samples during the two years of sampling. The residue levels of the OCs were in the range of < 0.00012 to 28.82 µg/kg (dry weight). A study carried out by Madadi (2005) reported the highest residue levels of OC in weed samples obtained from L.Victoria as 10.07 g/kg. This was rather a very high level as compared to the level of 28.82 µg/kg obtained in the current study.

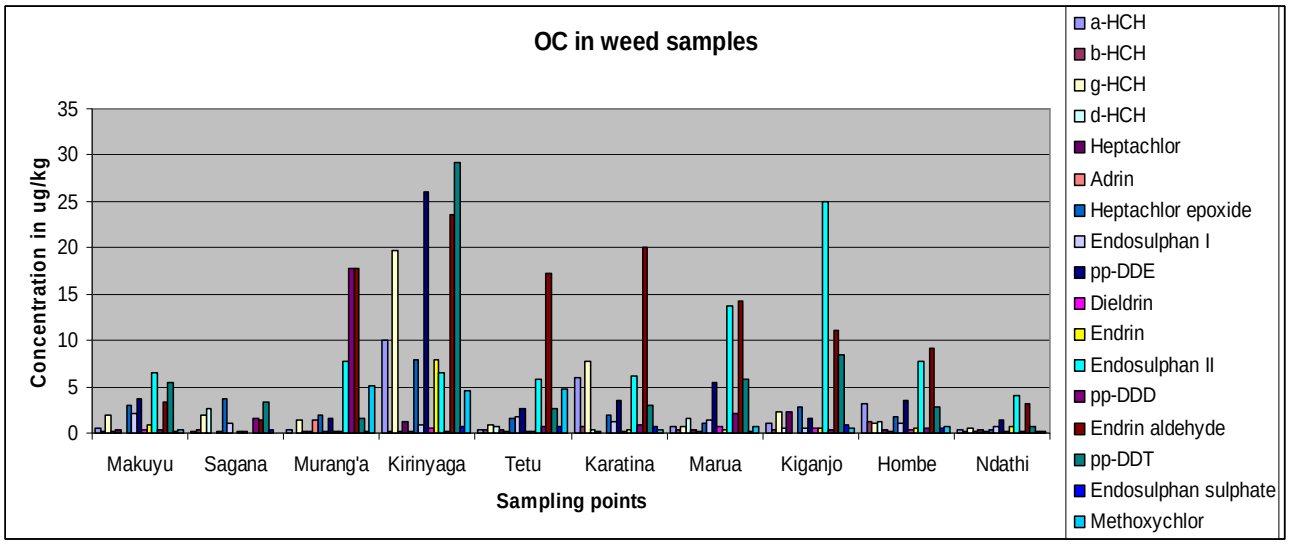


Figure 4.9 Distribution of OC compounds residue levels in weed samples

Endosulphan II had the highest total of the mean residue level of 166.65 µg/kg in weed samples and Adrin had the lowest total of the mean residue level of 2.77 µg/kg as shown in Figure 4.10 below.

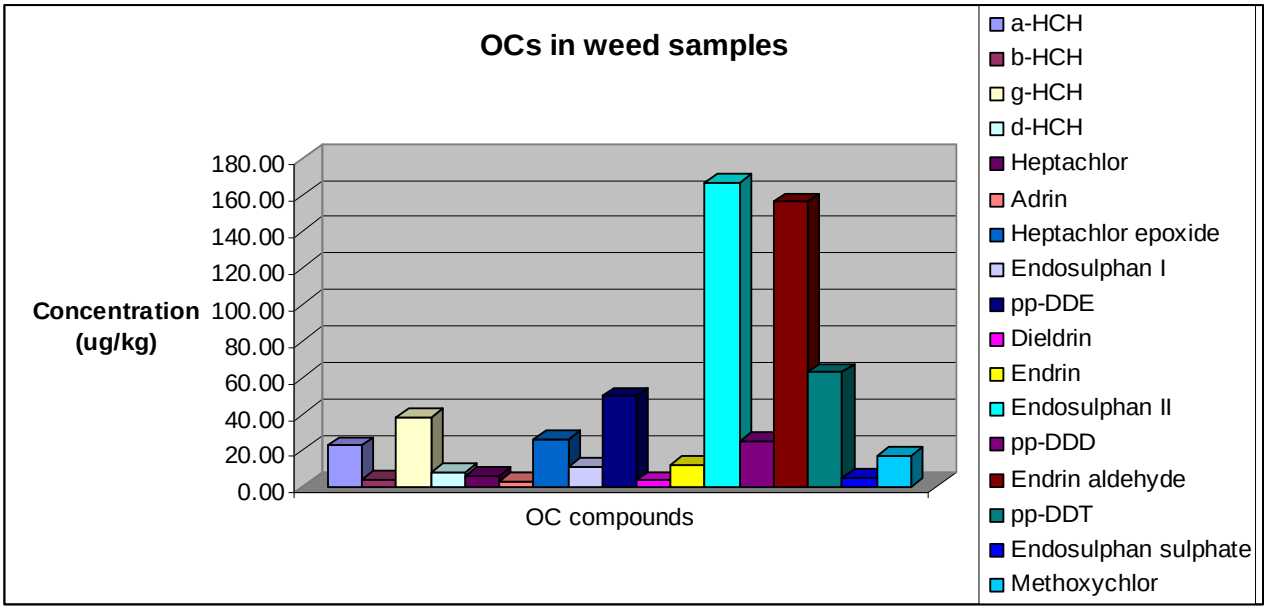


Figure 4.10: Mean of the total concentrations of each OC compound detected in all weed samples

The samples collected from the midstream section were still found with the higher total of the mean concentration residue level of OC of 302.55 µg/kg than those collected at the upstream and down stream areas which had 57.65 µg/kg and 160.40 µg/kg total of the mean concentration residue levels, respectively.

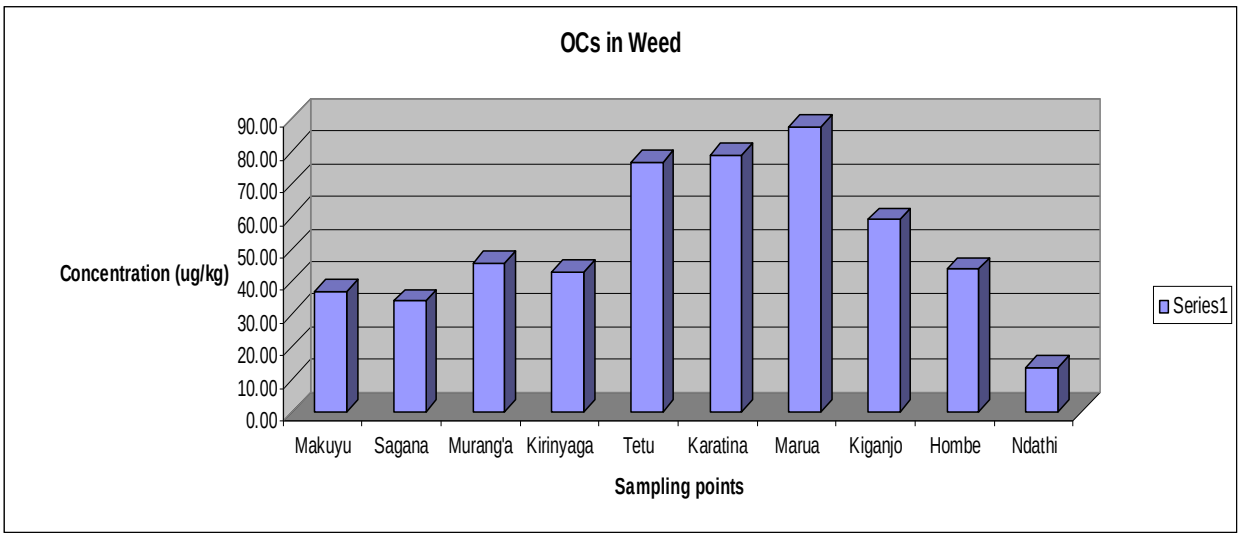


Figure 4.11: Mean of the total OCs in weed samples per site

Marua area, a point situated at the mid stream section had the highest total OC residue level of 87.65 µg/kg while Ndathi area at the source of Tana River had the lowest total of the mean concentration residue levels of 13.67 µg/kg over the period of the study as can be observed in Figure 4.11 above. As discussed earlier the mid stream section in encompassed with high potential of anthropogenic activities like crop and cattle farming, a possible cause of the high concentrations of the pesticides residues. Discharges from Marua coffee factory situated at Marua town could also have attributed to rise of the OC residue levels in the mid-stream.

4.3.2 Temporal distribution of organochlorines in weed samples

The total of the mean concentration residue levels of OCs in weed samples from the 10 sampling points during each sampling period are presented in Figure 4.12. Most of the samples sampled

during the dry seasons had higher concentrations of OC residue levels than the samples collected during the wet seasons. For example it can be observed from Figure 4.12 below that in December, 2008 which was during a dry season a total OC residue level of 22.17 µg/kg was realised, which was lower than the total OC residue level of 50.7 µg/kg obtained in February, 2009 (dry season) in point 1 (Makuyu) . The same thing happened in almost all the other points of sampling, apart from the month of June, 09.

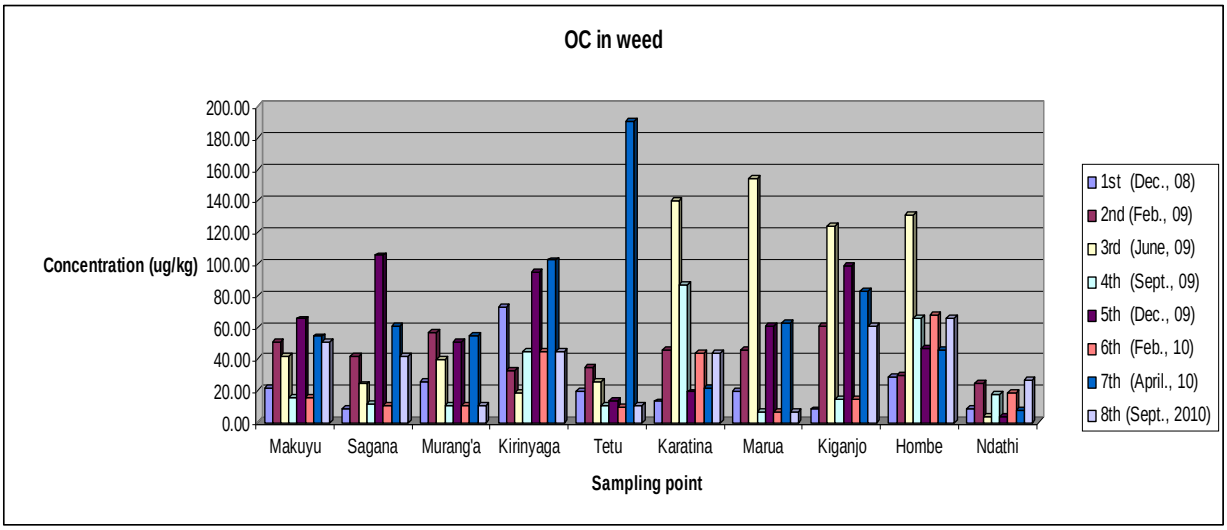


Figure 4.12: Temporal distribution of total OC levels in weed samples

In some cases like June, 2009, the total of the OC mean residue levels were high. The rains were low (of 68.2mm) during this season as compared to others, which could have contributed to high humidity level hence high usage of the pesticides due to vast number of pests and insects. This is because pest multiplies more in a humid weather than in a non-humid one. This also is an evident that farmers in the upper Tana River could still be using the banned OC pesticides in the area.

4.3.3 Seasonal variation of the organochlorines levels in weed samples

The concentration of the OCs in weed samples were also affected by the seasonal changes. The mean total OCs residue levels in weed samples were in the order of: dry season > short rains > long rains seasonally as indicated in Figure 4.13. The OCs concentrations in weed samples were also highest during the dry season. The average percentage moisture content in weed samples was found to be higher during the long rains (70 %) than during both the dry season (30 %) and short rains (55 %). The high moisture content in the weed samples could be the reason why the OC levels were low due to dilution effect.

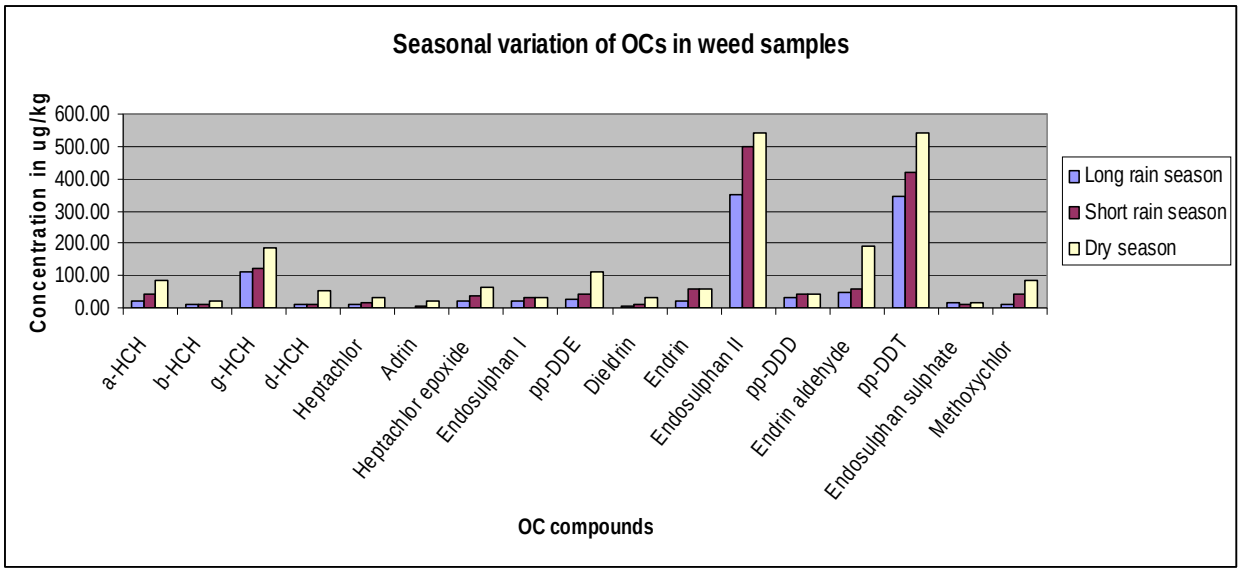


Figure 4.13: Seasonal variation of OCs in weed samples

4.4 Comparison of the total OC levels in water, sediment and weed samples

Most of the OCs residue levels were in the order of sediments samples > water samples > weed samples as shown in Figure 4.14. In general most organochlorine pesticides are highly hydrophobic and would partition from the aqueous media to sediments. On the other hand plants take in pesticides residues by absorption from sediments or water through the root systems, they

therefore bioaccumulate pesticides in their systems. The presence and persistence of these compounds also depends on the rate of metabolism. Other factors like age, physiological and species also influence the residue levels in biota (Munga, 1985).

The units for the water samples were converted from µg/L to µg/kg to make them comparable to the sediment and weed samples' residues levels. This was based on the assumption that the density of liquid water is normally given as 1 g/cm3.

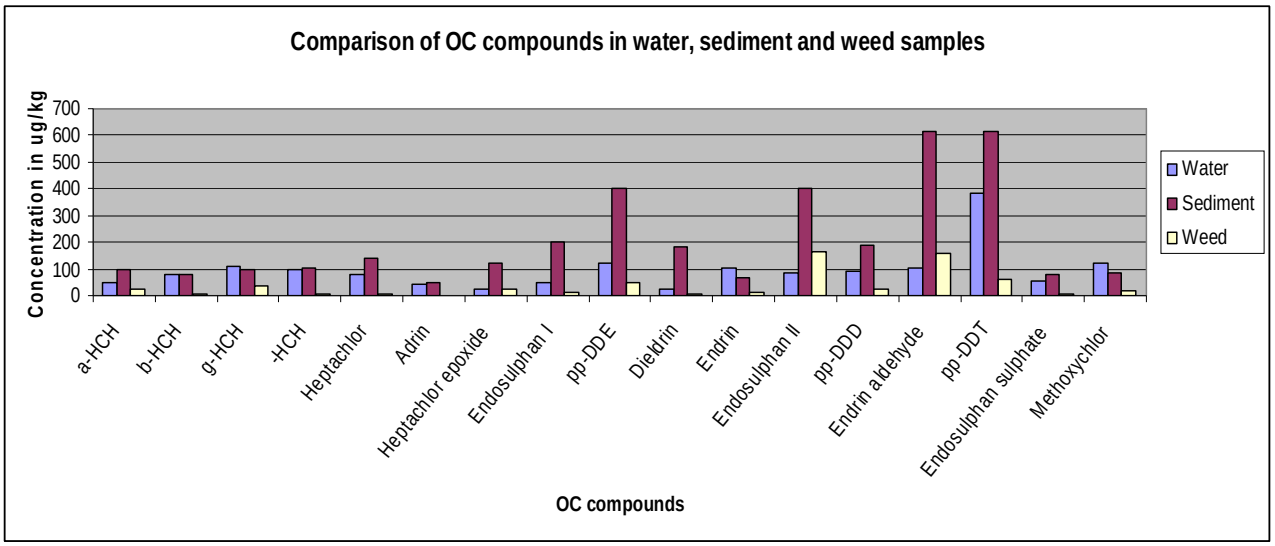


Figure 4.14: Comparison of OC residue levels in water, sediment and weed samples

The low total OC residue levels in weed samples could be attributed to the type and age of the weed analysed in the study. The main activities along the upper Tana River being farming, the ancient weeds around the river banks have been rooted out by the farmers in order to create more space for their crop farming activities. This has lead to diminishing of the ancient weeds species along the river banks. The weeds therefore analysed in this study were tender and therefore a possible reason why they had low OC concentration residue levels.

From all the three types of samples analysed (water, sediment and weed samples) in this study, □DDT comprising of p,p'-DDT, p,p'-DDD and p,p'-DDE showed the highest residues amounting to 1812.18 µk/kg, whereas □HCH consisting of a-HCH, B-HCH and g-HCH was 814.07 µk/kg, □Heptahlor comprising of heptachlor and heptachlor epoxide amounted to 325.35 µk/kg , □Endosulfan constituting a-endosulfan, b-endosulfan and endosulfan sulfate was 1074.79 µk/kg, □aldrin comprising of aldrin and dieldrin gave 218.07 µk/kg, □endrin and endrin aldehyde was 1095.11 µk/kg and □methoxychlor was 218.91 µk/kg .Therefore the total organochlorine pesticide residues in all the water, sediment and weed samples showed concentrations order as □DDT> □Endrin> □endosulphan> □HCH > □heptachlor> □methoxychlor >□endrin.

4.5 Chlorpyrifos residues in water samples

4.5.1 Spatial distribution

The objective in this case was to determine the residue levels of chlorpyrifos in water samples derived from upper Tana River. Table 4.6 shows the distribution of chlorpyrifos in water samples from the upper Tana River over the two years of sampling and analysis. The residues were in the range of < 0.0001 to 6.80µg/L. The highest level was found in Tetu situated at the mid-stream section. At the same time the highest chlorpyrifos average level of 5.24 µg/L was recorded at Point 6 (Karatina) located at the midstream and lowest average level of 1.02 µg/L was detected of point 10 (Ndathi) located at the upstream. The concentrations of chlorpyrifos residue levels were low at point 10 probably due to limited crop and cattle farming activities in the area.

The first column of Table 4.6 shows the points from which the samples were derived, while the first row shows the months and the years of sampling. All the water samples analysed for chlorpyrifos in this study had residue levels lower than the set guidelines for chlorpyrifos residue

levels in drinking water by WHO and New Zealand of 40 µg/L and 70 µg/L, respectively as shown in Table 4.3. A study by Mathur *et al.*, (2003), on the analysis of pesticides residues in bottled water, reported the highest concentration of chlorpyrifos as 9.6 µg/L. The level of 9.6 µg/L by Mathur was also below the set standards for chlorpyrifos residue levels in drinking water by WHO and New Zealand mentioned above. The study by Mathur is therefore comparable to the current study in that, the highest levels found for chlorpyrifos of 9.6 µg/L and 6.80 µg/L respectively were all below the set standards set by WHO and New Zealand for drinking water shown in Table 4.3.

Table 4.6: Distribution of chlorpyrifos residue levels in water samples in µg/L±sd

Sampling points/Sampling trips	Dec., 08	Feb., 09	June, 09	Sept., 09	Dec., 09	Feb., 10	April, 10	Sept., 10
Makuyu	2.99	4.47	3.11	3.18	1.79	1.27	3.17	2.76
SD	2.05	0.34	1.45	0.33	0.79	0.9	1.23	0.07
Sagana	3.82	1.32	4.82	2.73	3.21	2.14	3.24	2.45
SD	0.74	0.51	0.52	0.71	0.21	0.25	1.23	0.25
Murang'a	2.56	1.23	3.21	1.54	3.26	1.32	2.78	1.76
SD	0.64	0.02	0.09	1.10	1.41	0.01	0.97	0.16
Kirinyaga	2.92	< 0.0001	2.98	1.32	3.24	< 0.0001	3.98	< 0.0001
SD	1.11		0.42	0.01	0.69		0.26	
Tetu	6.66	2.17	6.80	6.61	5.66	3.07	4.76	2.09
SD	1.32	0.09	0.50	0.84	0.92	0.54	0.93	0.74
Karatina	5.57	6.21	6.73	6.21	3.61	3.55	4.47	5.55
SD	1.51	1.76	0.65	1.76	1.09	0.78	0.09	0.78
Marua	3.91	2.77	3.09	2.14	4.73	< 0.0001	6.35	4.74
SD	0.36	2.03	0.26	1.59	0.02		2.59	1.38
Kiganjo	2.47	6.14	1.94	3.24	3.22	2.68	4.17	< 0.0001
SD	0.91	0.64	0.21	0.98	1.08	0.55	1.25	
Hombe	2.34	1.70	3.10	1.32	3.43	< 0.0001	3.95	1.23
SD	1.97	0.09	1.32	0.11	1.55		1.96	0.01
Ndathi	1.43	< 0.0001	1.21	< 0.0001	2.01	0.23	2.11	1.19
SD	0.12		0.06		0.38	0.17	1.44	1.31

Key:

SD- Standard deviation

Higher total of the mean chlorpyrifos residue levels were recorded at the mid stream section (of 13.12 µg/L) than in both upstream and down stream section which had total of the mean concentrations of 7.85 and 2.53 µg/L respectively. According to the residence in the upper Tana River area, farmers use chlorpyrifos to control ticks in the cattle dips and on the farms to control flies, a probable reason why the levels were highest in the mid stream, where crop and cattle farming activities are highly practiced. The waste from the Marua coffe factory, Mtu Athi coffee factory and Nguguru coffee factory, may also have lead to high levels of chlorpyrifos due to discharges and wash off by the rain waters into the river.

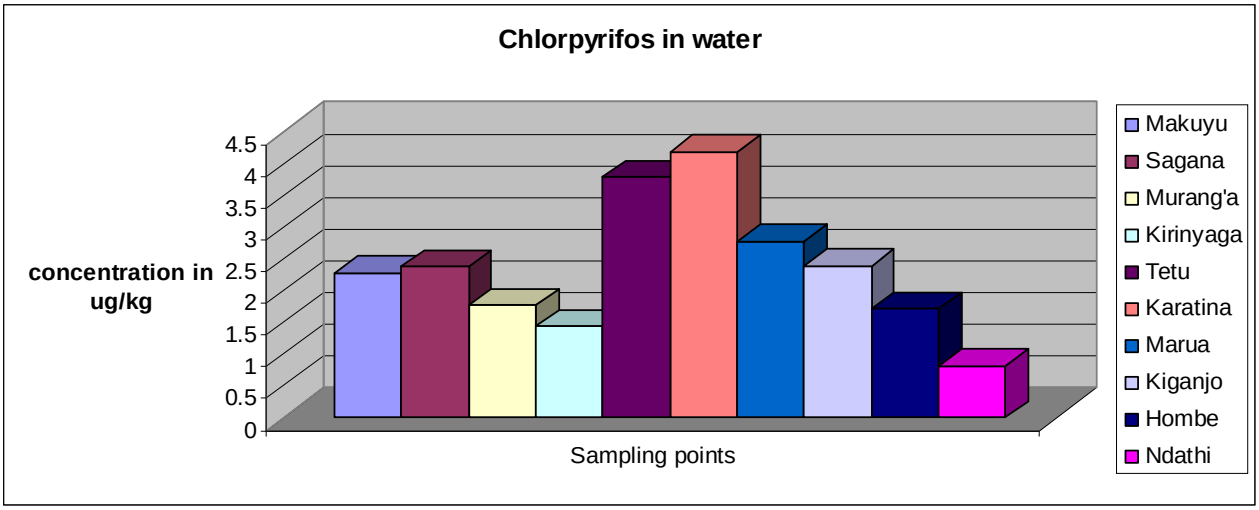


Figure 4.15: Total mean concentrations of chlorpyrifos residue levels in water samples per site

4.5.2 Temporal distribution of chlorpyrifos in water samples

High total of the mean of chlorpyrifos concentrations levels were realized during the samplings that were done during the wet seasons than during the dry seasons unlike the OCs as indicated in Figure 4.16. For example, high concentrations were recorded during the first sampling of December, 2008 of 34.67 µg/L, which was a wet season, while low concentration of 26.01 µg/L were observed during the second sampling of February, 2009, which was a dry season, as

indicated in (Figure 4.16). This could be attributed to the fact that chlorpyrifos (with half-life of 1 day) in water, degrade immediately after the application (Hayes and Laws, 1990), and therefore the residues could be available only from the recent use. The residues are therefore expected to be high during the rainy seasons because of the wash off from the cattle dips and cow shed into the water or residues persisting from previous contamination.

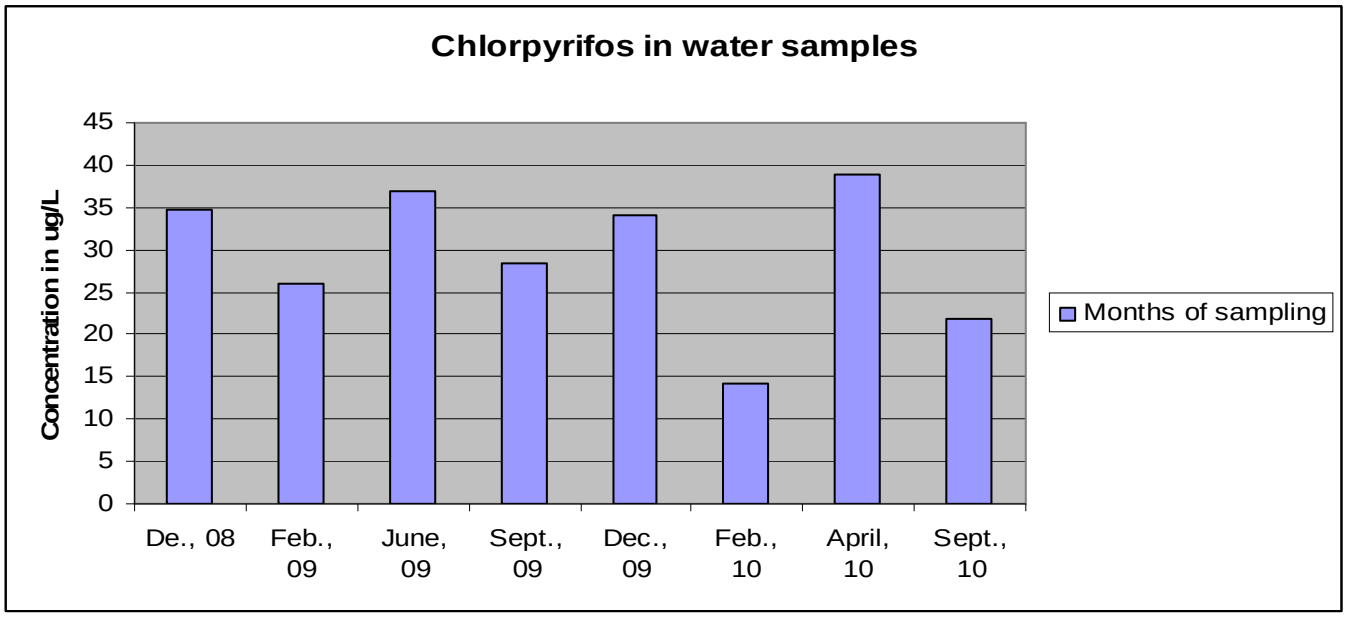


Figure 4.16: Temporal distribution of chlorpyrifos residue levels in water samples

4.5.3. Seasonal variation of chlorpyrifos in water samples

The concentrations of chlorpyrifos residue levels also were observed to be influenced by seasonal changes as with the case with the OCs residue levels in water samples. The residue levels in water samples depicted a general trend of concentration levels: long rains > short rains > dry season as can be observed from Figure 4.17. In this case it seems that during the long rains more chlorpyrifos were washed off into the waters than during the short rains because of heavy rains and splashes.

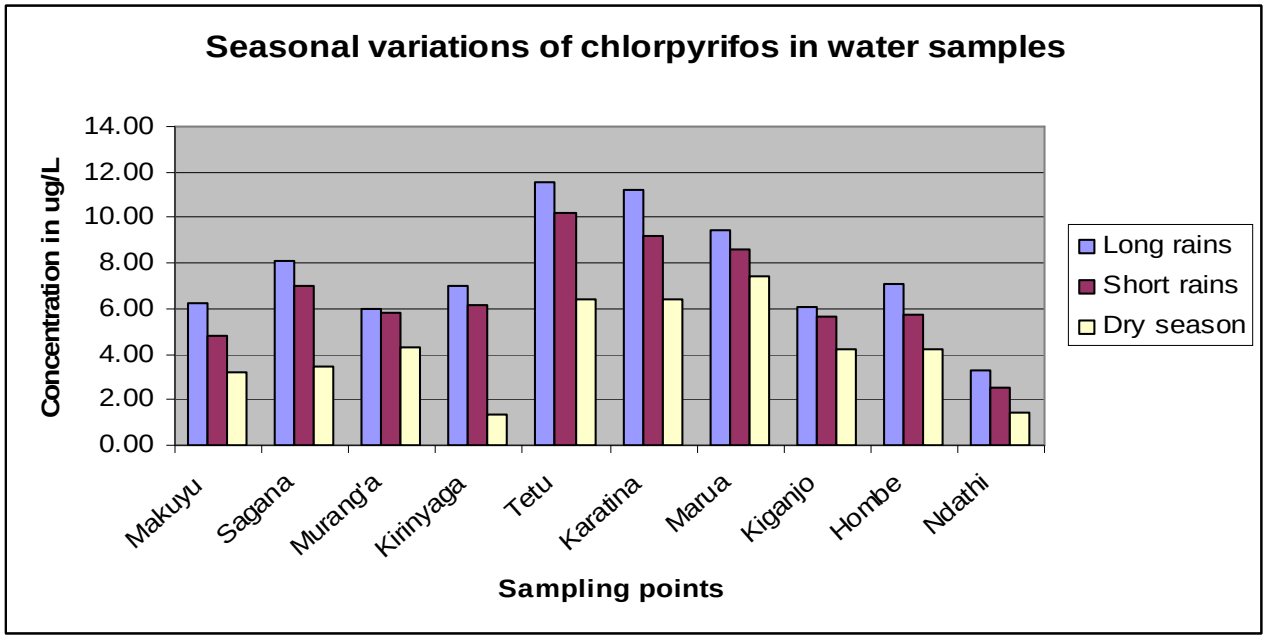


Figure 4.17: Seasonal variation of chlorpyrifos in water samples

4.6 Chlorpyrifos residues in sediment samples

4.6.1 Spatial distribution

The aim of this subsection is to determine the concentration residue levels of chlorpyrifos in sediment samples obtained from upper Tana River between December, 2008 and September, 2010. The chlorpyrifos residues levels in sediment samples ranged between < 0.0001 and 1.43 µg/kg based on dry weight as shown in Figure 4.18. The highsest of 1.43 µg/kg was recorded in June, 09 at point 6 (Karatina).

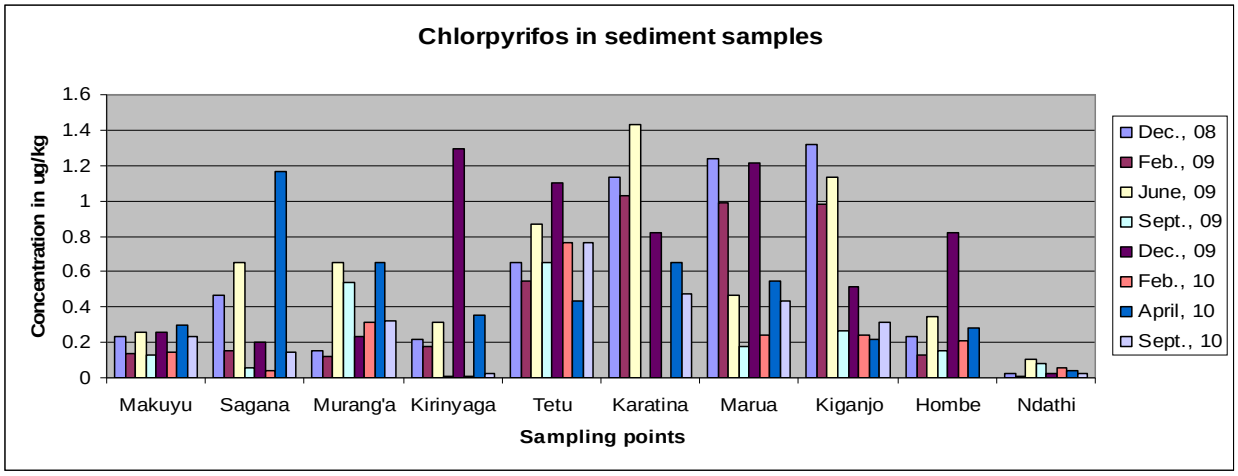


Figure 4.18: Distribution of chlorpyrifos residues levels in sediment samples

It can also be perceived from Figure 4.18 that the samples collected during the wet seasons had higher chlorpyrifos residue levels than the samples sampled during the dry seasons as it was the case with the water samples. A study by Otieno *et al.*,(2012) found out that the chlorpyrifos residue levels analysed in sediment samples that were obtained from Lake Naivasha were higher during the wet season (11.2-30.0 ng /g) than during the dry season (4.7-17.4 ng /g). This report agrees with the levels of chlorpyrifos residues in sediment samples found in the current study, in that the residues obtained during the dry seasons were lower than those determined during the wet seasons.

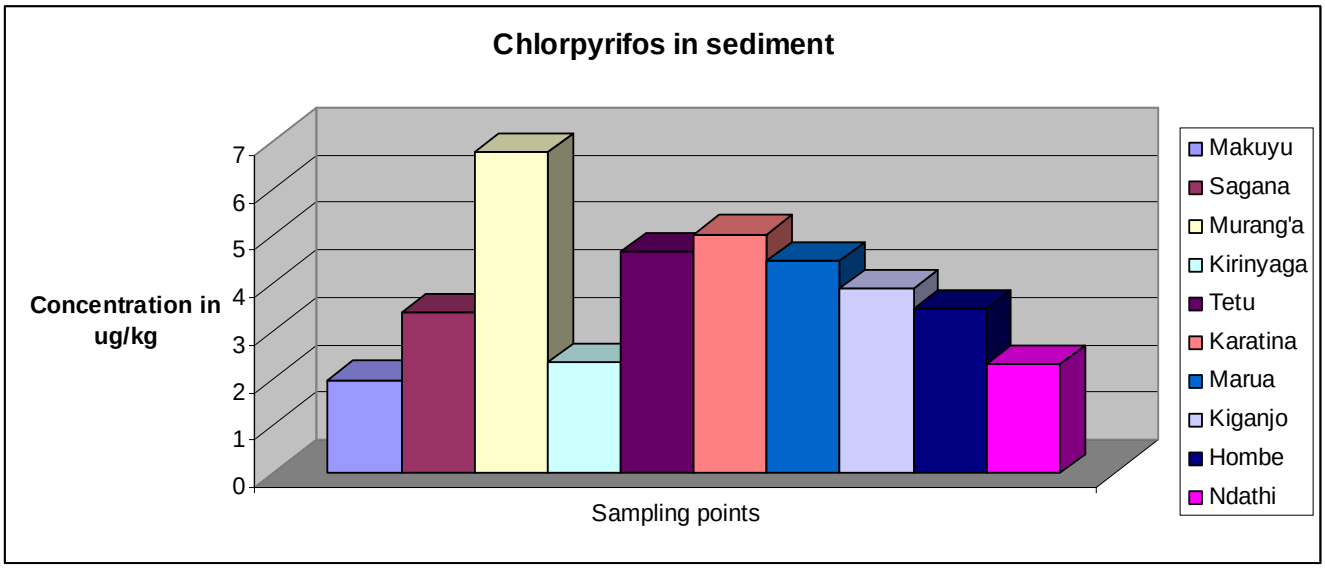


Figure 4.19: Mean chlorpyrifos residue levels in sediment samples

The highest chlorpyrifos average residue level of 6.72 µg/kg was detected at Point 3 (Murang'a and the lowest chlorpyrifos average level of 1.24 µg/kg was detected at Point 10 (Ndathi) found in the upstream at the source of Tana River as shown in Figure 4.19. On the other hand, the sediment samples collected from the mid stream had higher chlorpyrifos residue levels of total chlorpyrifos residues of 16.70 µg/kg than those analysed from up stream section of 11.86 µg/kg and down stream (1.24 µg/kg) respectively.

4.6.2 Seasonal variation of chlorpyrifos in sediment samples

The seasonal changes were also observed to influence the concentrations of chlorpyrifos in sediment samples from Upper Tana River. The residue levels in sediment samples depicted a general trend of total mean concentration residues levels as: long rains > short rains > dry season as is indicated in Figure 4.20. High levels during the rainy seasons could be as a result of wash off of the pesticides from the farms, cow dips and cow sheds immediately after the application into the water body.

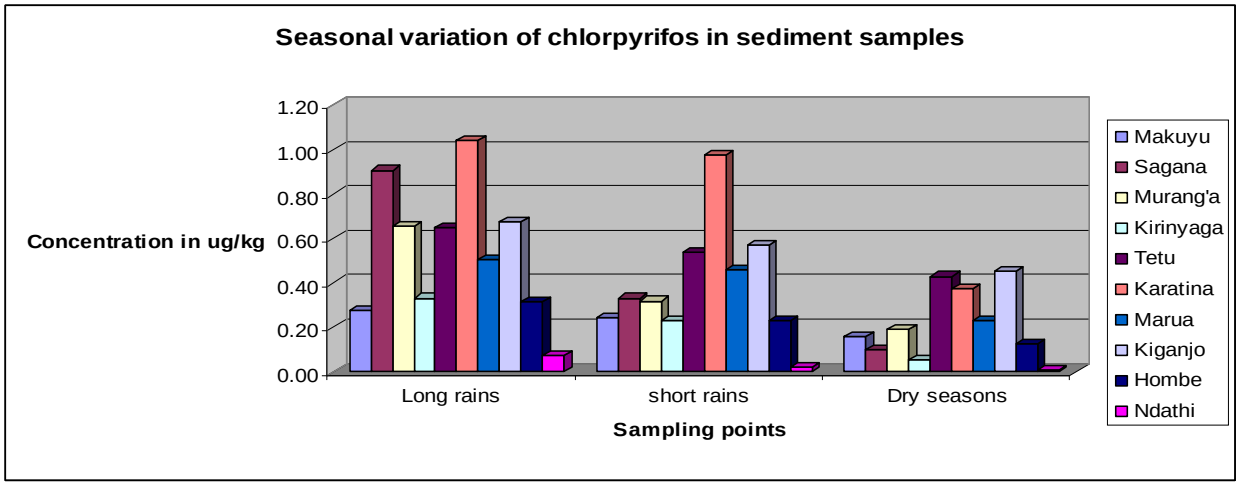


Figure 4.20: Seasonal variation of total chlorpyrifos residue levels in sediment samples

4.7 Chlorpyrifos residues in weed samples

4.7.1 Spatial distribution of chlorpyrifos in weed samples

The objective in this subsection was to investigate the chlorpyrifos residue levels in weed samples obtained from the upper Tana River. Table 4.7 shows the overall mean concentration of chlorpyrifos residue levels in weed samples during the two years of study. The residue levels were in the range of 0.01 to 2.57 µg/kg. The highest level of 2.57 µg/kg was detected at Point 7 (Marua), situated in the midstream. Amjad *et al*., (2010) analysed chlorpyrifos in wild plants (*Melilotus Indica*), in Lahore area, Pakistan. They found that the chlorpyrifos residue levels in the wild plant ranged between 20 and 710 µg/kg. Maximum limit of chlorpyrifos residue in these plants established by WHO and European Union (EU) are 50 and 500 µg/kg, respectively. Their highest level of 710 µg/kg was therefore above the limits set by the two bodies, while the lowest level of 50 µg/kg was below.

Table 4.7: The mean residue levels of chlorpyrifos residue levels in weed samples in µg/kg±sd

Point/Time of sampling	(Dec., 08)	(Feb., 09)	(June, 09)	(Sept., 09)	(Dec., 09)	(Feb., 10)	(April, 10)	(Sept., 10)
Makuyu	0.48	0.17	0.23	0.05	0.15	0.01	1.26	0.58
SD	0.17	0.11	0.08	0.01	0.01	0.01	0.59	0.01
Sagana	0.15	0.12	0.18	0.11	0.13	0.11	0.25	0.16
SD	0.04	0.09	0.07	0.08	0.01	0.04	0.08	0.01
Murang'a	0.11	0.07	0.46	0.05	0.00	0.10	0.85	0.20
SD	0.00	0.05	0.13	0.02	0.00	0.01	0.07	0.01
Kirinyaga	1.17	0.09	0.16	0.12	0.22	0.13	0.85	0.33
SD	0.09	0.07	0.01	0.08	0.11	0.05	0.01	0.02
Tetu	0.92	0.16	0.23	0.16	0.23	0.11	1.39	0.01
SD	0.11	0.08	0.02	0.11	0.14	0.10	0.60	0.01
Karatina	0.09	0.04	0.12	0.09	0.21	0.03	0.49	0.01
SD	0.03	0.02	0.05	0.09	0.07	0.01	0.03	0.01
Marua	1.52	0.10	2.57	0.21	0.21	0.02	0.73	0.02
SD	0.08	0.01	0.82	0.08	0.04	0.01	0.04	0.02
Kiganjo	1.95	0.22	0.37	0.16	0.92	0.39	0.89	0.34
SD	0.30	0.03	0.03	0.04	0.07	0.12	0.04	0.02
Hombe	1.46	0.17	0.19	0.05	0.13	0.07	1.00	0.01
SD	0.08	0.01	0.08	0.02	0.02	0.03	0.05	0.01
Ndathi	0.03	0.02	0.32	0.15	0.07	0.04	0.05	0.02
SD	0.01	0.03	0.01	0.08	0.07	0.01	0.02	0.02

KEY: SD – Standard deviation

The first column of Figure 4.21 shows the sampling points from where the samples were derived. The highest average level of chlorpyrifos for the two years of sampling was observed at Point 5 (Tetu) 0.68 µg/kg situated at the midstream section, while the lowest level of 0.09 µg/kg was detected at Point 2 (Sagana) located at the upstream as shown in Figure 4.21. This could be due to farming activities taking place in the area, which leads to high usage of chlorpyrifos to improve on their crop and animal production levels.

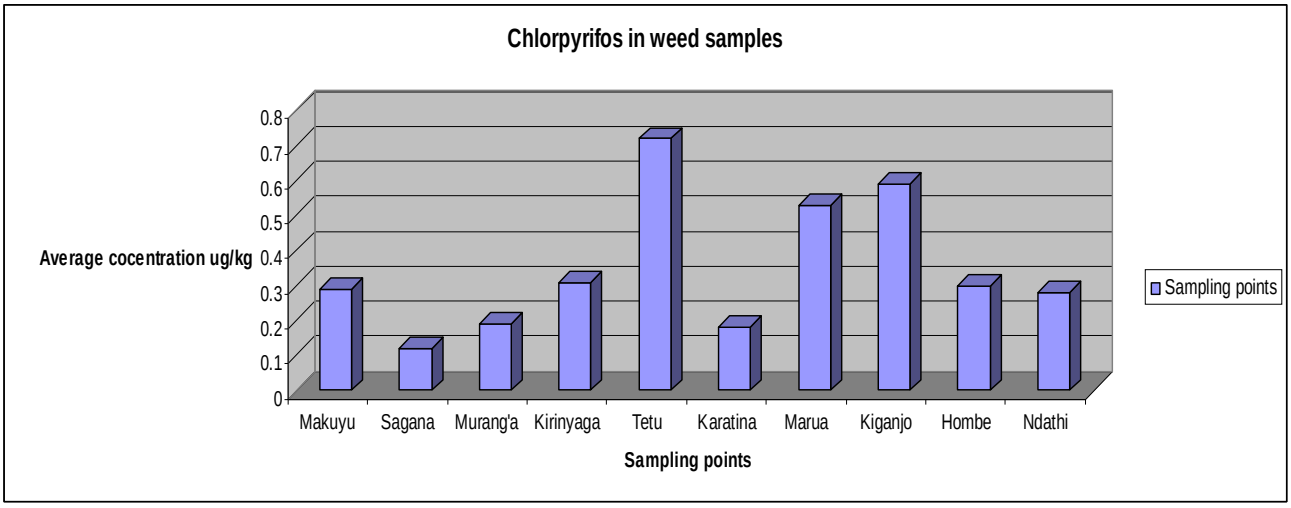


Figure 4.21: Total chlorpyrifos residue levels in weed samples from each point

4.7.2 Temporal distribution of chlorpyrifos in weed samples

The weed samples that were collected during the wet seasons had higher levels of chlorpyrifos than those collected during the dry seasons as was the case with water and sediment samples (Figure 4.22). For instance the samples collected in December, 2009 had higher total mean of chlorpyrifos residue level of 2.28 µg/kg than those collected in February, 2010 (1.02 µg/kg) as shown on Figure 4.22. According to the Meteological Departments; December, 2008 and April, 2010 had highest rainfall recorded as shown in Table 4.1 above a probable reason why the chlorpyrifos residue levels in weed samples detected were the highest.

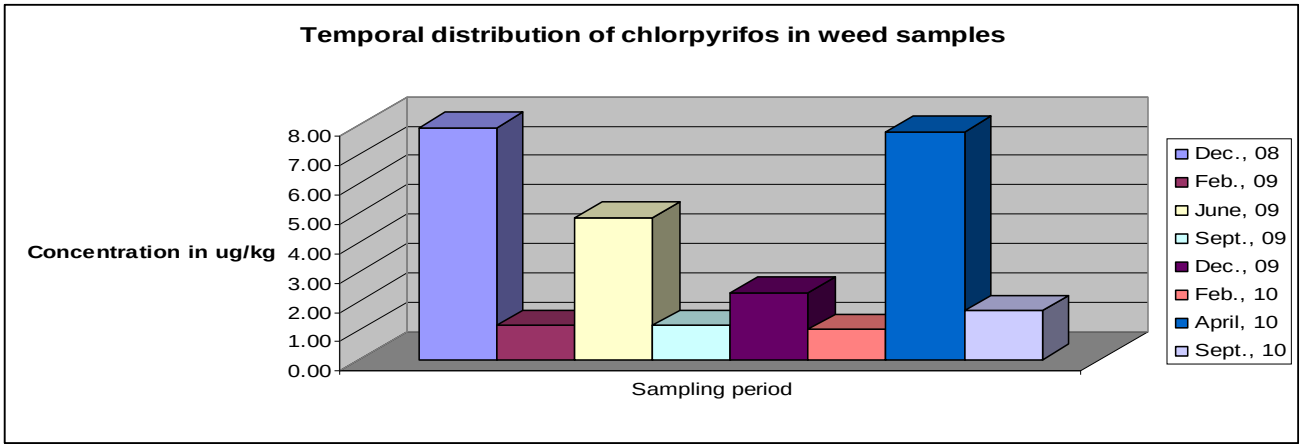


Figure 4.22: Temporal distribution of chlorpyrifos in weed samples

4.7.3. Seasonal variation of chlorpyrifos in weed samples

The concentration of chlorpyrifos residue in weed samples also were affected by the seasonal changes as was the case with the water and sediment samples. The residues in weed samples took a general trend of concentration levels: long rains > short rains > dry season as is indicated in Figure 4.23. The concentration of chlorpyrifos in weed samples was the lowest as compared to those in water and sediment samples. Since chlorpyrifos is not persistent (i.e has high degradability rate), its absorption into the plant roots system may be minimal unlike the organochlorine compounds.

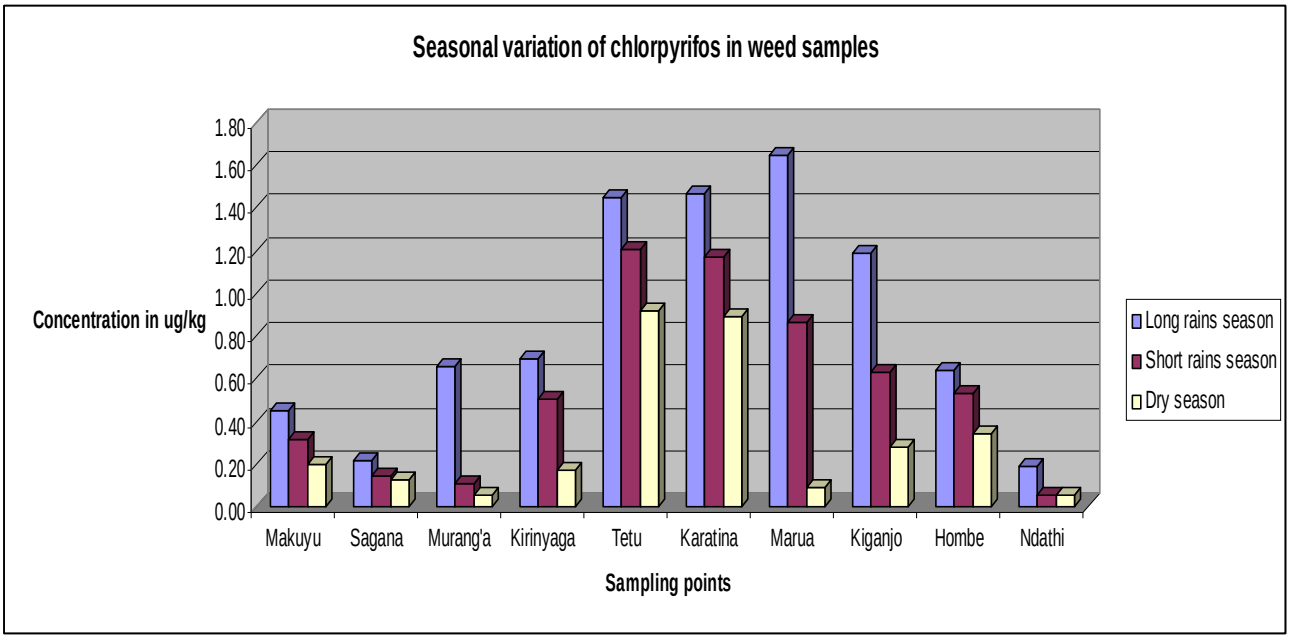


Figure 4.23: Seasonal variation of chlorpyrifos in weed samples

4.8 Comparison of the total chlorpyrifos in water, sediment and weed samples

The units of the water residue levels were converted from µg/L to µg/kg which corresponds to the sediment and weed samples' units. This was by assumption that the density of liquid water is normally given as 1 g/cm3. The total chlorpyrifos residue levels in all the samples analysed in this study portrayed a general trend as water > sediment > weed as shown in Figure 4.24. Water samples had the highest total chlorpyrifos residue levels of 29.39 µg/kg, followed by the sediment samples with a total concentration of 4.26 µg/kg residue levels and the weed samples had the lowest total chlorpyrifos residue levels of 3.46 µg/kg. Since chlorpyrifos degrades easily, very low amount is expected to adsorb on the sediment hence low concentration were observed in sediment samples as compared to those in water samples.

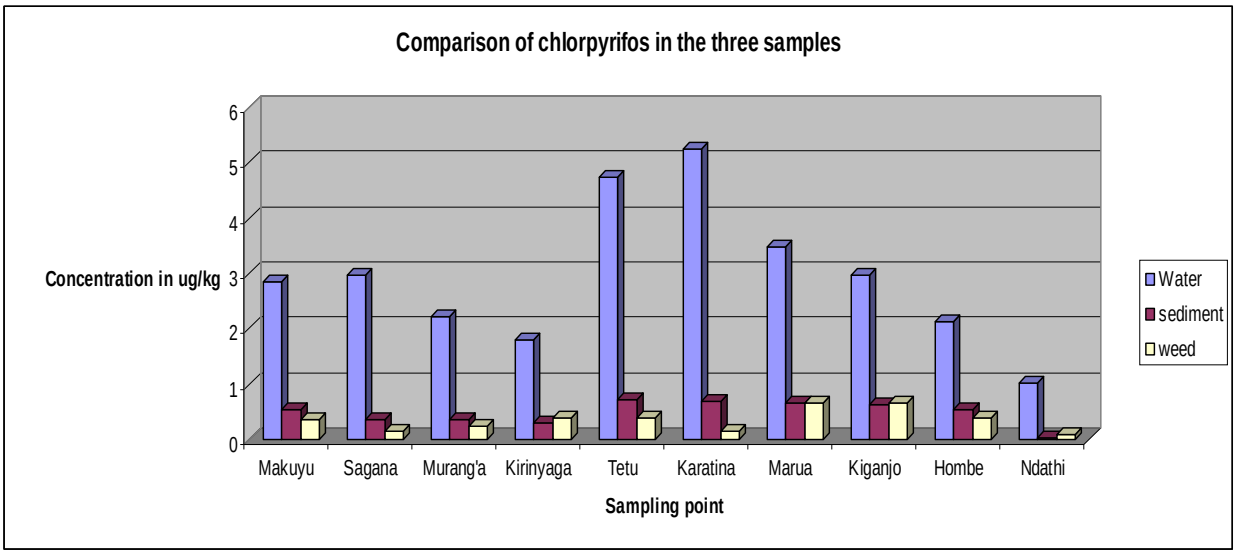


Figure 4.24: Comparison of chlorpyrifos residue levels in water, sediment and weed samples

4.9 The physico-chemical parameters

4.9.1 The pH levels in the water samples from the upper Tana River

The pH levels in the water samples ranged between 6.71 and 7.54 (as indicated in Table 4.8, with most samples having a near neutral pH, which falls within the range of 6.5-8.5 levels for natural water bodies recommended by the European Union. This could be attributed to the river's natural buffering capacity being adequate to withstand any basic or acidic discharges. The pH levels were within the permissible level of 6.5-8.5 for both irrigation and domestic water stipulated by Kenya Bureau of Standards (KeBS) and within the World Health Organization (WHO) recommended guideline which is between 6.5 and 8. They were also within the maximum allowable levels for both irrigation and domestic use by National Environment Management Authority NEMA of 6.5 -8.5 and within the acceptable levels permitted by Water Resources Management Authority (WRMA) of 6.5 -8. Therefore, there was no significant site and seasonal variations in water pH.

Table 4.8: Average pH levels in water samples

	Dec., 08	Feb., 09	June, 09	Sept., 09	Dec., 09	Feb., 10	April. 10	Sept., 10
Sagana	7.14±0.02	7.01±0.04	7.22±0.05	7.11±0.01	7.12±0.03	7.33±0.05	7.04±0.03	7.126±0.02
Murang'a	7.05±0.01	7.28±0.03	7.54±0.02	6.92±0.06	7.04±0.03	6.92±0.06	7.05±0.05	7.24±0.04
Kirinyaga	6.92±0.04	7.47±0.01	6.91±0.06	7.26±0.02	6.84±0.05	6.91±0.05	6.81±0.02	6.74±0.05
Makuyu	6.77±0.01	6.82±0.03	7.17±0.01	6.91±0.09	6.71±0.03	6.97±0.06	6.77±0.07	6.77±0.07
Tetu	7.15±0.02	7.01±0.01	7.22±0.04	7.11±0.03	6.76±0.01	7.33±0.05	7.14±0.05	6.98±0.08
Marua	7.25±0.03	7.28±0.03	7.54±0.06	6.92±0.05	7.04±0.02	6.92±0.06	7.05±0.03	7.45±0.06
Kiganjo	6.91±0.02	7.47±0.03	6.91±0.03	7.26±0.01	6.94±0.04	6.91±0.03	7.91±0.07	6.93±0.04
Hombe	6.97±0.01	6.72±0.01	7.07±0.02	6.91±0.04	6.75±0.02	6.87±0.04	6.76±0.06	6.78±0.03
Karatina	7.12±0.02	7.01±0.01	7.22±0.03	7.11±0.02	6.92±0.03	7.28±0.06	7.04±0.04	7.14±0.05
Ndathi	7.05±0.03	7.28±0.02	7.54±0.02	6.92±0.03	7.04±0.04	6.92±0.05	7.05±0.05	7.45±0.04

4.9.2 Electrical Conductivity in water sample

The Conductivity was lowest (57.02 µS) at the upstream (Ndathi), which is the source of Tana River as shown in Figure 4.25. The dissolved solids are few at the source because the waters are not contaminated much, due to limited anthropogenic activities in the area. There are no industry or factory activities going on in the up stream area, and hence a possible cause of low TDS mean levels. The highest conductivity of 373.43 µS was observed at Point 7 (Marua) situated at the mid stream. The levels were within the established EPA drinking water quality standards of 900 µS.

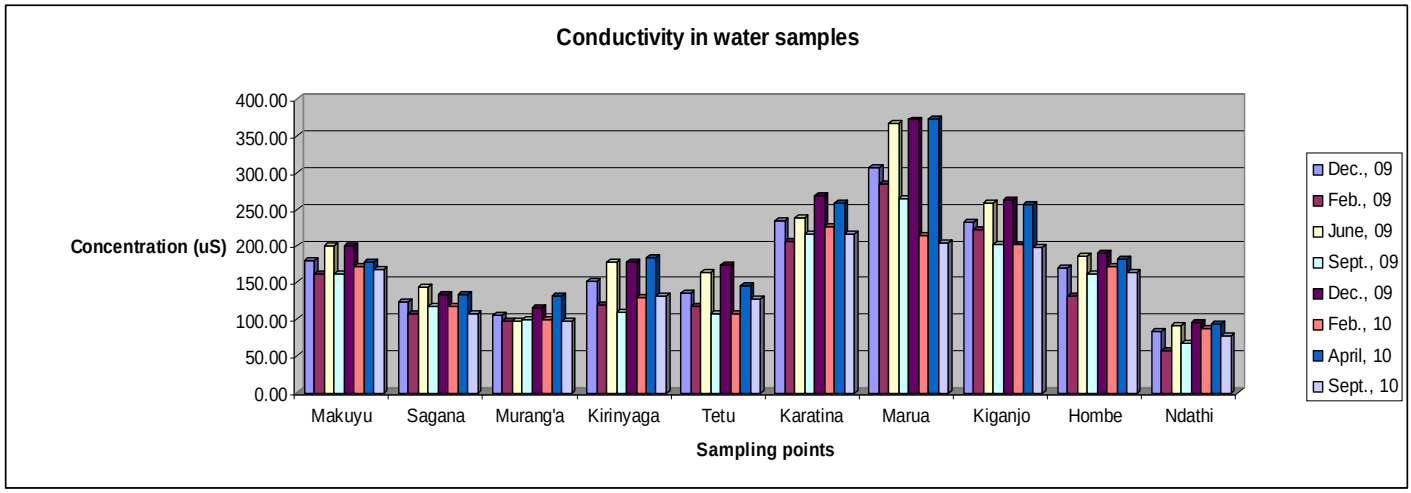


Figure 4.25: Average conductivity of the water samples

4.9.3 Total Dissolved Solids in water

The lowest recorded value for TDS was 39.91 mg/L at Point 10 (Ndathi) while the highest value of 261.40 mg/L was observed at Point 6 (Marua) as indicated on Figure 4.26. All the TDS values recorded were below WHO permitted level for drinking water of 1000 mg/L, they were below the permitted level of 1200 mg/l by KeBS which applies for both irrigation and domestic water and still they were within the established EPA drinking water quality standards of 500 mg/L.

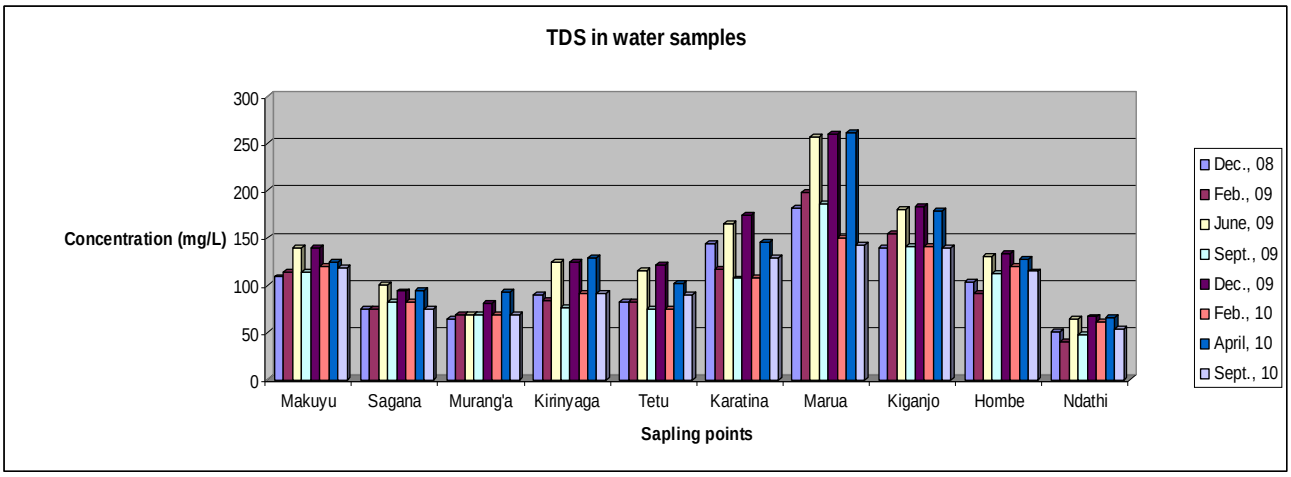


Figure 4.26: Average Total Dissolved Solids values in water samples

4.9.4 Total Suspended Solids (TSS) in water

Figure 4.27 below shows the TSS average levels in water samples analysed during the two years of the study. A Higher mean level of TSS of 432.45 mg/L was recorded at Point 8 (Kiganjo) and the lowest level of 5.33 mg/L was observed from Point 4 (Kirinyaga) as shown in Table 4.25 below. These levels were below the established levels by the United States of 500 mg/L, which were set to provide for palatability of drinking water (U.S. EPA, 1991). Suspended solids can be as result of erosion from farms algae growth or wastewater discharges. TSS is also closely linked to land erosion and to erosion of river channels which explains the high values recorded during most of the wet season.

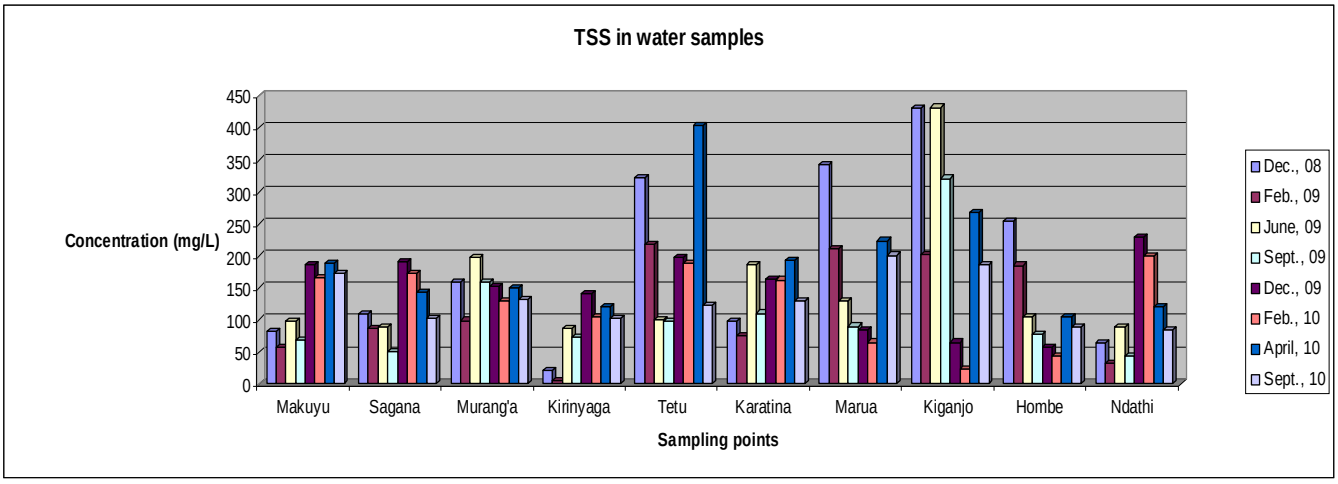


Figure 4.27: Average Total Suspended Solids in water samples

4.9.5 Salinity in water samples.

The salinity levels in water samples derived from upper Tana River are as indicated in Figure 4.28. The highest salinity level of 185.67 mg/L was recorded at Point 5 (Tetu), while the lowest level was recorded at Point 2 (Sagana) of 20.34 mg/L. The salinity levels in all the water samples

were below the Federal Environmental Protection Agency (FEPA) and WHO acceptable levels of 2000 mg/L and 600 mg/L, respectively (FEPA, 1991; WHO, 1986).

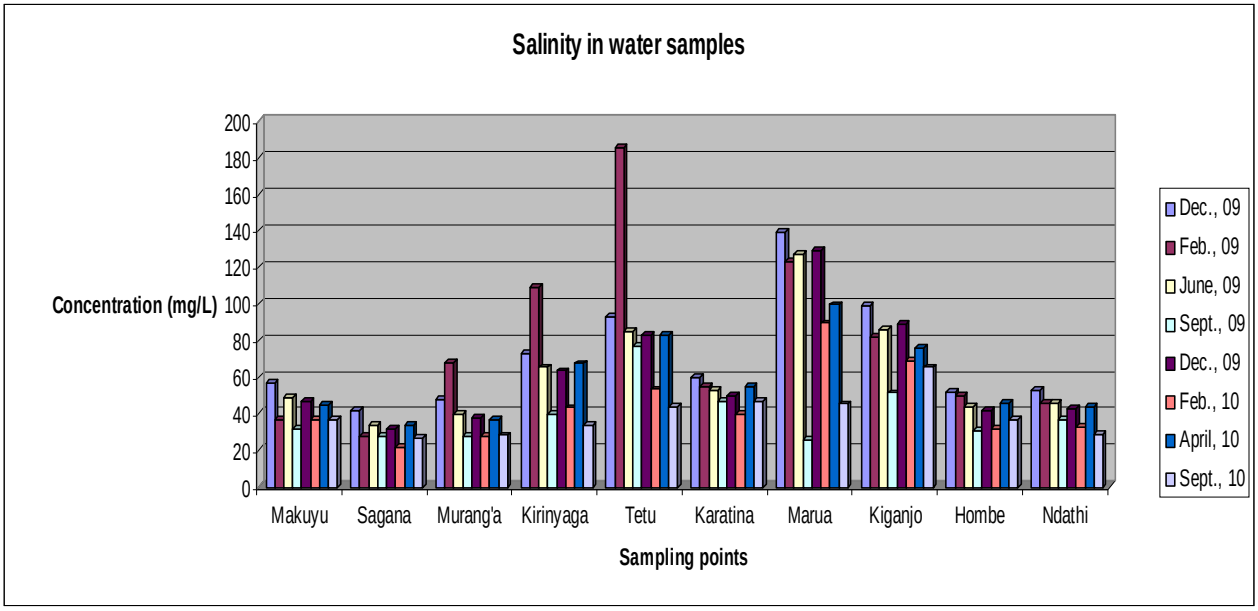


Figure 4.28: Average Salinity levels in water samples

4.10 Correlation of pesticides residue levels with physical-chemical parameters

Correlation of water samples from the upper Tana River showed high positive values for organochlorine pesticides and the physical-chemical parameters. In this case a high positive correlation coefficient of 0.925 was obtained for OCs and Salinity, while OCs –TDS and OCs-TSS both showed a correlation coefficient of 0.85 as shown in Appendix III (Table III A). Similarly, the correlation coefficients between chlorpyrifos residue levels with physical-chemical parameters showed positive correlation in most cases as indicated in Appendix III (Table III B). Chlorpyrifos-Conductivity, chlorpyrifos-TSS and chlorpyrifos- TDS showed a correlation coefficient of 0.379, 0.086 and 0.379, respectively. OCs tends to adsorb to the organic particles in water hence a possible reason for the positive correlation of OCs with TSS and also some elements of TDS are pesticides and PCBs arising from surface runoff.

4.11 The correlation of the pesticides in water, sediment and weed samples

Organochlorine pesticides residues in water, sediments and weed samples showed positive Pearson correlation coefficients. Correlation coefficients of 0.047 and 0.169 were obtained for water-sediment and water-weed, respectively, as can be observed from Appendix III (Table III C). On the other hand the chlorpyrifos residue levels in water also showed positive Pearson correlation coefficients of 0.699 and 0.619 for water-sediment and water-weed, respectively, as shown in Appendix III (Table III D).

4.12 Comparison of pesticides residue levels of this study with other researchers

4.12.1 International reports

The concentrations of OCs and chlorpyrifos detected in this work are consistent with earlier investigations; for instance: DDT residues in water, bottom sediments and certain non-target organisms from four different sites of the river Yamuna in Delhi (Capital of India) were monitored from 1976 to 1978. The concentration of total DDT residues ranged from 0.04 µg/L to 3.42 µg/L in water, 7 to 5630 µg/Kg in bottom sediments, 50 to 15240 µg/Kg in various invertebrates and 540 to 56310 µg/Kg in different fish (Aggarwal, 1986). The total DDT concentration in water at Wazirabad upstream was 2400 µg/L as compared to 558 µg/L at Wazirabad downstream, where the river receives water from Najafgarh drain (Aggarwal, 1986). This clearly shows high amount of DDT being consumed within Delhi. An Indo-Dutch study has shown alarming levels of pesticides in the Yamuna water supplies to Delhi. Organochlorines like aldrin, BHC, DDT, dieldrin were detected in the range of 0.001 - 1.064 µg/L (Agarwal, 1997). Organochlorine residues were detected in the sediments of the river Ganga. Of the various organochlorines detected g-HCH (0.002 - 0.014 µg/g), aldrin (0.0012 - 0.12 µg/g), dieldrin (0.002 - 0.014 µg/g), heptachlor (0.0014 - 0.008 µg/g) and heptachlor epoxide (0.002 - 0.018

µg/g) were more frequently present (Ahamad *et al*, 1996). The study above by Aggarwal *et al.*, (1986) reported high levels of DDT. Similarly, the current study also reviewed high p,p'-DDT residue levels in water and sediments samples of 107.33 µg/L and 190.07µg/kg respectively. This shows that DDT is still on use both in India and Kenya even though it has been banned.

Also in analyzed water samples of Rawal Lake (Pakistan) the average concentration of DDT (an organochlorine) and diazinon (an organophosphate) was higher. The pesticide residues were believed to have originated from agricultural or household uses (EPA, 2008). Several other studies conducted in India have shown organochlorine pesticide residues in human blood samples. According to a study conducted in Delhi, blood samples from 182 people were examined for DDT residues and showed that all except 8 contained DDT and its metabolites. The average total DDT concentration in the whole blood ranged from 0.177 to 0.683 mg/L in males and from 0.166 to 0.329 mg/L in females. The DDT metabolites detected were pp'- DDT, pp'-DDD and p,p'-DDE. DDE accounted for most of the total DDT (Agarwal *et al.,* 1976). This shows that the people in Delhi, India are exposed to very high DDT contaminations. Analysis of 27 samples of human whole blood of 19 males and 8 females from 21 to 57 year old, in Tokyo Metropolitan Research Laboratory of Public Health for polychlorinated terphenyls (PCTs), polychlorinated biphenyls (PCBs) and DDE showed a mean value of 3.2, 5.0 and 11.2 µg/L respectively (Doguchi and Fukano, 1975). Kenya being a developing country like India, may be involved in some similar anthropogenic activities which expose OCs to the environment and thus the results of this study are consistent with these reports from India.

4.12.2 Local reports

Another study by Safina, *et al.*, (2011) set out to survey pesticide usage and concentrations of their residues in lower Yala/Nzoia catchment areas of Lake Victoria, Kenya during the dry and rainy seasons of 2009. Water and sediment samples were analyzed for selected organochlorine and organophosphorus pesticide residues. The findings of the survey showed that the banned organochlorines are still being used in the catchment. Pesticide residue levels of organochlorines in water samples from Yala/Nzoia basin were below detection limit (BDL) both during the rainy and dry seasons. The residue levels detected in sediment samples collected during the rainy season ranged from 0.05 to 59.01 µg/kg, whereas during the dry season, they ranged from BDL-24.54 µg/kg. The results of Safina, 2011 agree with the current study, in that the OC residues realized in sediment samples during the dry season were higher than those detected during the wet season. Mugachia *et al.*, (1992) also investigated OC residue levels in fish from the Athi River estuary. Eight OC pesticide residues were detected in tissues from six species of fish with high levels of DDT of 702 µg/kg compared to breams and catfish of 213 and 145 µg/kg respectively. This study also agrees with the current study since in most cases p,p'-DDT showed the highest concentration of all other OC compounds, for instance in water and sediment samples p,p'-DDT had the highest levels of 107.33 µg/L and 190.07µg/kg, respectively.

Mwenda (2011) assessed OCs in sediment samples derived from Mbagathi River. Their concentration ranged between BDL and 4.24 g/kg with heptachlor having the highest levels.

Ndunda (2010) found high levels of PCB 28 (BDL- 718.98 ng/L) in water samples from Nairobi River and Gitari (2011) also found high levels of PCB (BDL-838.23 ng/L) in water ranging from BDL to 70.30 µg/kg in sediment samples from the Nairobi River basin. PCBs and OCs mostly

are considered together because they have similar methods of extraction and analysis, since they are both chlorinated organic compounds.

PCB congeners 28, 52, 101, 105, 118,153, 156 and 180 were detected along the shores of Lake Victoria (Wandiga and Madadi, 2009). PCB 28 was detected in sediments from River Sio in concentration of 8 µg/kg while PCB 52 was detected at concentration ranging from BDL to 60 µg/kg with the highest concentration emanating from a region with high agricultural and industrial activities. Other PCB congeners' concentrations ranged from BDL to 6.3 µg/kg of organic carbon at various sites (Wandiga and Madadi, 2009). Kituyi *et al.*, (1997) studied chlorfenviphos which is an organophosphate used to control ticks, in western Kenya and established that the concentration of chlorfenvinphos in milk samples varied between 0.52 and 3.90 mgk/g in the dry season and from 1.58 to10.69 mg/kg during the wet season, showing higher levels of residues in the dips during the dry season.

A total of 41 samples of maternal blood, milk, subcutaneous fat and umbilical cord blood were analysed from mothers giving birth by caesarean operation at Kenyatta National Hospital in Nairobi in 1986 (Kanja *et al*, 1992). The main contaminants found in all the samples were pp' – DDT (100 %), pp' DDE (100 %), op' DDT (59 %), dieldrin (27 %), transnonachlor (15 %), b-HCH (12 %) and lindane (2 %) of all the samples analyzed. The mean level (mg/kg fat) of t-DDT was 5.9 in subcutaneous fat, 4.86 in mother's milk, 2.75 in maternal serum and 1.9 in umbilical cord serum. The mean levels of betahexachlorocyclohexane (b-HCH) in subcutaneous fat and milk fat were 0.034 and 0.26 mg/kg fat, respectively (Kanja *et al*, 1992). This showed that most Kenyans could be at a danger of contracting pesticides related complications, like cancer and other diseases at that time.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSIONS

The OCs compounds; (*α-HCH, β-HCH, γ-HCH, δ-HCH, Heptachlor, Aldrin, Heptachlor epoxide, Endosulphan I, pp-DDE, Dieldrin, Endrin, Endosulphan II, pp-DDD, Endrin aldehyde, pp-DDT, Endosulphan sulphate and Methoxychlor),* and chlorpyrifos were assessed and found to be present water, sediment and weed in the upper Tana River.

The concentration of OCs in water samples ranged between < 0.00021 to 107.33 µg/L with the p,p'-DDT having the highest levels of 107.33 µg/L observed in Point 7 (Marua) located mid-stream stream. Only 10 % of the DDT and its isomers residue levels detected were below the WHO, Australia, the United States, New Zealand, Japan and Canada limit guidelines for drinking water, whereas 90 % were above the recommended values. 95 % of the other OCs compounds residue levels were below the WHO, Australia, the United States, New Zealand, Japan and Canada with only 5 % above the same levels showing that DDT and its metabolites are the main contaminants. In sediment samples OCs residue levels were in the range of < 0.00024-190.07µg/kg, whereby, p,p'-DDT had the highest OC residue levels in water samples. The OC residue level in weed samples were the lowest as compared to the residues in water and sediment samples and was in the range of < 0.00012 to 28.82 µg/kg.

On the other hand the chlorpyrifos residue levels were in the range of < 0.0001 to 6.80 µg/L in water samples. The highest chlorpyrifos average level of 5.24 µg/L was recorded at Point 6 (Karatina) located at the midstream section and lowest level of 1.02 µg/L was detected of Point 10 (Ndathi) located at the source. The concentration of chlorpyrifos residue levels were low at Point 10 probably due to limited crop and cattle farming activities in the area. All the water

samples analysed for chlorpyrifos had the residue levels lower than the set guidelines for chlorpyrifos residue levels in drinking water by WHO and Newzealand of 40 µg/L and 70 µg/L, respectively, indicated in Table 4.3. The sediment samples had chlorpyrifos residue levels in the range of < 0.0001 and 1.43 µg/kg while in the weed samples the levels were in the range of <0.0001 to 2.57 µg/kg. Concentrations of OCs and chlorpyrifos residue levels were highest in samples collected from the mid-stream of the upper Tana River, probably because of the intense crop and cattle farming. The mid stream area is also more loaded with factories, unlike up stream and down stream section, which include: Marua coffee factory in Marua, Mtu Athi coffee factory in Tetu together with, Nguguru and Gathugu coffee factories both in Karatina; a possible source of both OCs and chlorpyrifos residues discharged into the river body. Higher concentrations of OCs were detected during the dry season than during the wet season, unlike the chlorpyrifos concentration which was found to be higher during the wet seasons and low during the dry seasons. This could be attributed to fast biodegradation of the chlorpyrifos. The high residues of chlorpyrifos found during the wet seasons were probably as a result of recent wash off from the farms, cow dips and cow sheds in the area. Residues of both organochlorines and chlorpyrifos were also found at the source of Tana River (Ndathi). This could be attributed to settlement and some few farming activities taking place in the area. Since the area is preserved as rain catchments the anthropogenic activities like crop and cattle farming ought to be stopped. Zero grazing is also practiced at the source of Tana River a possible contribution of the chlorpyrifos residues detected in the area.

The physico-chemical parameters analysed in this study include pH, Electrical conductivity, TDS, TSS and Salinity. The pH levels in the water samples ranged between 6.71 and 7.54, with most samples having a near neutral pH, which falls within the range of 6.5-8.5 levels for natural

water bodies recommended by the European Union. This could be attributed to the river's natural buffering capacity being adequate to withstand any basic or acidic discharges. These levels were also within the permissible level of 6.5-8.5 for both irrigation and domestic water by Kenya Bureau of Standards (KeBS) and within the World Health Organization (WHO) recommended guideline which is between 6.5 and 8. They were also within the maximum allowable levels for both irrigation and domestic use by National Environment Management Authority (NEMA) of 6.5 -8.5 and within the acceptable levels permitted by Water Resources Management Authority (WRMA) of 6.5 -8. The electrical conductivity was in the range of 57.02 µS and 373.43. The levels were within the established EPA drinking water quality standards of 900 µS. The lowest recorded value for TDS was 39.91 mg/L at Point 10 (Ndathi) while the highest was 261.40 mg/L at Point 6 (Marua) as indicated on. All the TDS values recorded were below WHO permitted level for drinking water of 1000 mg/L, they were below the permitted level of 1200 mg/L by KeBS which applies for both irrigation and domestic water and within the established EPA drinking water quality standards of 500 mg/L. The TSS value ranged between 5.33 mg/L and 432.45 mg/L in the study. The highest salinity level of 185.67 mg/L was recorded at point 5 (Tetu), while the lowest level of 30.08 mg/L was recorded at point 2 (Sagana).

The correlation between water samples from the upper Tana River showed high positive values for organochlorine pesticides and the physico-chemico-parameters. In this case a high positive correlation coefficient of 0.925 was obtained for OCs and Salinity, while OCs –TDS and OCs-TSS both showed a correlation coefficient of 0.85. Similarly, the correlation coefficients between chlorpyrifos residue levels with physico-chemical parameters. Chlorpyrifos-Conductivity, chlorpyrifos-TSS and chlorpyrifos- TDS showed a correlation coefficient of 0.379, 0.086 and 0.379, respectively. OCs tends to adsorb to the organic particles in water hence a probable reason

for the positive correlation of OCs with TSS. Some elements of TDS are pesticides and PCBs arising from surface runoff.

Organochlorine pesticides residues levels in water, sediments and weed samples showed positive Pearson correlation coefficients. Correlation coefficient of 0.047 and 0.169 were obtained for water-sediment and water-weed, respectively. On the other hand the chlorpyrifos residues in water showed a positive Pearson correlation coefficient of 0.699 and 0.619 for water-sediment and water-weed, respectively.

5.2 RECOMMENDATIONS

1. The presence of organochlorine pesticides residue levels in the samples analysed in this study, implies that these residues are still in the environment. I therefore recommend for further studies looking into methods of remediation of pesticides pollution in the environment.

2. It is recommended that a policy be put in place to control the use and distribution of OCs and chlorpyrifos as well as implement routine monitoring programmes.

3. Further research should be carried out to determine point and non point sources of OCs and chlorpyrifos in the estuaries of the Tana River and in other aquatic environments and also the effectiveness of microbial degradation of OCs and chlorpyrifos in the environment for remediation such as waste water treatment before discharge into the river.

4. The presence of pesticide residues in the weed samples revealed the ability of weeds to extract pesticides from water and sediments or soil. Therefore, further studies are recommended to investigate bioconcentration factor for various plants to come up with suitable plant species that can be used in phytoremediation of the chemical contaminants from the environment.

5. Proper drainage should be adopted in the factories along Tana River profile in order to reduce water pollution with pesticides and other contaminants by use of suitable waste water treatment methods.

6. Alternative biological methods to chlorpyrifos application for pest control should be practiced in the mid stream area. This would be very helpful in preventing further contamination of the river with the chlorpyrifos residues and other pesticides.

REFERENCES

Abhik G., (2008). Impact of pesticides on human and ecosystem health: Scientific, Ethical and Policy Issues in: Proceedings of National seminar on Toxicity of chemicals and their hazards with special reference to heavy metal, pp 61-72 st. Edmund's College, Shillong.

Agarwal A., (1997). Homicide by Pesticides. State of Environment Series, No-4, pp 54

Agency for Toxic substances and disease Registry (ATSDR) (1989). Public Health Statement for Hexachlorocyclohexane. Atlanta, GA: US Department of Health and Human Services.

Agarwal H. C., Pillai M. K., Yadav D. V., Menon K. B. and Gupta R. K., (1976). Residues of DDT and its metabolites in human blood samples in Delhi, India. Bull. World Health Organ. 54:349-351.

Aggarwal H. C., (1986). DDT Residues in the river Jamuna in Delhi, India. Water Air and Soil Pollution 28: 89-104.

Ahamad S, Ajmal M. and Nomani A. A., (1996). Organochlorines and polycyclic aromatic hydrocarbons in the sediments of Ganges River (India). Bull. Environ Contamn Toxicol. 57:794-802.

AMAP (Arctic Monitoring and Assessment Programme) (2000). AMAP trends and effects programme, section B, trend monitoring programme, Table B2. Arctic Monitoring and Assessment Programme, Oslo, Norway.

Amjad I., Muhammed A. F., Attique R., Fahim A. and Sheraz A., (2010). Department of chemistry., GC. University, Katchery road, Lahore-54000, Pakistan.

APHA (American Public Health Association) (1992). Standard Methods for the Examination of Water and Wastewater. 18th Edn.

ATSDR (Agency for Toxic Substances and Disease Registry) (2000). Toxicological Profile for

Polychlorinated Biphenyls. US Public Health Service, Atlanta (GA), USA.

Baron, L., Cencil, L., Tettamant, M.; Derati, M., (2007). Evaluating the Environmental impact of various dietary patterns combined with different food production systems. *European journal of clinical Nutrition* 61 (2): 279-286. doi: 1038/sj.ejcn.1602522.PMID 17035955.

Birech R., Bernhard F., Joseph M., (2006). Conference in International Agricultural Research for Development towards reducing synthetic pesticide imports in favour of locally available botanicals in Kenya. Department of Crops, Horticulture and soils Egerton University, Kenya. Tropentag Boon.

Chapman, D., (1998). Water Quality Assessments: A guide to the use of biota, sediments and water in environmental monitoring, UNESCO-WHO-UNEP, by E&FN SPON.

Cheah U. B., and Lum K.Y., (1994). Pesticide residue and microbial contamination of water resources of rice agrosystem in Muda area. Proceeding of the seminar on Impact of pesticide on the Rice Agrosystem in the Muda area, Penang, 1-5.

CIA (Central Intelligence Agency) (2009). "Kenya". The World Factbook. Retrieved 23 January 2010. The contested Record of US Foreign Policy.

Damalas, C. A., and Ilias G. E., (2011). Pesticide Exposure, Safety Issues, and Risk Assessment Indicators. International Journal of Environmental Research and Public Health. *Web of Science*.

Doguchi M. and Fukano S., (1975). Residue levels of polychlorinated terphenyls, polychlorinated biphenyls and DDT in human blood. *Bull. Environ. Contam. Toxicol*. 13(1):57-63.

EPA, (2009). Illness Related to Sewage in Water. Accessed 0N 20th Feb.

EPA, (2008). Integrated Pest Management Principles. Retieved on 13th March.

Everaats, J. M., Van Weerlee, E. M., fischer, C. V., Hillbrand, M. T. J., (1997). Polychlorinated biphenyls and cyclic pesticides in sediments and macro vertebrates from Coastal regions of different climatical zones. Vienna, Austria 1-5 July. pp 1-18.

FAO (1997): Production Yearbook, Rome.

Farrelly, E., Hamer, M. J., and Hill, I. R., (1984). Toxicity to first instar Daphnia magma (Report No. RJ0359B, submitted to WHO by ICI). pp 321.

Feldmann R. J., and Maibach H. J., (1974). Percutanews penetration of some pesticides and herbicides in man. *Toxicol and Appl Pharmal.* 28: 126-32.

FEPA (Federal Environmental Protection Agency) (1991). Guideline and Standard for Environmental Pollution Control in Nigeria. Online.

Fifield F. W., Haines P. J., (2000). Environmental Analytical Chemistry. Blackwell Publishing, pp 4-5. ISBN 0-632-05383-6.

Fred F., (2002). Effects of pH on the stability of pesticides. University of Missouri, Department of Agronomy, Extension publications IPM 1017.

Freedman B., (1995). Environmental Ecology, the Ecological Effects of Pollution, Disturbance and other Stresses, 2nd edition, (page 213-275).

GEF, (2001). Persistent toxic substances (PTS), Food security and indigenous peoples of the Russian north. In: Kimstach 5th ed. *Arctic monitoring and assessment program*. Olso, Norway.

Gitari F. K., (2011). Assessment of polychlorinated biphenyls (PCBs) in water and sediments from Ngong and Mathare rivers. M.Sc Thesis, Department of Chemistry, University of Nairobi, Kenya.

Gregory K., McMillan., Robert A., Cameron, (2005). *Advanced pH measurement and control*. p. 3.

Hayes W. J., and Laws, E.R., (1990). Handbook of pesticide toxicology, general principles, Vol. 1 Academic Press, Inc., NY.

Helfrich L. A., Weigmann, D. L., Hipkins, P. and Stinson, E. R., (1996). Pesticides and aquatic animals: A guide to reducing impacts on aquatic systems. Virginia Cooperative Extension.

Hendricks D. W., (2007). Water Treatment Unit Processes: Physical and Chemical. Boca Raton, FL: *CRC Press* pp 44–62.

Hoff, H., Noel, S., (2007). Quantifying water usage and demand in the Tana River basin: an analysis using the Water and Evaluation and Planning Tool (WEAP). In: Dent, D. (Ed.), Green Water Credits. ISRIC - World Soil Information, Wageningen.

IADN (Integrated Atmospheric Deposition Network) (1994). Integrated atmospheric deposition network quality assurance program plan. US Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL, p 143.

IFAD/UNEP/GEF, (2004). Mount Kenya East Pilot Project for Natural Resource Management, Project brief report.

IPEP (International POPs Elimination Project) (2006). Approaches to Effective Malaria control that Avoid DDT in Kenya: Use of Bacillus thuringiensis israelensis (BTi).

IUPAC, (2003). Regulatory Limits for Pesticides Residues in water. Pure Appl. Chem. 75(8): 1123-1156.

Jones S., (1995). Food Market Reform. The changing role of the state. Food Policy, 20 (6): 551-560.

Kanja L.W.; Skaare J.U; Ojwang S.B.O. (1992); A comparison of organochlorine pesticide residue in maternal adipose tissue, maternal blood, chord blood and human milk from mothers infant pairs; Arch. Environ. Contam Toxic 22, 21-24.

Kituyi, E., Jumba, I. O., and Wandiga, S. O., (1997). Occurrence of chlorfenvinphos residues in cow milk in Kenya. *Bull Environ Contam Toxicol.* 58 (6): 969-75.

KMD (Kenya Meteorological Department) (2013). The outlook for the Mrch-April-May (MAM) 2013 "Long rain" season in Kenya. Ref. No. KMD/FCST/5-2013/SO/01. Dagoretti Corner.

KNBS (Kenya National Bureau of Statistics) 2009. Population and Housing Census results. Directorgeneral@knbs.or.ke USAID, UNFPA & SIDA.

Lalah J. O., (1993). Studies on the Dissipation and Metabolism of some Insecticides under Kenyan Environmental conditions; Ph. D. Thesis, Department of Chemistry, University of Nairobi: pp 138-146.

Leete D., (2001). A feasibility study for an abattoir in Laikipia. The Laikipia Farmemrs committee.

Lemaire G., Terouanne B., Mauvais P., Michel S. and Rahmania R., (2004). Effect of organochlorine pesticides on human androgen receptor activition in vitro. *Toxicology and Applied Pharmacology* 196 : 235-246.

Lewis E. L., (1982). The practical salinity scale of 1978 and its antecedents. *Marine Geodesy* 5 (4): 350.10.1080/15210608209379432.

Madadi O.V., (2005). Chemodynamic studies and assessment of pesticide residues in Lake Victoria catchment area for River Sio and Nzoia. M.Sc Thesis. UoN.

Mark., R., (2010). Environmental measurement matters: Factors affecting water quality; *Sper Scienfic*.

Mark, F. Z., (2003). Pesticide use in Zimbabwe. (Impact on Lake Kariba, a tropical freshwater ecosystem). IN: Pesticides Residues in Coastal Tropical Ecosystems. Published by Taylor and Francis, 11 New Fetter Lane, London EC4P 4EE.

Mathur, Sapna J., Rashmi M., Avinash K. and Bhupinder S., (2003). Centre for Science and Environment 41, Tughlakabad Institutional Area, New Delhi 110062.

Meister, R. T., (1992). Farm chemicals handbook. Meister publishing company. Willoghby, OH.

Michaud J. P., (1994). Measuring Total Suspended Solids and Turbidity in lakes and streams. *A Citizen's Guide to Understanding and Monitoring Lakes and Streams.* State of Washington, Department of Ecology.

Mogako H., Gichere, S., Davis R. and Hirji R., (2006). Climate variability and water resources degradation in Kenya: Improving water resources development and management. World Bank, Washington DC.

Mugachia, J. C., Kanja, L., and Gitau, F., (1992). Organochlorine pesticide residues in fish from Lake Naivasha and Tana River, Kenya. *Bull Environ Contam Toxicol.* 49(2): 207-10.

Munga, D., (1985). DDT and Endosulfan residues in Fish from Holla irrigation Scheme, Tana River, Kenya: M.Sc thesis, Chemistry Department, University of Nairobi: pp 95-140.

Mwaisaka P., (1999). Government applauds efforts. *Agrochem News*, Nairobi, Kenya:5 (11):1.

Mwenda. J.N., (2011). Assessment of organochlorine pesticides residues in cow milk, sediments and water from Nairobi West region. M.Sc Thesis, Department of Chemistry, University of Nairobi, Kenya.

Ndunda E. N., (2010). Analysis of polychlorinated biphenyls in sediments and water in Nairobi River by Gas Chromatography. M.Sc Thesis, Department of Chemistry, University of Nairobi, Kenya.

NEAP, (The Kenya National Environment Action Plan) (1994). Report for the Ministry of Environment and National Resources. Nairobi, Kenya: Ministry of Environment and Natural Resources.

Nick, M., Jirat, J., Kosata, B., (2006). Matrix (in analysis. IUPAC Compendium of Chemical Terminology (Online ed.). DOI:10.1351/goldbook.M03758. ISBN 0-9678550-9-8.

Nyandiko H.O., (2001). Policy and Legal Framework for the Tea subsector and the impact of liberation in Kenya. Kenya Institute for Public Policy Research and Analysis (KIPPRA).

Notter, B., MacMillan, L., Viviroli, D., Weingartner, R.and Liniger, H.-P., (2007). Impacts of environmental change on water resources in the Mt. Kenya region. Journal of Hydrology 343, 13.

Ogallo, L. A. and Mwangi, R. W., (1996). Implications of the expected climate changes on the low-lying parts of Kenya. IN: Environment and development, A public lecture series. KNAS press, Nairobi.

Otieno P.O., Schramm K., Pfister C., Lalah J. O., Ojwach S.O. and Virani M., (2012). Spatial distribution and temporal trend in concentration of Carbofuran, diazinon and chlorpyrifos residue in sediment and water in L. Naivasha, Kenya. Environ. Contam. Toxical 88: 526-532.

PCPB, (2012). Annual Report, July 2011/June 2012, © 2010 Pest Control Products Board, Nairobi, Kenya. Page 9-10.

PCPB (Pest Control Products Board) (2008). Annual Report, July 2007/June 2008. Pest Control Products Board, page 10-13.

PCPB (Pesticide Control Products Board) (2005). Pest Control Products Board, July, 2004 – June, 2005 Annual Report.

Ritter L, Solomon, K. R. and Foget J., (2007). Persistent Organic Pollutants. An assessment report on DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls, dioxins and furans. International programme on chemical safety (IPCS).

Robert L., (2002). Metcalf "Insect Control" in Ullmann's Encyclopedia of Industrial Chemistry" Wiley-VCH, Weinheim, doi:10.1002/14356007.a14_263.

Robert P., and Adams, (2007). Identification of Essential Oil Components By Gas Chromatography/Mass Spectrometry. Allured Pub Corp. ISBN 1-932633-21-9.

Safina M., John W. G., Phillip O. R. and Christopher M. A., (2011). Organochlorine and organophosphorus pesticide residues in water and sediment from Yala/Nzoia River within Lake Victoria Basin, Kenya. *Kari Org*. KARI REPORT.

UNEP, (2007). POPs Training Project. Practical Training Course in Nairobi, Kenya at University of Nairobi, Department of Chemistry.

UNEP, (2001). Final act of the conference of plenipotentiaries on the Stockholm convention on persistent organic pollutants. United Nations Environment Programme, Geneva, Switzerland, p 44.

UNEP, (1999). Guidelines for The identification of PCBs and Materials containing PCBs. Inter-Organization Programme for the Sound Management of Chemicals. First Issue, United Nations Environmental Programme.

UNEP, (1984). Marine and coastal conservation in East Africa region. UNEP Regional Seas Reports and Studies nr 39. Geneva: Gegional Seas Programme Activity Centre, pp 39.

UNEP/GEF, (2010). POPs Training Project. Practical Training Upper Lakes Reference Group, (1977). The waters of Lake Huron and Lake Superior. Report to the International Joint Commission, Vols. I-III, Parts A and B. *Windsor, Canada, International Joint Commission*.

(UNWA, 2011) UN Water Africa, (2011). The Africa Water Vision for 2025: Equitable and Sustainable use of water for socioeconomic development, pg 8.

Upper Lakes Reference Group (1977). The waters of Lake Huron and Lake Superior. Report to the International Joint Commission, Vols. I-III, Parts A and B. *Windsor, Canada, International Joint Commission*.

U.S. Environmental Agency, (2007). What is a pesticide? epa.gov. guide.pdf.

U.S. Environmental Protection Agency, (2003). "National Management Measures to Control Nonpoint Source Pollution from Agriculture.". Document No. EPA 841-B-03-004.

U.S. Environmental Protection Agency (1991). Washington, D.C. "Guidance for Water Quality-Based Decisions: The TMDL Process." Doc. No. EPA 440/4-91-001.

Course in Nairobi, Kenya at University of Nairobi, Department of Chemistry.

U.S. Environmental Protection Agency, (1988). Dichlorvos: Initiation of special review. Fed. Regist. 53: 5542-49, 1988.5-11.

Victoria A. R., (2009). Acid-Alkali Balance. Natural medicine.suite101.com/article.cfm/acid alkali_balance.

Wagner, S. L., (1989). The acute health hazards of pesticides. In Chemistry, Biochemistry, and Toxicology of Pesticides. Witt, J. M., Ed. Oregon State University Cooperative Extension Service, Corvallis.

Wandiga S.O., (2001). Use and Distribution of Organochlorine Pesticides, the Future in Africa. Pure applied chemistry 73:1147-1155.

Wandiga S. O., and Madadi V. O., (2009). Water Issue in Eastern Africa. In: Handibook of Water purity and quality, pp 50-62. Satinder Ahuja. In Elsevier, Academic Press.

Wania F, and Mackay D., (1996). Tracking the distribution of persistent organic pollutants. *Environ. Sc.* and T 30 (a). Pp 390-396.

WHO, (1996). Guidelines for drinking water quality , 2nd ed. Vol. 2. Health criteria and other supporting information. World Health Organization, Geneva.

WHO (World Health Organisation). (1989). DDT and its Derivatives. *Geneve:* p. 83. ISBN 92-4-154283-7.

WHO, (1986) World Health Organization International Standards for drinking water, 3rd ed. WHO, Geneva.

WHO/UNEP, (1990). Public health impact of pesticides used in Agriculture. Total Suspended Solids_247238_7.

WHO/UNEP, (1989). Global freshwater quality. Oxford, Alden Press.

World Bank, (2007). Project appraisal document on a proposed credit in the amount of sdr 46.0 million (US$68.5 million equivalent) to the government of Kenya for a natural resource management project. World Bank pp 176.

WRMA (Water Resource Management Authority (2012). Securing water and land in the Tana Basin: The resource book for water and Practitioners. pp 8; 3rd water secretariat.

WRMA (Water Resource Management Authority) (2008). Tana water catchment area; Catchment management strategy. CMS - Tana_1st Edition doc. pp 55.

Yugi, P.O., (2000). Distribution of Organochlorine Pesticides Residues in the Marine Environment along the Coastal Region of Kenya, MSc. Thesis, Department of Chemistry, University of Nairobi.

APPENDICES

APPENDIX I

Table I A: Some of the OC compounds analysed in this study

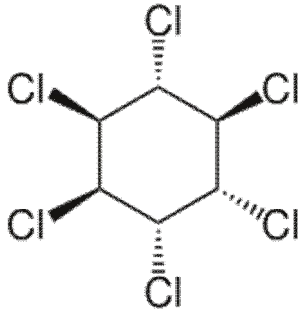
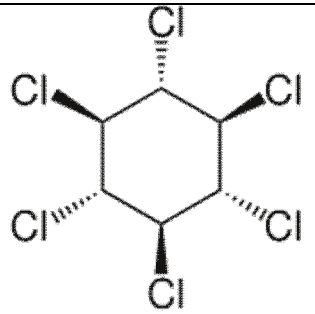
OC compound	**Structure**	**Half-Life**
α-HCH (α-hexachlorocyclohexane)		26 years at pH 8 and 5°C 63 years at pH 8 and 0° 14 years in water 45 years in soil
β-HCH (β-hexachlorocyclohexane)		12 years in water 7.2 years in blood 7.1 years in lipid
OC compound	**Structure**	**Half-Life**

Table I A: Some of the OC compounds analysed in this study contd.,

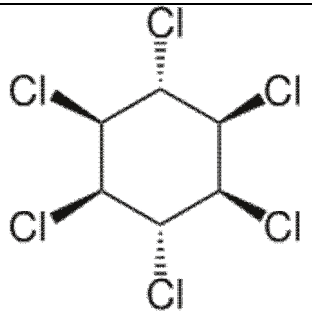
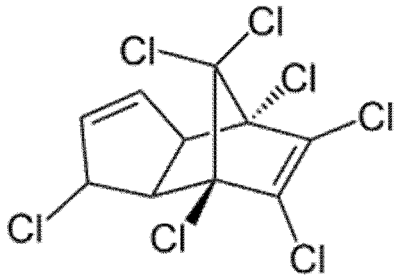
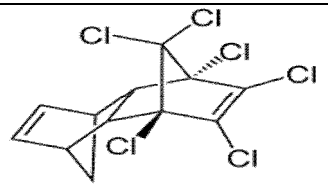
OC compound	**Structure**	**Half-life**
γ-HCH (γ- hexachlorocyclohexane) (Lindane)		14 years in water 32 years in soil
Heptachlor		16 years in soil 4.2 days in air and 0.11 years in water
Adrin		5 years in soil and 2 years in water

Table I A: Some of the OC compounds analysed in this study contd.,

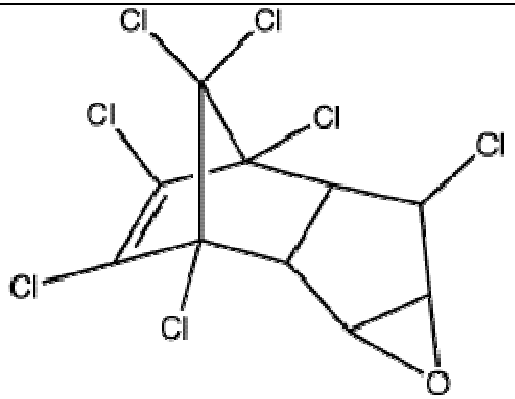
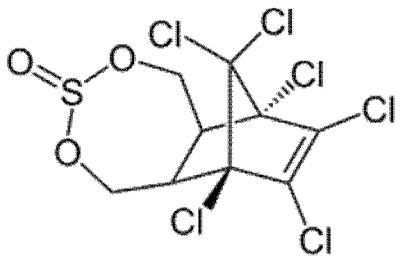
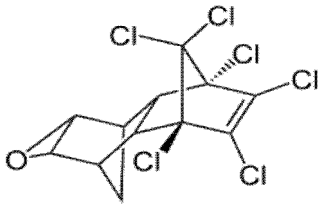
OC compound	Structure	Half-life
Heptachlor epoxide		14 years in soil and 6 years in water
Endosulphan I		5 days in water 5 Months in acidic condition 7 days in plants and 1 day in basic condition
Dieldrin		12.8 years in soil 96 and 116 days in fat 4 Months in water

Table I A: Some of the OC compounds analysed in this study contd.,

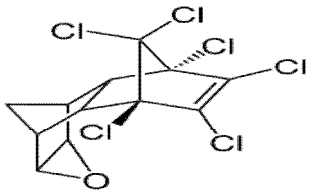
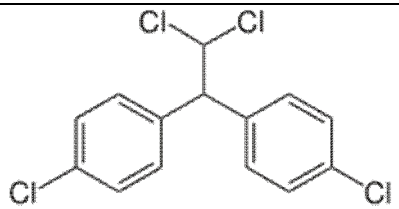
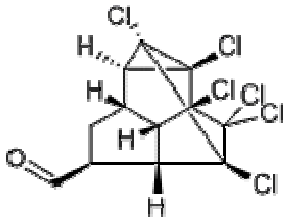
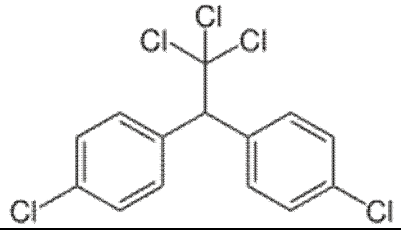
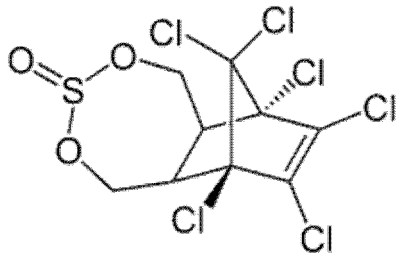
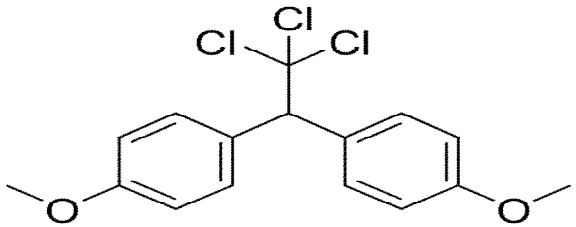
OC compound	Structure	Half-life
Endrin		14 years in soil 6 years in water
p,p'-DDD (Dichlorodiphenyldichloroethane)		150 years in soil/sediment 10 years in water
Endrin aldehyde		14 years in soil 4 years in water
p,p'-DDT		30 years in soil 56 days in water

Table I A: Some of the OC compounds analysed in this study contd.,

OC compound	**Structure**	**Half-life**
Endosulphan sulphate		1 week in water 5 months in soil 11 weeks in plants
Methoxychlor		120 days in soil 5 hours in water

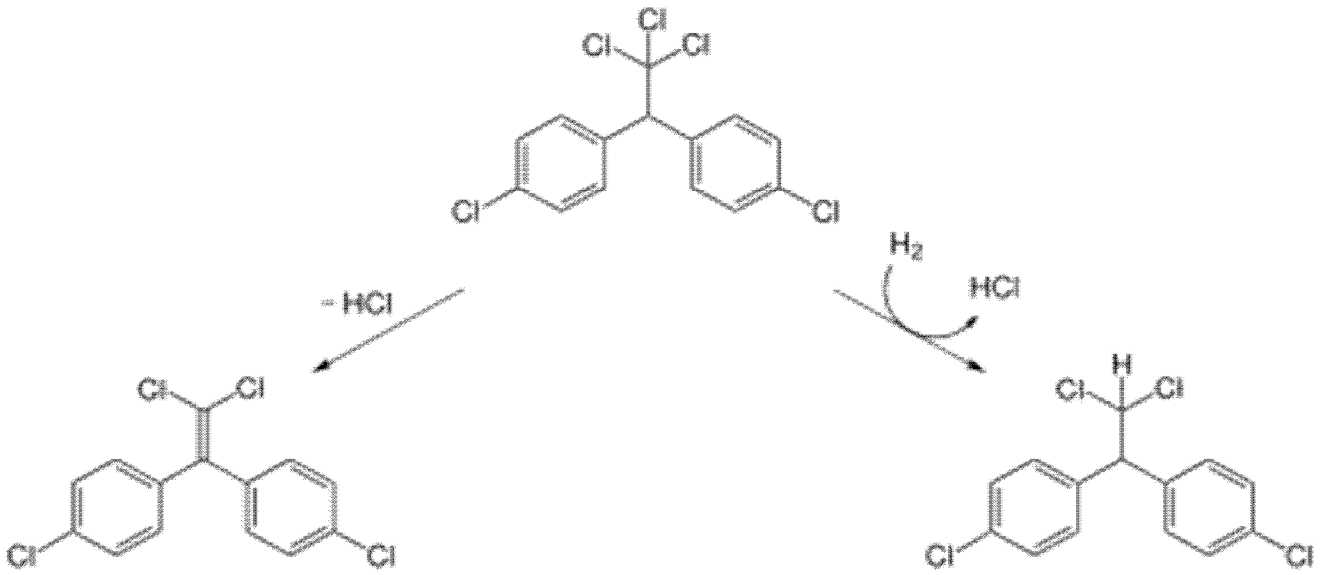


Figure I A: Degradation of DDT to form DDE and DDD

APPENDIX II

GC-MS model**:** Varian CP8912

Analysis software: Agilent EvironQuant ChemStation software

Injector mode: Splitless

Column parameters

(i) Description: VF-1MS

(ii) Model: CP8912

(iii) Manufacture: Varian

(iv) Actual length (m): 30

(v) Internal diameter (µm): 250.00

(vi) Film thickness (µm): 0.25

GC Serial: CN10620074

Inject Volume (µl): 1

Syringe size (µl): 10.00

Plunger speed: Fast b

Carrier gas: White spot nitrogen, 2.7 ml/min, constant flow

Oven parameters: 40°C (1 min) at 6°C/min to 100°C to 240°C (7 min) at 10°C/min

Detector: MS

Figure II A: The conditions of the GC-MS used in the study

APPENDIX III

Table III A: Correlation between the OC residues and the physico–chemical parameters

Correlations

		OCs	Ph	TSS	Salinity	TDS	Conductivity
OCs	Pearson Correlation	1	-.360	.552	.925**	.850**	.850**
	Sig. (2-tailed)		.307	.098	.000	.002	.002
	N	10	10	10	10	10	10
Ph	Pearson Correlation	-.360	1	-.143	-.195	-.256	-.256
	Sig. (2-tailed)	.307		.693	.590	.475	.475
	N	10	10	10	10	10	10
TSS	Pearson Correlation	.552	-.143	1	.651*	.611	.611
	Sig. (2-tailed)	.098	.693		.041	.060	.060
	N	10	10	10	10	10	10
Salinity	Pearson Correlation	.925**	-.195	.651*	1	.909**	.909**
	Sig. (2-tailed)	.000	.590	.041		.000	.000
	N	10	10	10	10	10	10
TDS	Pearson Correlation	.850**	-.256	.611	.909**	1	1.000**
	Sig. (2-tailed)	.002	.475	.060	.000		.000
	N	10	10	10	10	10	10
Conductivity	Pearson Correlation	.850**	-.256	.611	.909**	1.000**	1
	Sig. (2-tailed)	.002	.475	.060	.000	.000	
	N	10	10	10	10	10	10

Table III B: Correlation between chlorpyrifos and the physico–chemical parameters

Correlations

		Chlorpyrifos	pH	Conductivity	TDS	Salinity	TDS
Chlorpyrifos	Pearson Correlation	1	-.087	.379	.379	.161	.086
	Sig. (2-tailed)		.811	.280	.280	.656	.813
	N	10	10	10	10	10	10
pH	Pearson Correlation	-.087	1	-.245	-.257	-.196	-.144
	Sig. (2-tailed)	.811		.496	.473	.588	.692
	N	10	10	10	10	10	10
Conductivity	Pearson Correlation	.379	-.245	1	.999**	.901**	.599
	Sig. (2-tailed)	.280	.496		.000	.000	.067
	N	10	10	10	10	10	10
TDS	Pearson Correlation	.379	-.257	.999**	1	.909**	.611
	Sig. (2-tailed)	.280	.473	.000		.000	.060
	N	10	10	10	10	10	10
Salinity	Pearson Correlation	.161	-.196	.901**	.909**	1	.651*
	Sig. (2-tailed)	.656	.588	.000	.000		.041
	N	10	10	10	10	10	10
TDS	Pearson Correlation	.086	-.144	.599	.611	.651*	1
	Sig. (2-tailed)	.813	.692	.067	.060	.041	
	N	10	10	10	10	10	10

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table III C: The correlation of organochlorines in water, sediment and weed samples

Correlations

		Water	Sediment	Weed
Water	Pearson Correlation	1	.047	.169
	Sig. (2-tailed)		.897	.641
	N	10	10	10
Sediment	Pearson Correlation	.047	1	.747*
	Sig. (2-tailed)	.897		.013
	N	10	10	10
Weed	Pearson Correlation	.169	.747*	1
	Sig. (2-tailed)	.641	.013	
	N	10	10	10

*. Correlation is significant at the 0.05 level (2-tailed).

Table III D: The correlation of chlorpyrifos in water, sediment and weed samples

Correlations

		Water	Sediment	weed
Water	Pearson Correlation	1	.699*	.616
	Sig. (2-tailed)		.025	.058
	N	10	10	10
Sediment	Pearson Correlation	.699*	1	.746*
	Sig. (2-tailed)	.025		.013
	N	10	10	10
Weed	Pearson Correlation	.616	.746*	1
	Sig. (2-tailed)	.058	.013	
	N	10	10	10

*. Correlation is significant at the 0.05 level (2-tailed).

Appendix IV

Table IV A: Banned Pesticides in Kenya

No.	Common name	Use	Date Banned
1.	2,4,5 T (2,4,5 – Trichloro-phenoxybutyric acid)	Herbicide	1986
2.	Chlordane	Insecticide	1986
3.	Chlordimeform	Insecticide	1986
4.	DDT (Dichlorodiphenyl Trichloroethane)	Agriculture	1986
5.	Dibromochloropropane	Soil Fumigant	1986
6.	Endrin	Insecticide	1986
7.	Ethylene dibromide	Soil Fumigant	1986
8.	Heptachlor	Insecticide	1986
9.	Toxaphene (Camphechlor)	Insecticide	1986
10.	5 Isomers of Hexachlorocyclo-hexane (HCH)	Fungicide	1986
11.	Ethyl Parathion	Insecticide All formulations banned except for capsule suspensions	1988
12.	Methyl Parathion	Insecticide All formulations banned except for capsule suspensions	1988
13.	Captafol	Fungicide	1989
14.	Aldrin	Insecticide	2004
15.	Benomyl, Carbofuran, Thiram combinations	Dustable powder formulations containing a combination of Benomyl above 7%, Carbofuran above 10% and Thiram above 15%	2004
16.	Binapacryl	Miticide/Fumigant	2004

Table IV A: Banned Pesticides in Kenya contd.,

No.	Common name	Use	Date Banned
17.	Chlorobenzilate	Miticide	2004
18.	Dieldrin	Insecticide	2004
19.	Dinoseb and Dinoseb salts	Herbicide	2004
20.	DNOC and its salts (such as Ammonium Salt, Potassium salt & Sodium Salt)	Insecticide, Fungicide, Herbicide	2004
21.	Ethylene Dichloride	Fumigant	2004
22.	Ethylene Oxide	Fumigant	2004
23.	Fluoroacetamide	Rodenticide	2004
24.	Hexachlorobenzene (HCB)	Fungicide	2004
25.	Mercury Compounds	Fungicides, seed treatment	2004
26.	Pentachlorophenol	Herbicide	2004
	Phosphamidon	Insecticide, Soluble liquid formulations of the substance that exceed 1000g active ingredient/L	2004
27.	Monocrotophos	Insecticide/Acaricide	2009
28.	All Tributylin Compounds	All compounds including tributyltin oxide, tributyltin benzoate, trybutyltin fluoride, trybutyltin lineoleate, tributyltin methacrylate, tributyltin naphthenate, tributylin chloride	2009
29.	Alachlor	Herbicide.	2011
30.	Aldicarb	Nematicide/Insecticide/Acaricide.	2011

Table IV B: Rectricted Pesticides in Kenya (PCBP, 2008)

Common name	**Remarks**
Benomyl, Carbofuran/Thiram Combinations	Dustable powder formulations containing a combination of Benomyl below 7%, Carbofuran below 10% and Thiram below 15%.
DDT (Dichlorodiphenyl trichloroethane)	Insecticide, restricted use to Public Health only for mosquito control for indoor residual spray by Ministry of Health. Banned for agricultural use.
Ethyl Parathion	Insecticide, capsule suspension formulations allowed in 1998.
Methyl parathion	Insecticide, capsule suspension formulations allowed in 1998.
Phosphamidon	Insecticide, Soluble liquid formulations of the substance that is below1000g active ingredient/L.

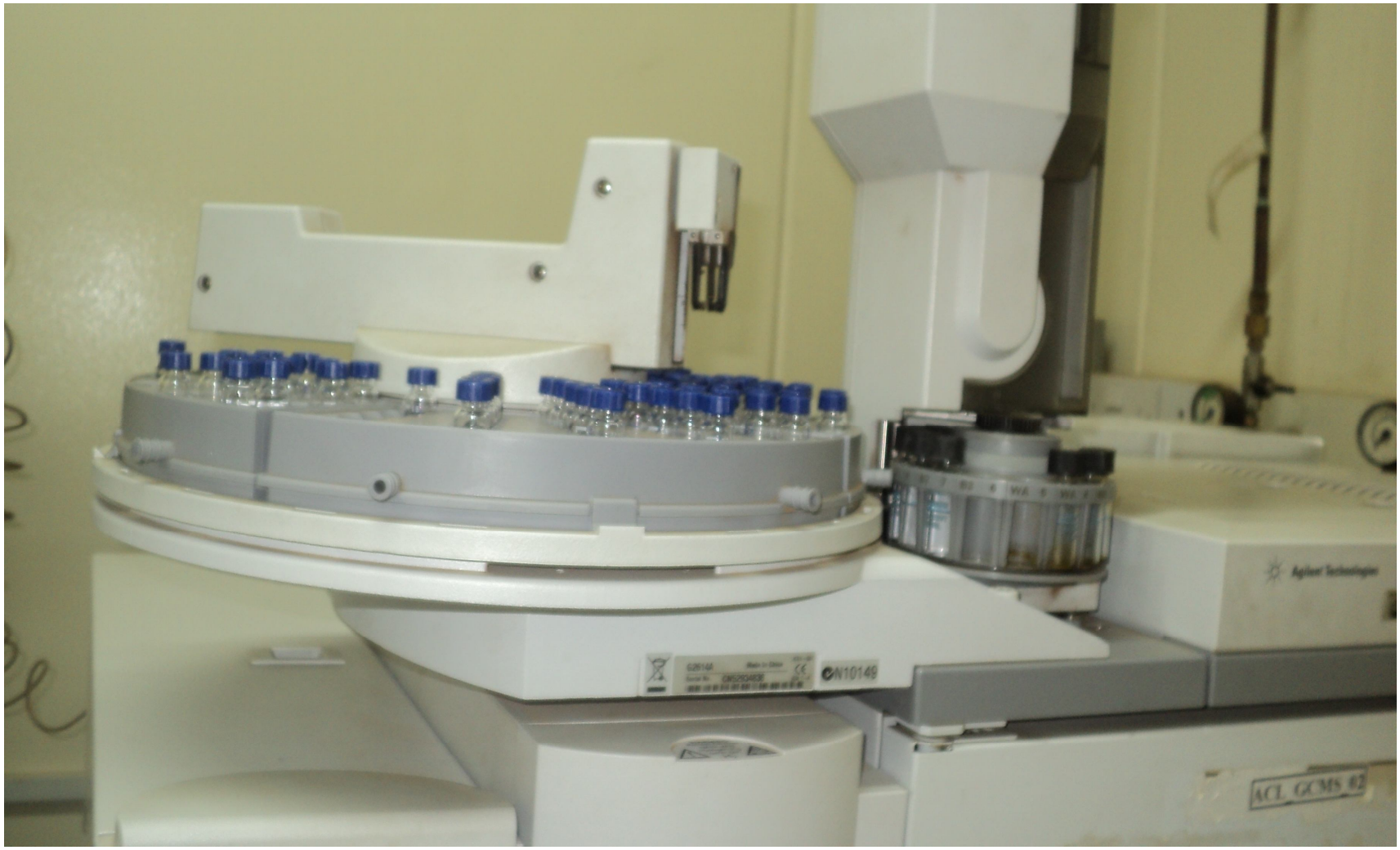


Figure IV A: An image of GC-MS used in the study

Appendix V

Tables used to develop graphs in the text

Table V A: Total of the mean concentrations of each OC in water samples in µg/L±sd

OCs	**Overall Concentration**
α-HCH	48.2±7.02
β-HCH	81.56±5.28
γ-HCH	107.32±1.29
δ-HCH	97.8±0.50
Heptachlor	77.8±3.50
Adrin	44.91±8.03
Heptachlor epoxide	27.12±3.82
Endosulphan I	49.43±4.61
pp-DDE	123.05±2.47
Dieldrin	25.1±3.82
Endrin	101.3±1.41
Endosulphan II	84.29±2.48
P,p'-DDD	89.43±0.62
Endrin aldehyde	105.53±1.52
pp-DDT	384.04±5.51
Endosulphan sulphate	54.97±6.07
Methoxychlor	120.06±1.05
OCs	**Overall Concentration**

Table V B: Total OC levels in water samples per sampling point in µg/L±sd

Sampling Point	**Total OCs Compounds**	**Standard deviation**
Makuyu	75.84	13.03
Sagana	84.92	10.13
Murang'a	154.22	43.79
Kirinyaga	169.76	21.14
Tetu	205.55	11.92
Karatina	240.49	13.72
Marua	321.02	29.38
Kiganjo	208.57	23.11
Hombe	89.53	13.78
Ndathi	70.01	10.94

Table V C: Temporal distribution of OCs in sediment samples in µg/kg±sd

Sampling points/time of sampling	1st (Dec., 08)	2nd (Feb., 09)	3rd (June, 09)	4th (Sept., 09)	5th (Dec., 09)	6th (Feb., 10)	7th (April., 10)	8th (Sept.,10)
Makuyu	56.43	259.66	76.45	123.76	109.76	254.34	98.34	243.23
Sagana	91.64	319.43	120.23	208.65	97.91	202.38	79.45	102.54
Murang'a	227.73	331.06	245.23	352.87	216.23	265.57	232.12	251.71
Kirinyaga	256.34	356.43	234.32	319.09	276.9	421.87	151.02	209.12
Tetu	675.45	765.43	543.98	598.78	167.77	249.6	213.87	347.92
Karatina	564.34	645.34	456.32	543.98	234.98	117.03	102.92	167.98
Marua	453.34	467.47	356.34	432.98	143.89	166.46	282.1	149.63
Kiganjo	476.45	559.25	245.08	321.9	136.31	235.65	166.24	197.09
Hombe	198.56	216.23	163.55	287.12	78.09	183.94	42.58	154.53
Ndathi	154.43	213.34	143.21	298.01	101.09	143.98	132.98	154.76

Table V D: Total of the mean concentrations of each OC compound in sediment samples in µg/kg±sd

OC compounds	Concentration
a-HCH	99.9±7.67
b-HCH	79.47±4.29
g-HCH	96.53±1.85
d-HCH	104.19±1.3
Heptachlor	137.53±1.63
Adrin	45.85±0.72
Heptachlor epoxide	121.926±3.09
Endosulphan I	202.8±3.00
pp-DDE	404.44±12.77
Dieldrin	182.38±2.82
Endrin	66.64±2.40
Endosulphan II	399.945±4.78
pp-DDD	189.22±1.56
Endrin aldehyde	613.31±14.94
pp-DDT	616n.51±8.51
Endosulphan sulphate	77.21±3.39
Methoxychlor	84.02±1.53

Table V E: Total of the mean of OCs in weed samples in µg/kg

Sampling points	**Total of the mean of OCs per site**
Makuyu	37.26
Sagana	34.23
Murang'a	45.68
Kirinyaga	43.23
Tetu	76.87
Karatina	78.98
Marua	87.65
Kiganjo	59.05
Hombe	43.98
Ndathi	13.67

Table V F: Comparison of OC in water, weed and sediment samples in µg/kg±sd

OC compound	Water samples	Sediment samples	Weed samples
a-HCH	48.2±7.02	99.9±12	22.62±17.17
b-HCH	81.56±5.28	79.47±05	3.84±2.32
g-HCH	107.32±1.29	96.53±21	37.93±19.35
-HCH	97.8±0.50	104.19±23	7.77±4.18
Heptachlor	77.8±3.50	137.53±21	5.79±5.43
Adrin	44.91±8.03	45.85±31	2.77±3.30
Heptachlor epoxide	27.12±3.82	121.92±09	26.24±21.82
Endosulphan I	49.43±4.61	202.8±12	10.89±5.43
pp-DDE	123.05±2.47	404.44±23	49.64±48.92
Dieldrin	25.1±3.82	182.38±21	3.36±2.04
Endrin	101.3±1.41	66.64±43	11.78±28.15
Endosulphan II	84.29±2.48	399.94±09	166.65±136.77
pp-DDD	89.43±0.62	189.22±05	24.73±7.09
Endrin aldehyde	105.53±1.52	613.31±34	156.36±126.16
pp-DDT	384.04±5.51	616.51±22	62.81±12.33
Endosulphan sulphate	54.97±6.07	77.21±11	4.74±2.67

Table V G: Distribution of chlorpyrifos in sediment samples in µg/kg±sd

Sites	Dec., 08	Feb.,	June, 09	Sept., 09	Dec., 09	Feb., 10	April, 10	Sept., 10	Average	Sites	Dec., 08
Makuyu	0.23	0.14	0.26	0.13	0.25	0.14	0.30	0.23	0.21	Makuyu	0.23
SD	0.02	0.03	0.05	0.02	0.07	0.04	0.03	0.04	0.04	SD	0.02
Sagana	0.46	0.15	0.65	0.06	0.20	0.04	1.16	0.15	0.36	Sagana	0.46
SD	0.02	0.02	0.05	0.03	0.06	0.01	0.32	0.03	0.07	SD	0.02
Murang'a	0.15	0.12	0.65	0.54	0.24	0.31	0.65	0.32	0.37	Murang'a	0.15
SD	0.03	0.07	0.02	0.19	0.02	0.08	0.03	0.02	0.06	SD	0.03
Kirinyaga	0.21	0.17	0.31	0.01	1.30	0.01	0.35	0.02	0.30	Kirinyaga	0.21
SD	0.04	0.01	0.02	0.01	0.19	0.01	0.02	0.01	0.04	SD	0.04
Tetu	0.65	0.54	0.87	0.65	1.10	0.77	0.43	0.77	0.72	Tetu	0.65
SD	0.03	0.09	0.08	0.08	0.15	0.12	0.02	0.05	0.08	SD	0.03
Karatina	1.13	1.03	1.43	< 0.0001	0.82	< 0.0001	0.65	0.47	0.69	Karatina	1.13
SD	0.02	0.03	0.32		0.07		0.03	0.04	0.06	SD	0.02
Marua	1.23	0.99	0.47	0.18	1.21	0.24	0.54	0.43	0.66	Marua	1.23
SD	0.01	0.02	0.05	0.01	0.08	0.05	0.13	0.09	0.05	SD	0.01
Kiganjo	1.32	0.98	1.13	0.27	0.52	0.24	0.22	0.31	0.62	Kiganjo	1.32
SD	0.03	0.07	0.12	0.05	0.23	0.04	0.03	0.07	0.08	SD	0.03
Hombe	0.23	0.13	0.35	0.15	0.82	0.21	0.28	< 0.0001	0.27	Hombe	0.23
SD	0.04	0.04	0.03	0.09	0.74	0.07	0.08		0.14	SD	0.04
Ndathi	0.02	0.01	0.10	0.08	0.02	0.06	0.04	0.02	0.04	Ndathi	0.02
SD	0.02	0.01	0.02	0.01	0.01	0.03	0.01	0.01	0.02	SD	0.02
Total of the mean	5.66	4.27	6.22	2.07	6.47	2.03	4.64	2.73	**4.26**	Total of the mean	5.66

Key:
SD- Standard deviation
BDL- Below Detection Limit

Table V H: Seasonal variations of chlorpyrifos in weed samples in µg/kg±sd

Sampling point	Long rains season	Short rains season	Dry season
Makuyu	0.45±0.33	0.32±0.09	0.20±0.03
Sagana	0.21±0.08	0.14±0.02	0.12±0.05
Murang'a	0.65±0.10	0.10±0.01	0.06±0.02
Kirinyaga	0.69±0.01	0.51±0.10	0.17±0.06
Tetu	1.45±0.31	1.21±0.13	0.92±0.07
Karatina	1.47±0.04	1.17±0.05	0.89±0.03
Marua	1.65±0.43	0.86±0.06	0.09±0.03
Kiganjo	1.19±0.03	0.63±0.19	0.28±0.05
Hombe	0.64±0.06	0.53±0.05	0.34±0.02
Ndathi	0.19±0.01	0.06±0.01	0.05±0.03

Appendix VI

Some of the Chromatograms and Spectra in the study

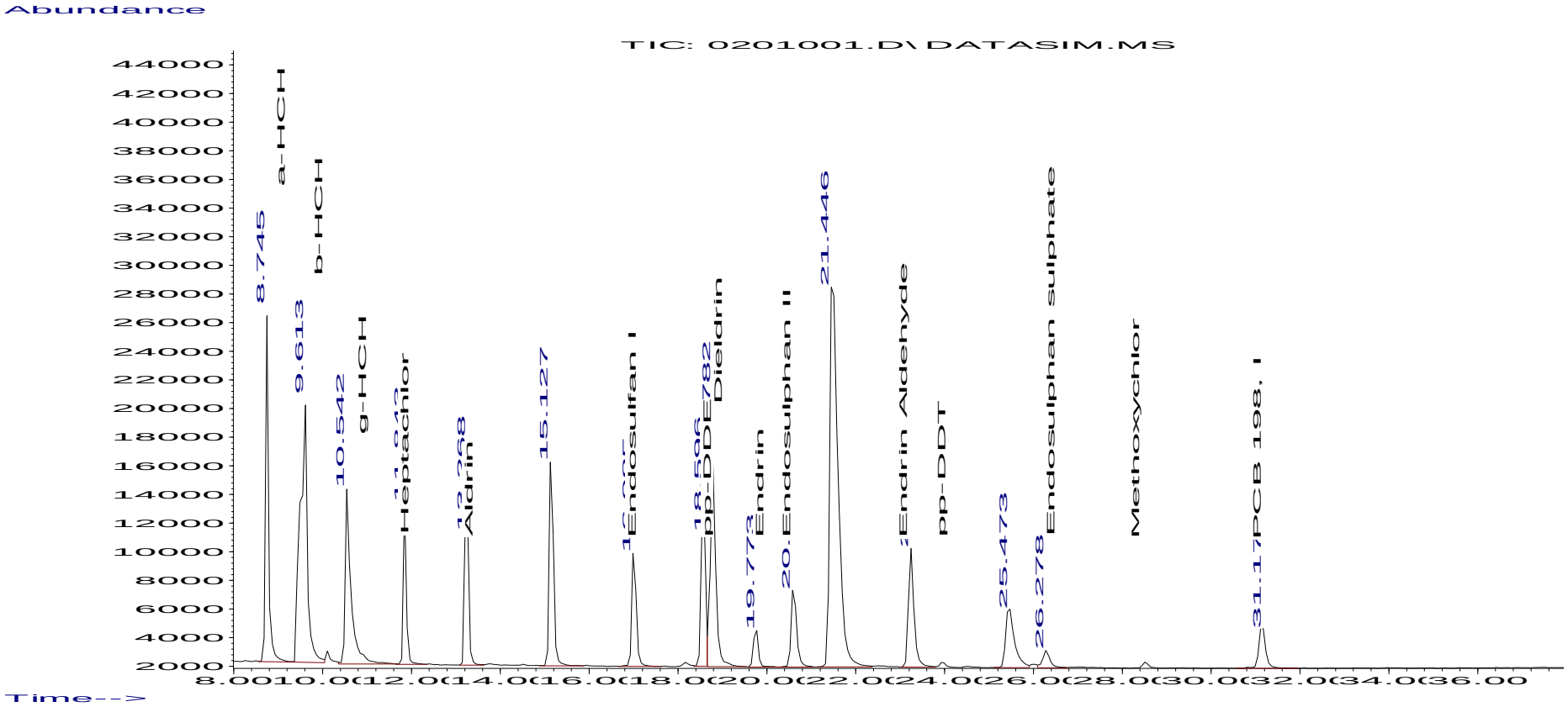


Figure VI A: Chromatogram of OC's Standards mixture using GC-MS

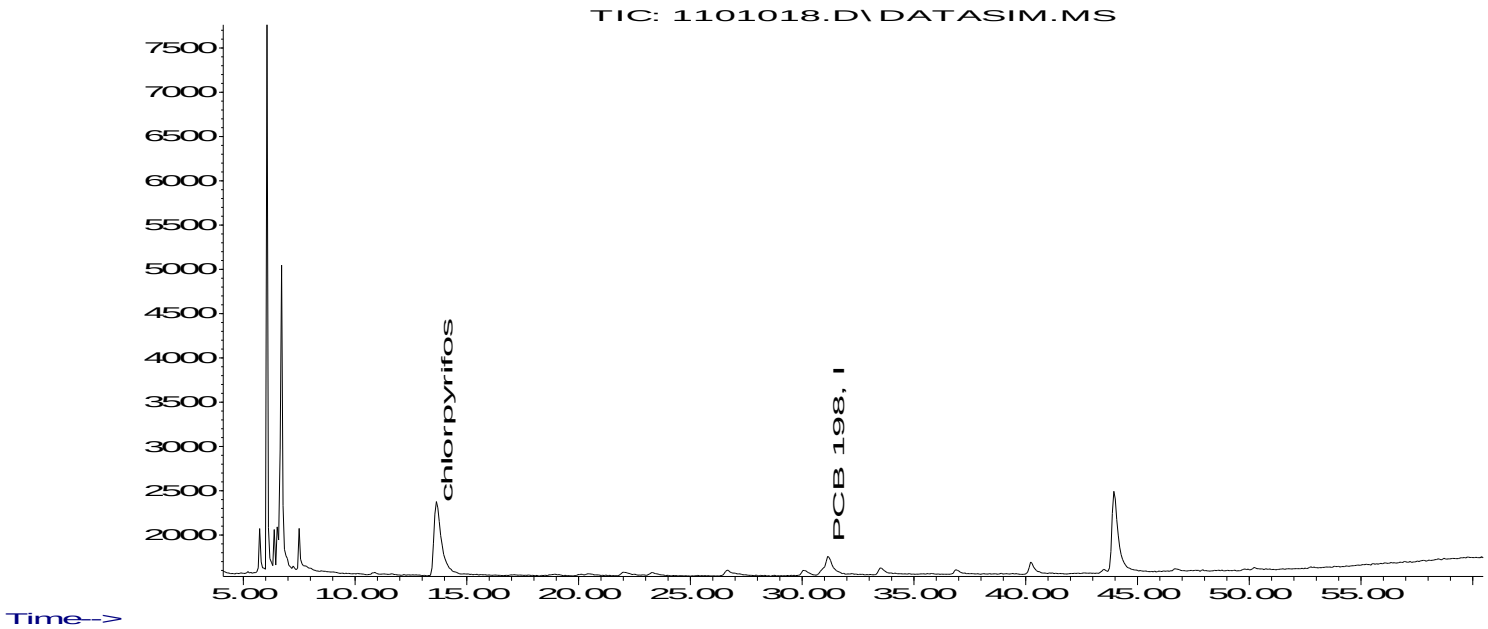


Figure VI B: Chromatogram of chlorpyrifos Standard using GC-MC

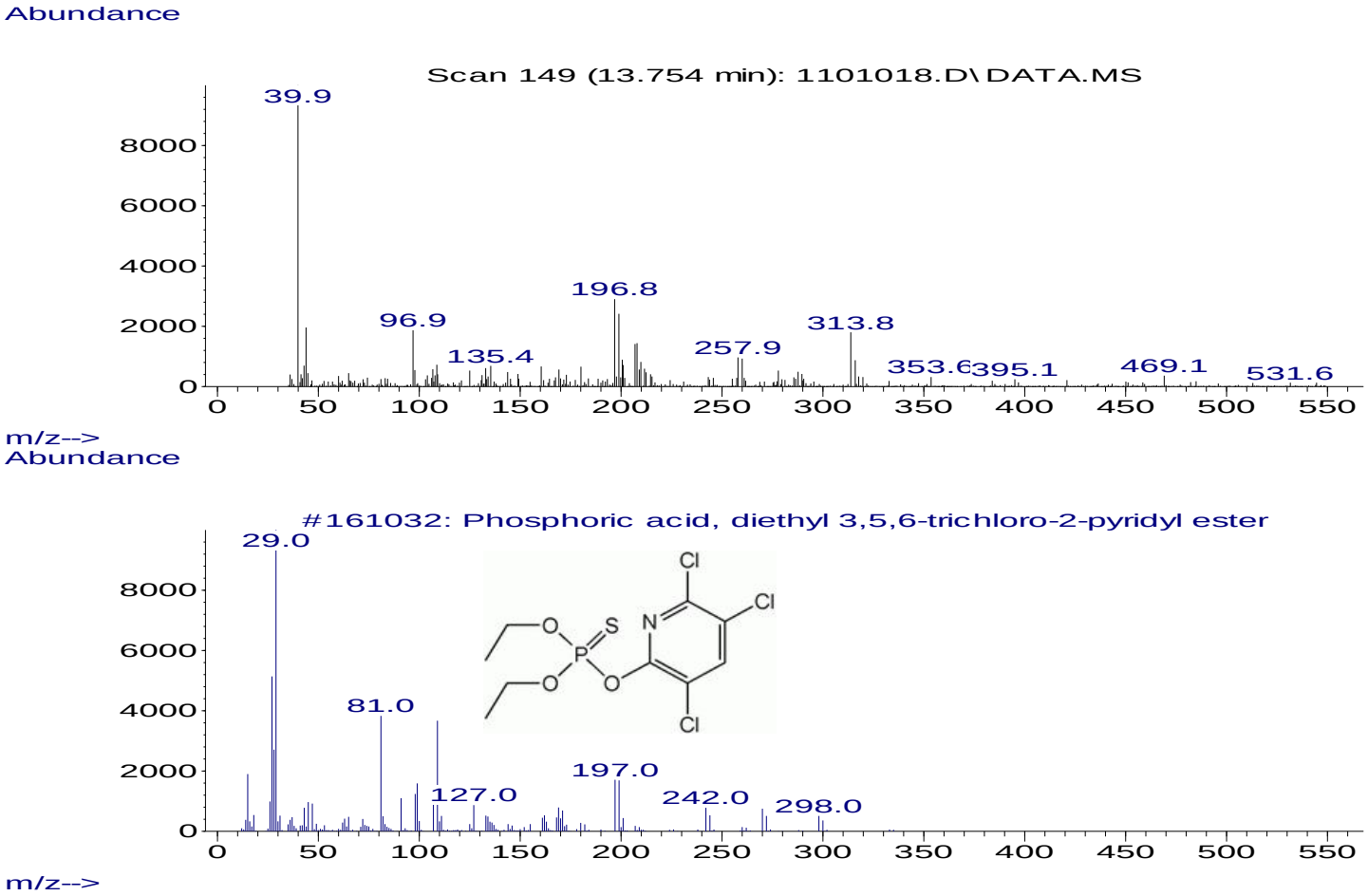


Figure VI C: The TIC and SIM of chlorpyrifos spectrum

Key: TIC- Total Ion Count; SIM- Single Ion Mode

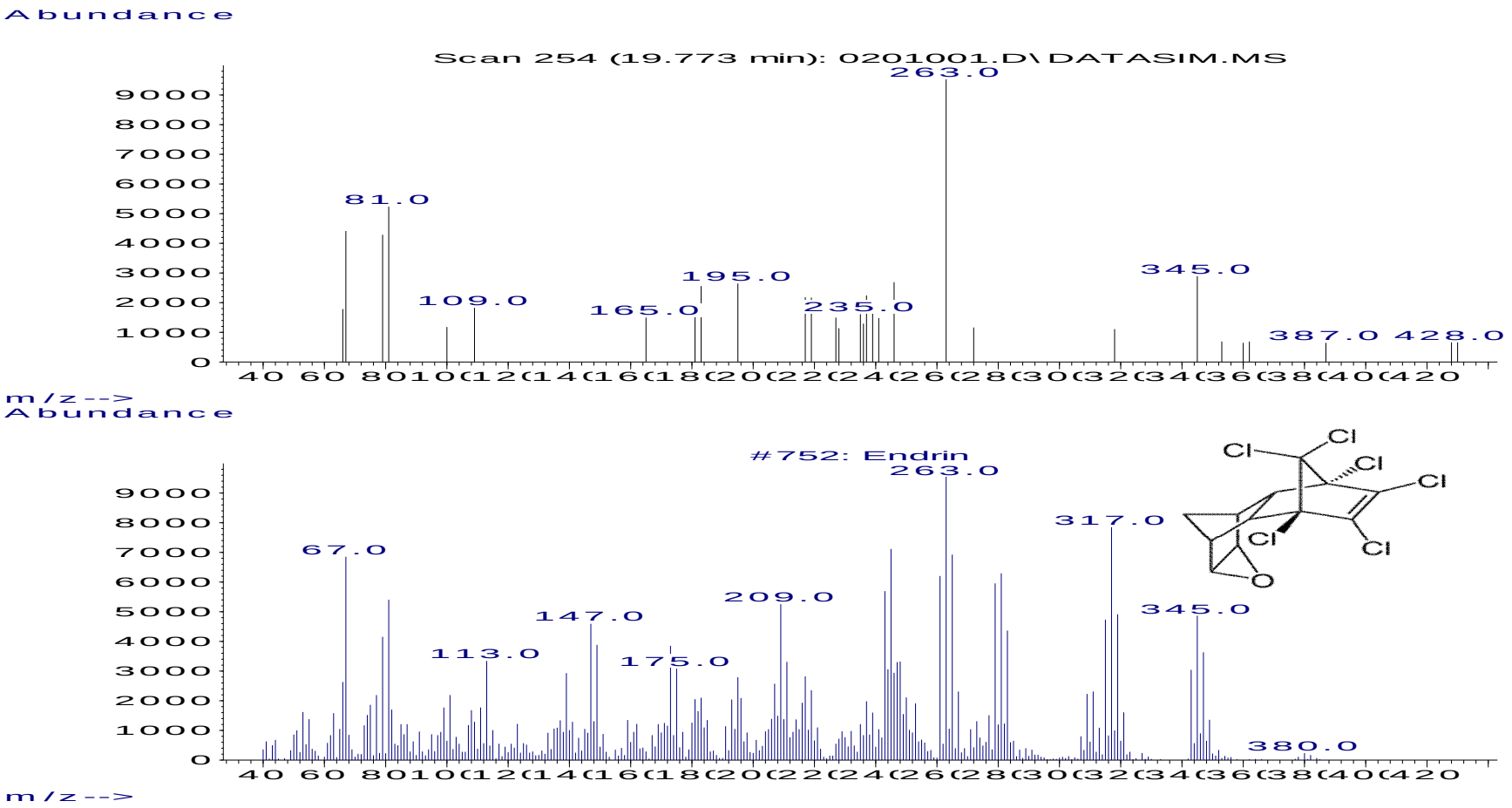


Figure VI D: The TIC and SIM of Endrin spectrum

Key: TIC- Total Ion Count; SIM- Single Ion Mode

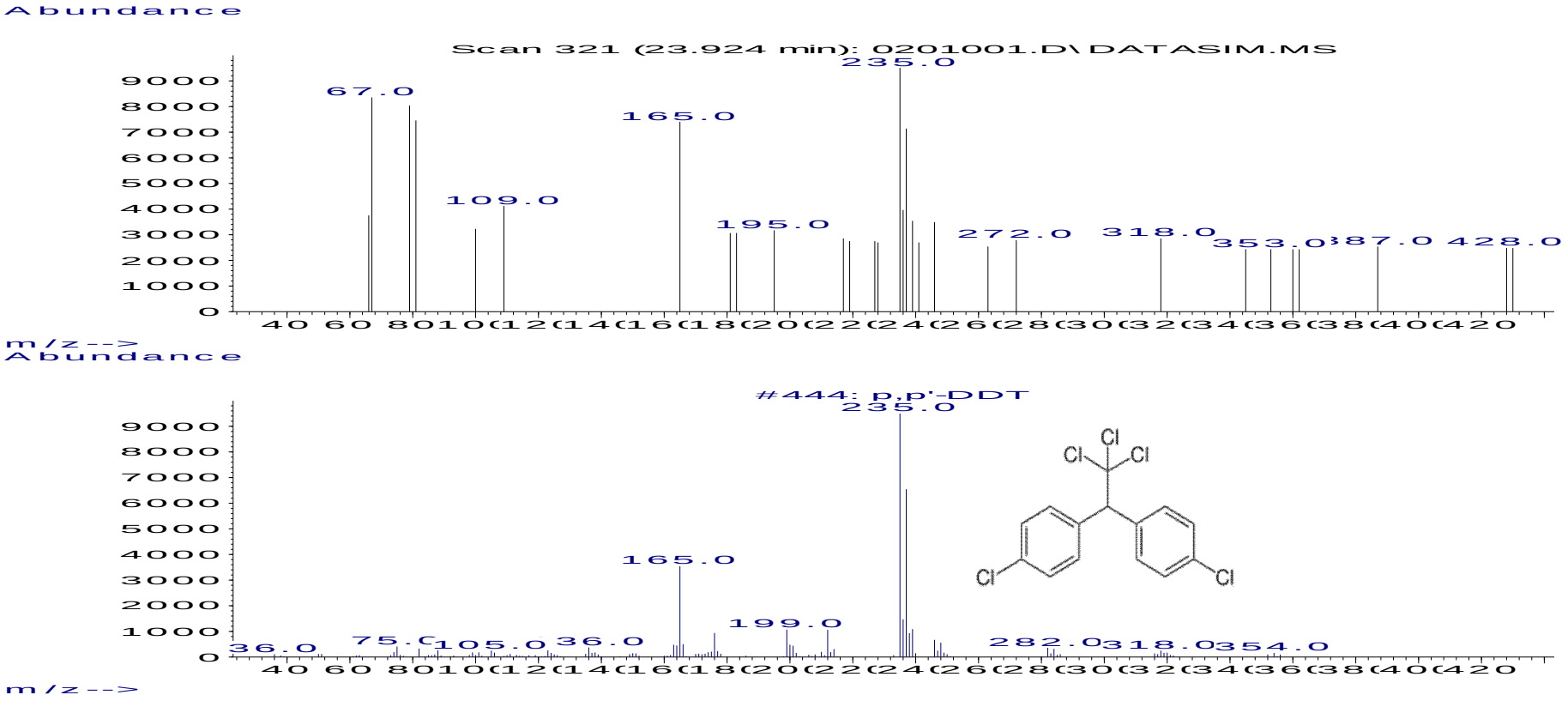


Figure VI E: The TIC and SIM of p,p'-DDT spectrum

Key: TIC- Total Ion Count; SIM- Single Ion Mode

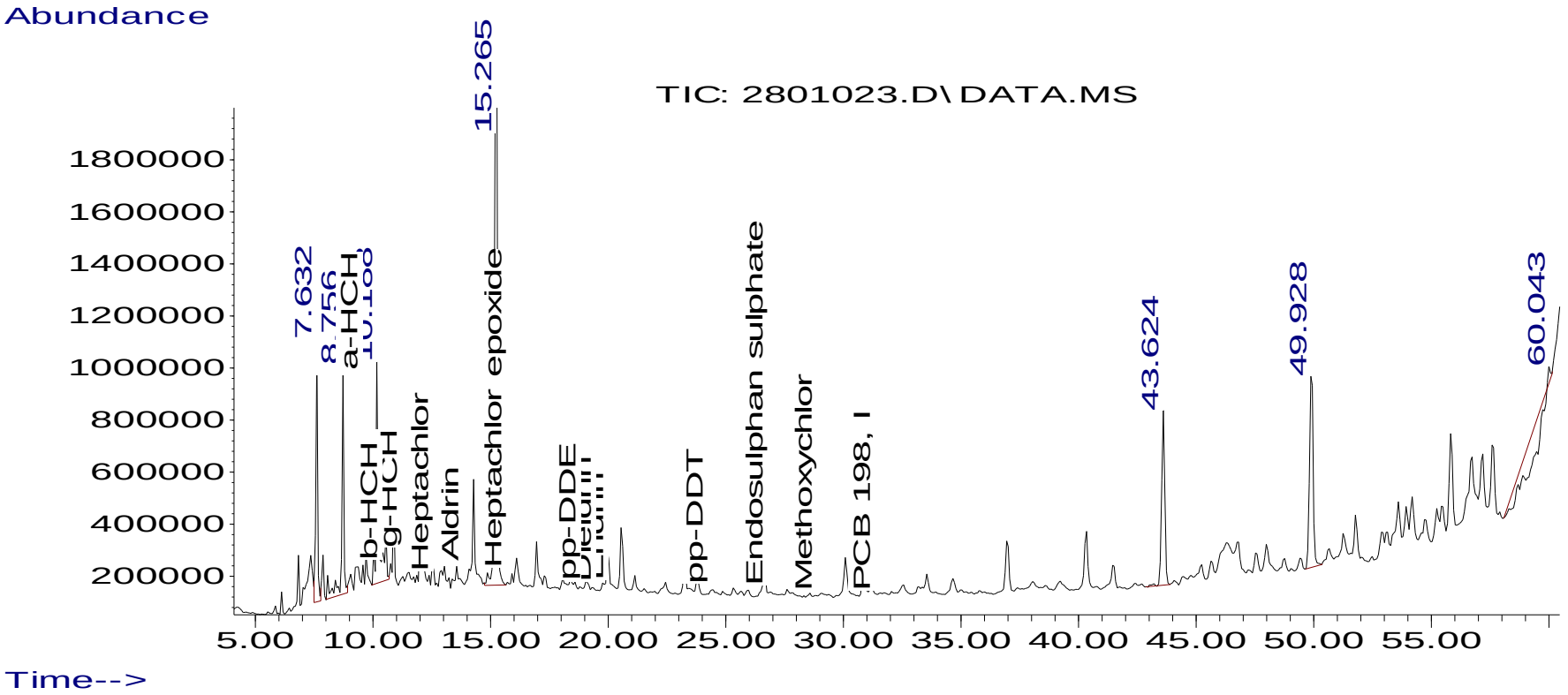


Figure VI F: OCs chromatogram of a sediment sample

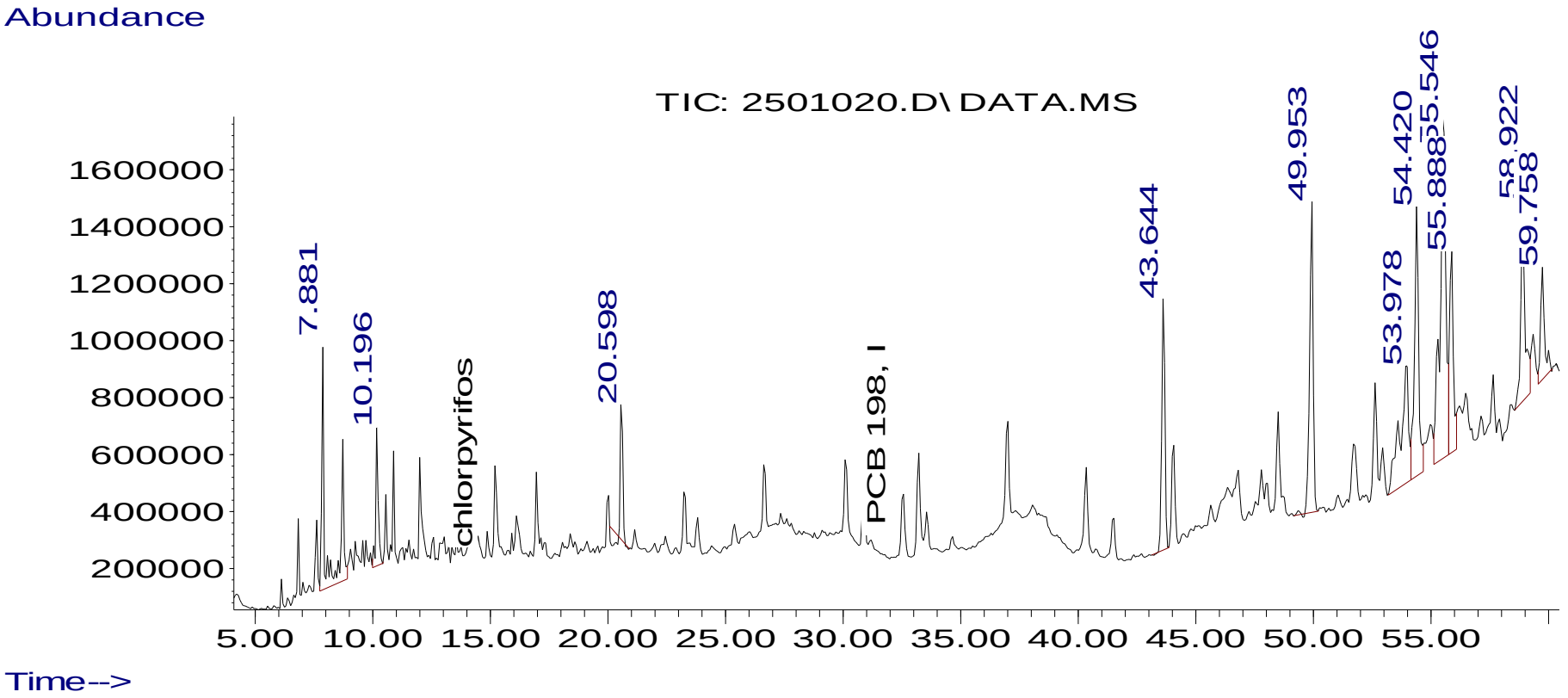


Figure VI G: Chlorpyrifos chromatogram of a sediment sample

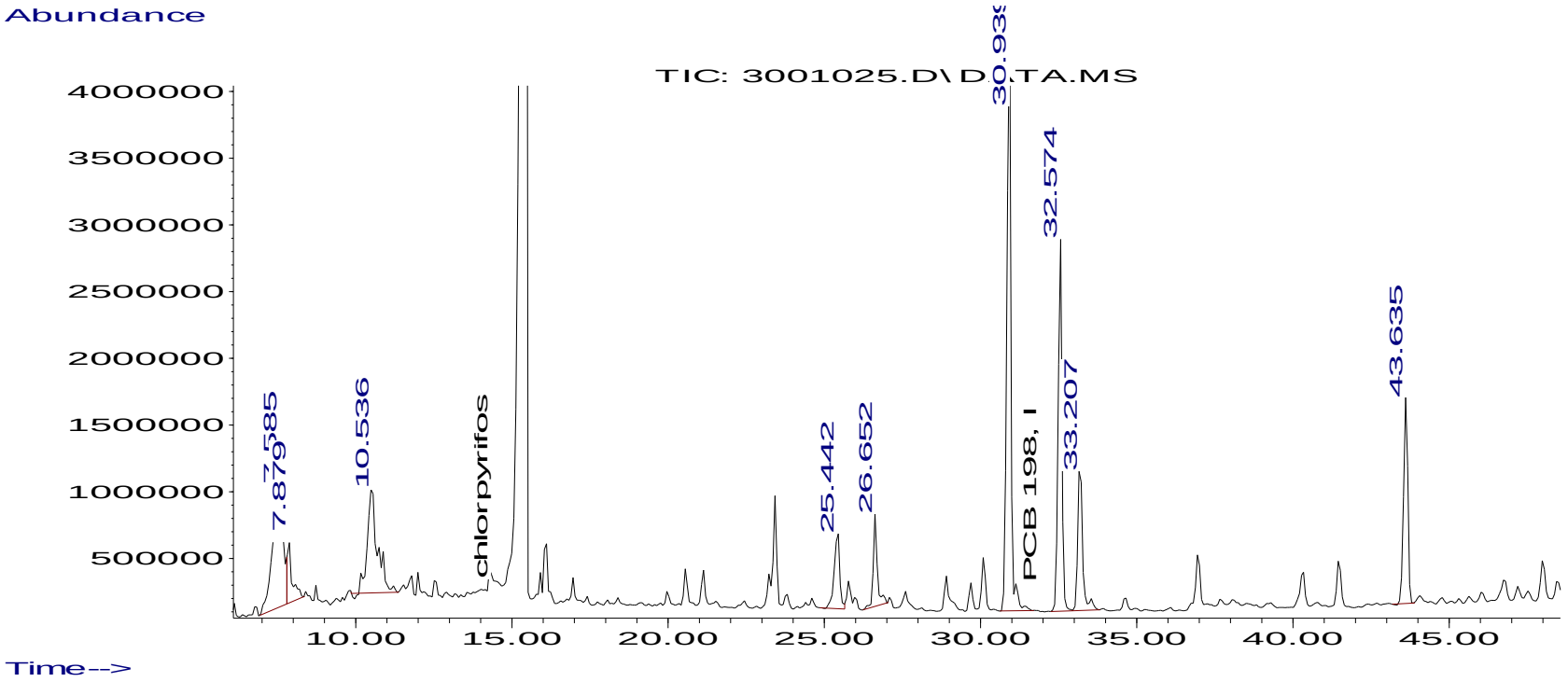


Figure VI H: Chlorpyrifos chromatogram of a water sample

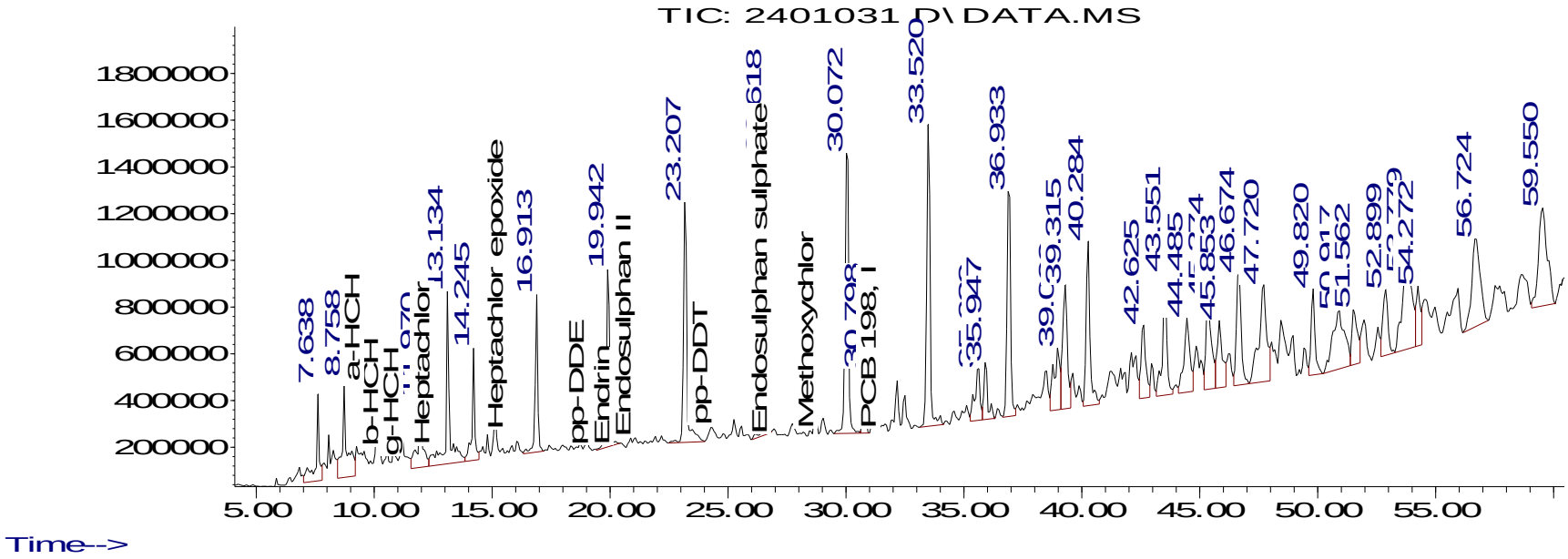


Figure VI I: OCs chromatogram of a water sample

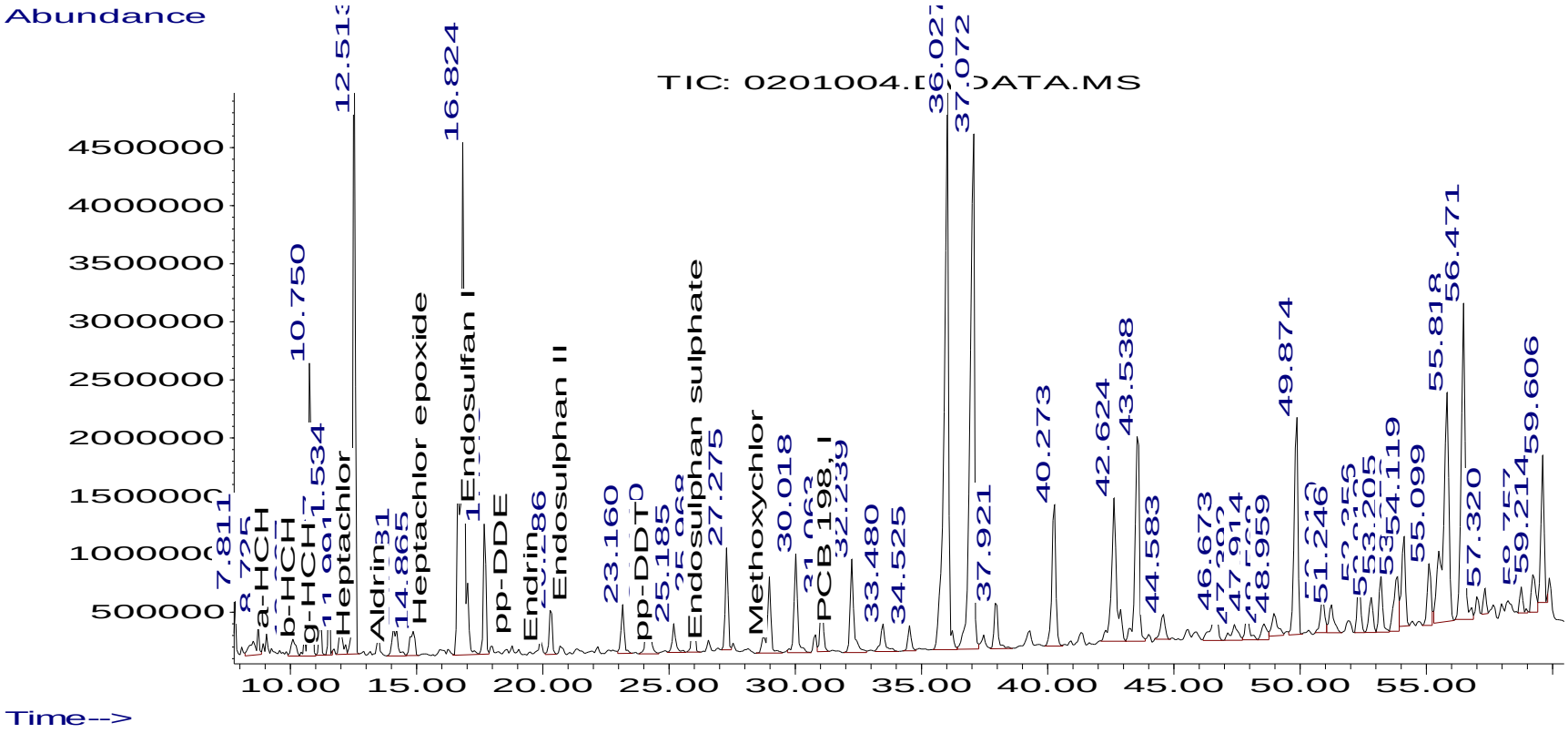


Figure VI J: OCs chromatogram of a weed sample

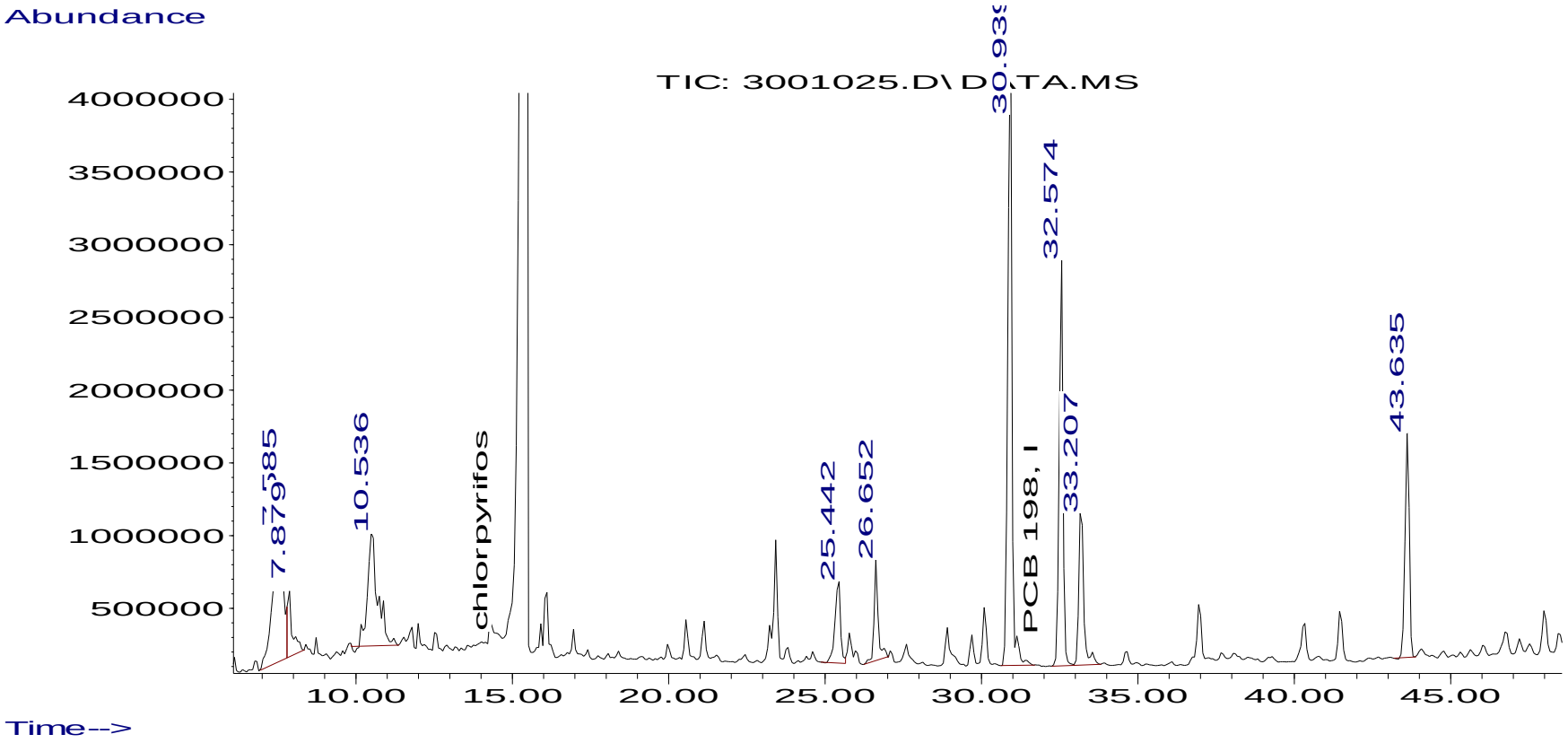


Figure VI K: Chlorpyrifos chromatogram of a weed sample

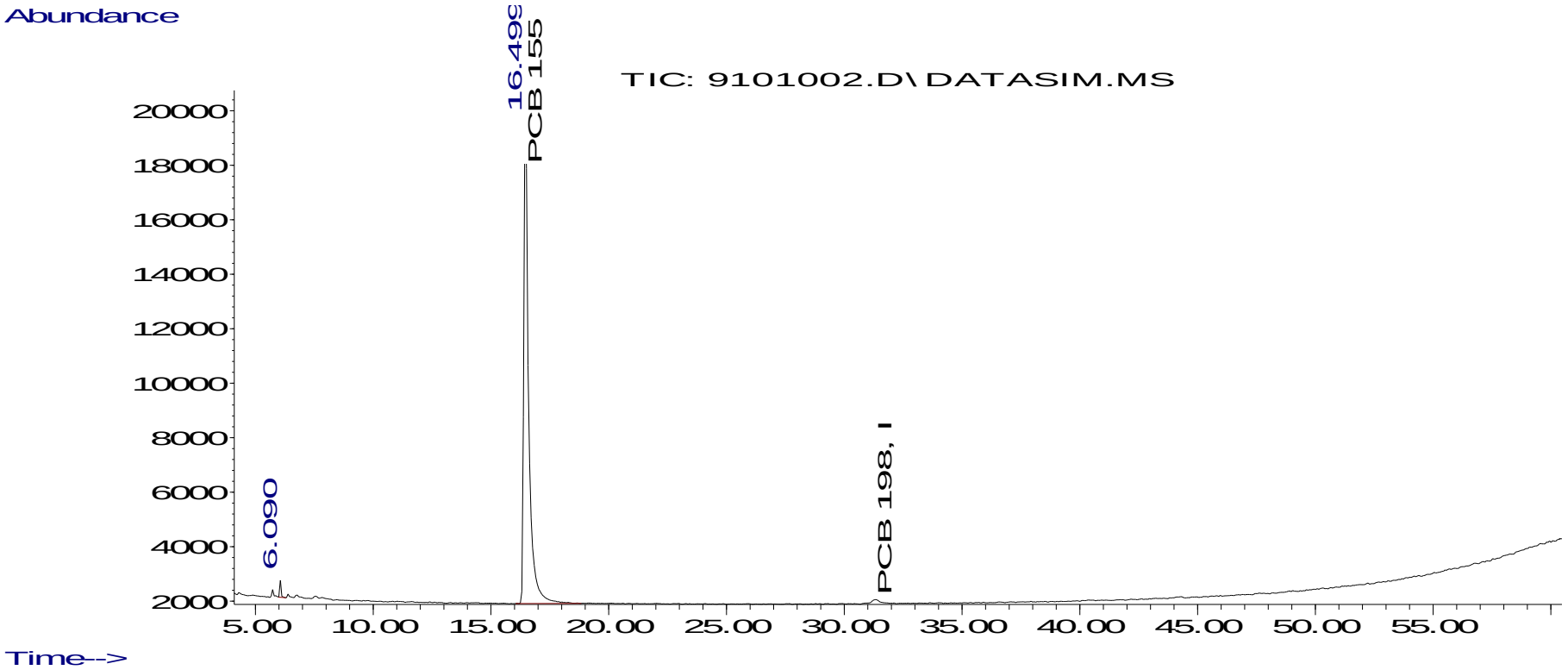


Figure VI L: PCB 155 and PCB 198 standards chromatogram