# ASSESSMENT OF SPATIAL AND TEMPERAL TRENDS OF PESTICIDE RESIDUES IN SEDIMENTS AND WATER FROM NAIROBI RIVER

**BY**

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**(I56/71225/07)**

Thesis Submitted to the Board of Postgraduate in Partial Fulfillment of the Requirements of the

Degree of Master of Science in Environmental Chemistry of the University of Nairobi

**November, 2015**

# DECLARATION

This thesis is my original work and has not been presented for a degree in any other University

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# DEDICATION

This thesis is dedicated to my lovely wife Jennifer, my daughter Myra, Parents, Brother and Sisters for their moral support.

# ACKNOWLEDGEMENT

I thank my Supervisors Prof. Shem. O. Wandiga, Prof Paul M. Shiundu and Dr. Fredrick D. O. Oduor of the Department of Chemistry University of Nairobi for their continual guidance, support and encouragement during the period of the study. I wish to express my gratitude to KEPHIS for granting me time off and allowing me to use their GC-MS for the sample analysis.

Further acknowledgment goes to the teaching and non-teaching staff of the University of Nairobi and fellow researchers. Special recognition to Nicholas Mwenda for the assistance he provided when sampling and continued moral support during the research, many thanks to Nusrat, Edna, Madadi, Ooko, Florence, Elizabeth, Dorice, Wanyama who greatly assisted with the technical information that enabled completion of the project. I would also like to acknowledge Abraham Lagat for his help in statistical analysis of data.

My deepest gratitude goes to my entire family for their support, encouragement and understanding throughout the course of my study.

# ABSTRACT

The Nairobi River water is laden with pollutants which emanate from industrial and municipal effluents discharged directly into the river. In the catchment area, riparian agricultural activities and large scale farms contribute to chemical load in the river. The water pollution brings both environmental and health risks to the direct users of the river especially the urban dwellers that use it for irrigation, domestic use, watering animals and in worst case scenario for drinking.

This study was conducted to establish temporal and spatial distribution of the 16 OC and 14 OP pesticides in water and sediment samples from selected sites along the Nairobi River. In addition physicochemical parameters (TSS, TOC, EC, TDS and pH) were determined and correlated with pesticide concentrations. A total of 144 samples comprising of 72 sediment and 72 water samples were collected for six times over a period of six months. The extraction was done using Soxhlet extraction and Liquid-Liquid partitioning techniques and cleaned up using deactivated florisil. The extracts were analysed with Agilent 6890 Gas chromatograph coupled with a 5890 Mass spectrometer system. The statistical data was analysed using Microsoft Excel and Statistical Package for Social Sciences (SPSS). The seasonal pesticide concentrations in sediments ranged between 0.88 to 1385µg/kg and 0.68 to 1984.03 µg/kg for OC and OP pesticides, respectively. p,p’ DDT and a-HCH were dominant and constituted 25% and 11% of the OC pesticides, respectively. The highest average concentrations for p,p’ DDT and a-HCH were recorded at Naivasha Bridge and Muthangari Bridge respectively. Malathion and Chlorpyrifos had the highest average concentrations amongst the OP pesticides at 38% and 27% respectively both recorded at Muthangari Bridge. Muthangari Bridge recorded the highest concentrations of ∑OCP and ∑OPP at 5025.47 µg/kg and 3611.97 µg/kg respectively. ∑OCP were dominant compared to ∑OPP and constituted 58% of total pesticides detected. In water samples OC pesticides concentrations ranged between 0.02 to 31.79 µg/L, p,p’-DDT and Endrin were dominant and constituted 8% of total OC pesticides, Outering Bridge recorded the highest concentrations of the two pesticides The OP pesticides concentrations ranged between 0.01 to 44.99 µg/L. Ethoprophos recorded the highest average concentration of 19.21 µg/L at Outering Bridge and constituted 58% of total OP pesticides. Outering Bridge recorded the highest ∑OCP and ∑OPP concentrations at 114.19 µg/L and 116.82 µg/L respectively. Positive Pearson correlation coefficients were observed between pesticides, TDS and TSS. A comparison of ∑16 OCP, TSS and TDS in water gave values of 0.485 and 0.424 for TDS and TSS respectively. Similar comparison with ∑OPP gave p values of 0.145 and 0.818 for TDS and TSS respectively. Inter matrix Pearson correlations between ∑16 OCPS and ∑14 OPPS were stronger for sediments which had a p value of 0.905 compared to water, p=0.747.

Fifty six percent of the Nairobi river water samples exceeded the pesticide limit (OC and OP pesticides) of 0.5µg/l in drinking water as set by EC directive 98/83/EC. Comparatively in water the ∑OPPS exceeded ∑OCPS by 1.1 times, signifying higher solubility’s of OP pesticides in river water. This implied that use of Nairobi river water for irrigation and drinking purposes could pose health risks from OP pesticide poisoning to communities that depend on it. The data from this study may form a basis for policy formulation by regulatory authorities.

# ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| NRBP | Nairobi River Basin Programme |
| OPs | Organophosphates |
| OCs | Organochlorines |
| GC-ECD | Gas Chromatography Electron Capture detector |
| GC MS | Gas Chromatograph Mass Spectrometer |
| USEPA | United States Environment Protection Authority |
| POPS | Persistent Organic Pollutants |
| EMCA | Environmental Management Coordination Act |
| UNEP | United Nations Environment Programme |
| DDT | Dichlorodiphenyltrichloroethane |
| DCM | Dichloromethane |
| DDD | Dichlorodiphenyldichloroethylene |
| DDE | Dichlorodiphenyldichloroethylene |
| EPA | Environmental Protection Agency |
| KEPHIS | Kenya Plant Health Inspectorate Service |
| PCPB | Pest Control Products Board |
| SPSS | Statistical Package for Social Scientist |
| ADMIS | Automated Mass Spectral Deconvolution and Identifcation System |
| NIST 05 | National Institute of Standards |
| RTL PEST | RetentionTime Locking Pesticides Database |
| EU | European Union |
| ∑OPP | Total Organophosphates |
| ∑OCP | Total Organochlorines |
| EC | European Commission |

# UNITS OF MEASUREMENT

| | |
|---|---|
| µS | Micro Siemens |
| ppm | Parts per million |
| ppb | Parts per billion |
| ng | Nanogram |
| nm | Nanometre |
| ml | Millilitre |
| µg | Microgram |
| L | Litre |
| $^{o}$C | Degree Celsius |
| g | Gram |
| Kg | Kilogram |
| µl | Microlitre |
| M | Molar |

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# CHAPTER ONE

## INTRODUCTION

### 1.1 Background Information

Nairobi name comes from the Maasai phrase “enkare Nairobi” which means a “place of cool waters”. It originated as the headquarters of Kenya Uganda Railway established when the railhead reached Nairobi in 1899. The city grew into British East African commercial and business hub and by 1907 became the capital city of Kenya (Mitullab 2003, Rakodi 2007). It is the most populous city of East Africa with a current population of 3.1Million projected to reach 3.8 Million by 2015 according to the national census report (KNBS, 2008).

The city occupies an area of 700km2 at the South Eastern end of Kenya’s agricultural heartland. The western end of the city is the highest with a rugged topography while the eastern side is lower and generally flat. At an altitude of 1600 to 1850 m above sea level it enjoys tolerable temperatures year round (CBS, 2001, Mitullah 2003). The capital city has temperate climate moderated by the altitude, the hot seasons are sunny and warm while the cold seasons are cool with the mean daily temperatures ranging between 12°C and 26°C (CBS, 2001). The rainy months are between April and May and between November and December with an average annual rainfall of 1000mm. The dry months are between June and September and January and March.

Agriculture accounts for about 24% of Kenya’s GDP with an estimated 75% of the population depending on the sector either directly or indirectly. Much of the intermittent strength and overall weakness in GDP and income growth in Kenya can be attributed to changes in agricultural performance. As an agricultural economy, Kenya’s demand for pesticides is relatively high. The import demand is further fuelled by regional consumption in land locked countries like Uganda, Rwanda and Burundi. Kenya imports approximately 7,000 metric tonnes of pesticides worth billions of Kenya shillings (US$ 50 million), (PCPB, 2005). These pesticides are an assortment of insecticides, fungicides, herbicides fumigants, rodenticides, growth regulators, defoliators, proteins, surfactants and wetting agents. Of the total pesticide imports, insecticides account for about 40% in terms of volume (2,881 metric tonnes) and 53% of the total cost of pesticide imports (PCPB, 2005).

The risks of using pesticides are serious (Pimentel, 2009b). Most of them are highly toxic to humans and the environment. Pesticides and their metabolites flow into the atmosphere, soils and rivers, resulting in the accumulation of toxic substances and thus threatening human health and the environment.

Contamination of river water by pesticides arises primarily from their application. Surface water contamination can occur as a result of spray drift from aerial spraying or runoff from agricultural areas as a consequence of rain and to a lesser extent, leaching from the soil and wind dynamics. Hence runoff water contains dissolved pesticides residues as well as chemicals sorbed onto particulate matter. Contamination of river water by pesticides can also arise from accidental or intentional discharges of pesticides and pesticide waste and rinses from mixing areas (on farm) and from manufacturing plants. Pesticide concentrations tend to be higher in small catchments with intensive agriculture and when older spraying equipment is used (Fischer et al., 1998).

Pesticides can also be transported sorbed on airborne particulates and then washed into aquatic environment by rainfall. Pesticides applied on fields have been known to volatilize and be deposited in areas far from the point of application. Volatile pesticides have been observed to dissipate more rapidly in tropical agro-systems because of high temperature associated with this region. Several studies involving volatile organochlorines insecticides such as DDT and HCH have shown volatilization to be a major route of dissipation of these chemicals from tropical agro-ecosystems and other tropical environments (Abdullah et al., 1997).

Once in the aquatic environment, either through runoff, direct application or atmospheric fallout pesticides undergo a number of interactions with all the components of the system. They interact with suspended matter in water, sediments and in organisms (Warren et al., 2003).The nature of interactions with the suspended matter and sediments depend on the solubility of the pesticide and characteristics of the sediments such as organic content and hence humic material show increased tendencies to sorb pesticides. Natural sorbents, like sediments, can indirectly control processes in the water phase by release or uptake of pesticides. Hence, natural sorbents form buffers that influence the reactivity of pesticides in a considerable way (Warren et al., 2003).

A pesticide in the aquatic environment is also subject to accumulation in aquatic environment and degradation by biotic and abiotic factors. Aquatic organisms take up pesticides from the surrounding water by passive diffusion through the gill, epithelial tissues or gastrointestinal tract (Huckle and Millburn, 1990).

The Kikuyu wetlands, Ngong and Thogoto forests are the major sources of the Nairobi River Basin. They support a diverse and rich assemblage of biodiversity. They are important water catchments areas and have other environmental, socioeconomic and cultural benefits to the rural communities living around these areas.

## 1.2 Problem Statement

Fifty percent of the population in Nairobi live in low income areas and live below poverty line, earning less than one US dollar per day (MPND, 2003). As a way of securing self employment and income generation, about 150,000 households are involved in urban agriculture where 94% of them depend wholly on farming (Foeken and Mwangi, 2000).

Further studies on urban agriculture by Memon and Smith, (1996) showed that land used for agriculture was 32% private residential land, 29% roadside land, 16% along river banks, and 16% in other publicly owned areas.

The pressure to increase agricultural production for subsistence and economic purposes leads to enhanced use of pesticides by farmers to protect crops against pests and diseases. However, lack of awareness on the hazardous effects of these chemicals by many farmers has led into improper use thus leading to environmental contamination. The upperparts of Nairobi River are dominated by riparian agriculture with farmers encroaching the river banks for vegetable growing; mid stream major flower companies like Magana exploit the river water for irrigation. Light industries including cottage agrochemical firms are scattered along the river at Eastleigh, Kimathi, Jerusalem and Jericho and discharge effluent into the river waters. This has consequently lead to heavy pollution and adverse effects to communities relying on this water. The concern for the quality of the Nairobi river water has therefore contributed to the interest in the current study.

## 1.3 Justification of the Study

Scanty information is available on organochlorines and organophosphate pesticides in Nairobi River. A review of Nairobi river data from past studies indicate that Malathion, Ridomil, Ambush, Lindane and p,p’-DDT were reported between 1992 and 1996. Grace (1996) reported that 2 distinct groups of organochlorines were detected in the upper parts of the Nairobi River from the source (Ondiri swamp) to the sampling points at the Naivasha road bridge and again at the lower parts after the sewage works at Dandora. These were p,p’-DDE, p,p’-DDD, o,p’-DDT, o,p'-DDD and Lindane. Shadrack (1992) reported DDT, 0.000086 mg/l, Malathion 0.00039mg/l, Ambush 0.1413mg/l and Ridomil 0.147mg/l in river water. However, no data was reported for residues in sediments.

Lack of current data on pesticides in Nairobi River is serious given the heavy agricultural activities in the catchments and therefore this study seeks to collect data on the extent of contamination levels of organochlorine and organophosphate pesticides in Nairobi river water and sediments.

### 1.4 Overall objective

To determine the extent of organochlorine and organophosphate pesticide pollution in water and sediments in the Nairobi River.

### 1.5 Specific objectives

1. To identify and quantify organochlorine and organophosphate pesticides in Nairobi river water and sediments.
2. To determine temporal and spatial variations of Organochlorine and organophosphate pesticides in Nairobi river water and sediments.
3. To determine physicochemical parameters (*pH, EC, TDS, TSS, TOC)* in Nairobi river water and sediments.
4. To correlate physicochemical parameters and pesticide residues in the Nairobi River water and sediments.

# CHAPTER TWO

## LITERATURE REVIEW

### 2.1 Global Pesticides Use

Worldwide pesticide application dates back to around 1940s when DDT was accidentally discovered to be an insect killer. Synthesis of other organo chlorine pesticides followed in quick succession. Today several organochlorine pesticides have been or are in use and include DDT, Lindane, Dieldrin, Aldrin, Endrin, Endosulfan and Heptachlor.

For the last few years, the pesticides market has grown considerably. Worldwide trading figures for chemicals was valued at 1,700 billion Euros in the year 2000 (Bruno, 2006). In the USA, the use of pesticides has doubled from 1960 to 1980 but the total use has remained stable or fallen. In 1999, 2.6 million tonnes of active ingredients were used. Most pesticides are used in agriculture but in 1999 about 74% of households in the USA were reported to use at least one pesticide in the home (USEPA 1998-1999).

Pesticide use has increased worldwide to secure the food supply of the swelling global population. Especially in tropical regions, agricultural intensification has led to higher pesticide consumption (Racke et al., 1997).

According to UNEP (1985), 2-3 million tonnes of pesticides products are scattered all over the environment each year in an attempt to control pests and diseases. Although this results in the consumer having better supply of food, inappropriate and or excessive use of pesticides has various undesirable side effects regarding the environment and human health.

## 2.2 Pesticide Use in Kenya.

The control of the general use and handling of pesticides in Kenya traces its way back to the colonial era. Acaricides with varying application rates, residual action periods, stripping rates, stability were among the first pesticides introduced to combat disease vectors (Keating, 1983).

Sodium Arsenate was the only acaricide in use in Kenya between 1912 and 1949 for vector control of serious livestock diseases such as East Coast Fever whereas Benzene Hexachloride (BHC) and Hexachlorocychlohexane (HCH) were introduced in 1949 (Keating 1983)

The development of tick strains resistant to Arsenic and HCH led to increased use of toxaphene, a chlorinated camphene which was introduced in 1950 (Keating, 1983) pp -DDT and Dieldrin were introduced in 1956 and 1961 respectively. Other compounds used in the 1950s included dinitrocresol (DNC) and organophosphate compounds such as dioxathion, coumophos, TEPP (Tetraethyl Pyrophosphate) and Schradon. However due to the development of tick resistance the organochlorine acaricides were banned in 1976 (Keating, 1983).

Organophosphate (OPs) compounds were introduced in 1959 (Keating, 1983). The OPs were used in combination with arsenic, HCH, and Toxaphene. The acaricides still in use in Kenya include Carbaryls, Quatifos, Chlorfenviphos, Coumaphos and formamidines. Three major areas of pesticide use in Africa have been and still remain agriculture, livestock development, and human health (Wandiga, 2001).

Between the year 2005 and 2006 approximately 7708 metric tonnes of pesticides with a value of Kshs 4.5 billion were imported into the country. The major active substances involved were Glyphosate, 1,3-dichloropropene, Amitraz, Mancozeb, Imiprothrin, D’allethrin, Chlorothalonil, Copper hydroxide, Cuprous Oxide, Dimethoate, Metolachlor+Atrazine; Sulphur, Diazinon, Methyl Bromide, Deltamethrin, 2, 4-D Amine and Cobox in order of decreasing volume. The table 1 below shows a summary of quantity and value of imports in 2005/2006 financial year (PCPB, 2006).

Table 1: Quantities and values of the various pesticide groups imported 2005/2006

|  | 2003/2004 |  | 2004/2005 |  | 2005/2006 |  |
|---|---|---|---|---|---|---|
| Category | *Quantity in tones* | *Value in '000 000'Kshs* | *Quantity in tones* | *Value in '000 000'Kshs* | *Quantity in tones* | *Value in '000 000'Kshs* |
| Insecticide | 2465 | 2411 | 2881 | 2077 | 2844 | 2,031 |
| Fungicide | 1657 | 925 | 2031 | 1113 | 2361 | 1,506 |
| Herbicide | 1396 | 571 | 1538 | 650 | 1311 | 620 |
| *Others | 723 | 142 | 597 | 133 | 1192 | 337 |
| TOTAL | 6241 | 4049 | 7047 | 3973 | 7708 | 4,494 |

Source: Pest Control Products Board Annual Report July 2005 to June 2006

## 2.3 Pesticide Regulations in Kenya

The earliest recorded legislation dates from 6th September 1921 when the Public Health Act Cap 242 was passed by the colonial government. 16 years later a second Act of parliament dealing with cattle cleansing Cap 358 was passed on 27th April 1937.

The most comprehensive law regulating pesticides is the Pest Control Products Act which came into law on 19th May 1983. It was established to regulate the importation, exportation, manufacture and distribution of products used for the control of pests and of organic function of pesticides in plants and animals (Wandiga et al., 2003).

Environmental Management Coordination Act (EMCA, 1999), sections 94 to 100 offer national guidelines for safe use and handling of pesticides in Kenya.

## 2.4 Pesticide Processes in Rivers

From large-scale studies that have monitored herbicide losses to surface water it can be concluded that, on average, less than 2% of the total mass applied within large catchments is ultimately lost to surface waters and that losses occur primarily during and right after the application period (Capel et al. 2001). Furthermore, such studies show that weather conditions, soil type, land use, intrinsic properties of the compound, as well as point sources are crucial factors influencing the overall herbicide loss from a watershed (Kreuger, 1998; Capel et al., 2001).

Kreuger and Tornqvist (1998), Neumann et al.,(2002) and Tesfamichael and Kaluarachchi (2006) found that the amount applied in the catchment region is more important than the octanol–water partition coefficient $K_{ow}$, in influencing the load of pesticides occurring in the river for all pesticide classes considered.

Natural sorbents, like sediments, can indirectly control processes in the water phase by release or uptake of pesticides. Hence, natural sorbents form buffers that influence the reactivity of pesticides in a considerable way.

For hydrophobic organic substances and for soils and sediments with a total organic carbon content higher than 0.1%, it is has been proven that the content of natural organic carbon is the dominant sorbent (Karickhoff, 1984; Ying and Williams, 2000; Chefetz et al., 2004). Sorption is often described by a constant normalized for the organic carbon content $K_{OC}$ (Karickhoff, 1984; Warren et al., 2003).

While pH seems to have little influence on sorption of chlorinated hydrocarbons, it does have a marked effect on pesticides containing acidic functional groups (Hassett et al., 1975). For sediments with low organic carbon content, the sorption of polar compounds (acids/bases) is proportional to the cation exchange capacity, to the sediment specific surface and to pH (Rae et al., 1998; Madsen et al., 2000; Ertli et al., 2004; Weber et al., 2004).

The pesticide that is associated with suspended material eventually enters the sediment. In the sediment it may be re-released into the water, taken up by organisms, degraded by microorganisms or simply buried. In natural systems, the pathways and rates of microbial degradation will depend on type of substrate, temperature, oxygen availability, nutrient supply, similarity of the compound to other food sources, previous exposure to the compound or similar ones and previous environmental conditions which controls the current population make-up (Warren et al., 2003). In the sediment, many types of compounds degrade more slowly below the oxic zone of bed-sediment and may therefore be persistent once buried (Warren et al., 2003).

The movement of these pesticides across the biological membrane is influenced by various parameters which include the lipid and water solubility, degree of ionization, chemical stability and the molecular shape of the chemical. The rate of movement is also influenced by the metabolic activity of aquatic organisms and indirectly by factors such as water, temperature, pH, salinity, hardness and presence of other chemicals. The compound taken up from water either through the external body surface or from the gut wall distributes into various organs of the body with the circulatory fluid or blood.

During distribution, the pesticide is subject to deposition in fatty tissues, transformation and excretion. The extent to which a compound will accumulate in organism at a given time is therefore determined by the competing processes such as uptake, distribution, metabolism and excretion (Huckle and Millburn, 1990).

## 2.5 Pesticides in Fresh Water and Estuarine Ecosystems

Global studies of pesticide contamination of runoff and stream water reveals presence of pesticides in the aquatic environment. The first and second order streams, Brown and Horquets respectively, which are located in the main area of soybean production in Argentina, were examined for insecticide contamination caused by runoff from nearby soybean fields. The insecticides most widely used in Argentina (Chlorpyrifos, Cypermethrin and Endosulfan) were detected in sediments suspended particles and water.

The highest concentration in suspended particles was 318 ug/kg for endosulfan in the stream Horqueta, while 226 ug/kg Chlorpyrifos, and 13.2 ug/kg cypermethrin were measured in the stream Brown. The highest Chlorpyrifos concentration in flood water was 0.45 ug/L in Brown stream. However endosulfan was not detected in the water phase. In runoff water the highest concentration measured were 0.3 ug/L for cypermethrin in Brown stream (Jergentz et al, 2005). The occurrence of OCPs was studied in the surface waters of Northern Turkey for a period of three seasons in 1999. The levels of pesticide residues found ranged widely, from 0.0003 µg /l to 0.2505 µg/ l for OCPs (Geyikçi et al, 2009)

A review of research activities in Kenya indicates prevalence of pesticide residues in water. The study on pesticide residues in rivers Nzoia and Sio reported p,p'-DDT, o,p'-DDE, p,p'-DDD, µ-α-γ-ß-HCH, aldrin, dieldrin, endrin, α- ß- endosulfan sulphate, heptachlor epoxide, ethyl parathion, Malathion, Fenitrothion, Dimethoate and Diazinon (Madadi, 2005; Madadi et al., 2006). The residue levels ranged from <0.002-0.439 ug/l in water.

Getenga et al, (2004), found α-BHC, ß –BHC, Lindane, Endosulfan, Heptachlor epoxide, Dieldrin, Endrin and Methxychlor residues in water samples collected from rivers draining the sugarcane fields constituting the Lake Victoria Basin. They found residues of Lindane and α-

BHC to be the highest with α-BHC showing concentrations of 0.21 ± 0.09 mg/L for six points except one point that showed concentration as high as 0.69 mg/L. The same study reported the highest concentration of Lindane in water as high as 1.240 mg/L (Getenga et al., 2004).

## 2.6 Pesticides in Soils and Sediments

A number of laboratory studies have been carried out to establish the behavior of organochlorine residues in soils. The studied organochlorines include DDT, DDE, Lindane, Endosulfan Sulphate, Dieldrin, Heptachlor and Heptachlor Epoxide.

Everaats et al. (1997) examined pesticide residues in sediments and macro invertebrates along the Kenyan coast. They found Polychlorinatedbiphenyls (PCBs) and pesticide residues in sediments samples from two shallow coastal stations at the mouth of Sabaki River. PCBs congeners 28, 52,101,153 and 138 were detected at the two sites in a concentration range of 7.1 to 62.2 ng $g^{-1}$ of organic carbon. Similarly p, p’-DDE was measured at concentrations ranging from 32.1 to 508.8ng $g^{-1}$ organic carbon.

## 2.7 Pesticides in Animals, Birds and Humans

Pesticides have been detected in cow’s milk (Kituyi et al., 1997), human milk (Kinyamu et al., 1998) and in eggs (Kahunyo et al., 1986).

Kituyi et al, (1997) measured Chlorfenviphos residues in cow’s milk in Kenya. Concentrations ranged between 0.52 and 3.90mg $kg^{-1}$ in the dry season and from 1.58 to 10.69 mg $kg^{-1}$ during the wet season. Milk collected from plunge dipped cows had higher concentrations than milk obtained from hand sprayed animals.

Studies by Kinyamu et al., (1998), on 219 milk samples for organochlorine pesticide residues established p,p’-DDT, p,p’-DDE, p, p’-DDD, o,p’-DDT, α-HCH, ß-HCH, Lindane and Dieldrin.

p,p’-DDT and p,p’-DDE were the most detected pesticides with frequency of 78.8% and 99.5% respectively, whereas the sum of DDT ranged between 0.04 and 6.312 mg/kg fat.

Kahunyo et al. (1986) found high levels of DDT and dieldrin in eggs from Embu district. Pesticides accumulation in this case may have been favored by the practice of allowing chicken to forage freely for food thus exposing them to residue around the farm.

## 2.8 Pesticides in Air

Pilot air monitoring activities conducted in 15 African countries including Kenya to investigate POPs levels in ambient air revealed presence of 9 POPs pesticides at varying concentrations Kitengela in Kenya elucidated the problem of obsolete pesticide storages sites with very high atmospheric levels of DDTs, Hexachlorocyclohexanes (HCHs) and Hexachlorobenzene (HCB). (APMR, 2008).

## 2.9 Health Impacts of Pesticides

Chronic adverse effects of pesticides on human health, due to prolonged periods of exposure, were first recognised in the 1960s. Several of the POP pesticides are carcinogenic in experimental animals and therefore are possibly carcinogenic to humans. Some are also suspected to depress the immune system (Repetto and Baliga, 1996).

organochlorine pesticides and DDT have raised environmental concerns globally especially in developed countries. The tendency of DDT and other Organochlorines pesticides to persist in the environment for a long time together with their ability to accumulate in animal adipose and other tissues and organs have contributed significantly to their impacts in animal species. Many studies have been carried out to investigate the health effects of organochlorines and DDT. Reported abnormalities in laboratory animals and wildlife exposed to endocrine-disrupting chemicals include feminization of males, abnormal sexual behaviour, birth defects, altered sex ratios, decreased sperm density, decreased size of testes, breast cancer, testicular cancer, reproductive failure and thyroid dysfunction (Crisp et al., 1998; Vom Saal et al., 1998).

Epidemiologic studies involving workers have found associations between exposure to specific pesticides or industrial chemicals and levels of thyroid stimulating hormone (TSH), testosterone and prolactin in adults (Steen land et al., 1997; Sweeney et al., 1997-98; Manzo et al., 1996).

Some of these studies have also found significant associations with other relevant end points, including diminished sperm quality, impaired sexual function and testicular cancer (Hardell, 1997; Whelan et al., 1996).

Rodents exposed to a single low dose of an organophosphate pesticide in a critical period of neonatal life have been found to have permanently decreased brain density of muscarinic receptors and hyperactive behaviour when tested as adults (Ahlbom et al., 1995). The subsequent contamination of the inhabitants is influenced by local environmental pollution, diet, duration of exposure, age, capacity for elimination by metabolism, and number of nursed infants (Brunetto et al. 1996; Czaja et al 1997; Laden et al. 1999; Smith 1999; Waliszewski et al. 1998a; Laden et al., 1999).

### 2.10 Pesticides analysis by GC-MS

The Gas Chromatography- Mass Spectrometry is a hyphenated analytical technique that combines the separation properties of gas –liquid chromatography with the detection feature of mass spectrometry to identify different substances within a test sample.

GC is used to separate the volatile and thermally stable substitutes in a sample whereas GC-MS fragments the analyte to be identified on the basis of its mass. Components of the GCMS system are shown in figure 2.1 below.

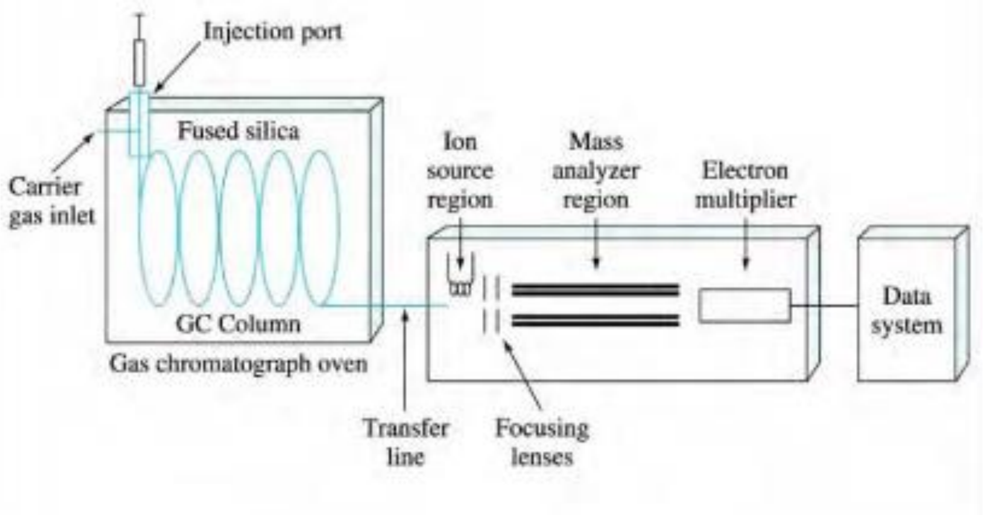

Figure 2.1: Components of a GCMS equipment

GC-MS technique represents the mass of a given particle (Da) to the number (z) of electrostatic charges (e) that the particle carries. The term m/z (mass to charge) is measured in DA/e. GC-MS commonly uses electron impact (EI) and chemical ionization (CI) techniques.

Other GC techniques employ conventional detectors such as Electron Capture Detector (ECD) and Flame Ionization Detector (FID), which present major drawbacks such as insufficient proof of the nature of detected compounds. This is because analyte identification is based on retention time matching which may be inaccurate and misleading.

The GC-MS has superior features which include, enhanced molecular ion capabilities, improved confidence in sample identification, significantly increased range of thermally labile and low volatility samples amenable for analysis, much faster analysis and improved sensitivity particularly for compounds that are hard to analyze. Therefore the GCMS is highly recommended for monitoring and tracking of organic pollutants in the environment such as determination of chlorophenols, Poly aromatic hydrocarbons (PAH), unleaded gasoline, dioxins, dibenzofurans, herbicides and pesticides in soil and water.

# CHAPTER THREE

## MATERIALS AND METHOD

### 3.1 Description of the Study Area

The Nairobi River Basin consists of three major rivers namely Nairobi, Ngong and Mathare Rivers whose catchments are found within Kikuyu and Limuru hills.

The source of Nairobi River is Ondiri swamps. Farmers in the Ondiri swamp use the water to irrigate their land. The upper parts of the Nairobi River which include the Kikuyu township area are characterized by intensive smallholder farms of kales, cabbages, onions, maize, beans and tomatoes where agrochemicals such as pesticides and fertilizers are applied. Along the riverine edges of the Nairobi River at Kikuyu springs before the confluence with Nyongera River there are small scale farms of kales, managu, arrow roots and Napier grass and numerous large scale flower farms such as Magana flowers.

The river passes through Kawangware, Kangemi, Lavington, Kileleshwa and Chiromo which are characterized by residential houses, solid wastes, dumpsites and vegetable farming along the riverbanks.

It then passes through the central business district which comprises of commercial offices, chemical industries and motor vehicle garages. The river then goes through Eastleigh, Kariobangi collecting effluents from small scale industries and sewage from informal settlements. Further down stream Ngong River and Mathare River join Nairobi river to form the bigger Nairobi River which finally joins Athi River known downstream as the Sabaki. The Athi

River eventually discharges its waters into the Indian Ocean at Malindi on the East African Coast.

In this study four sites located along the river were chosen namely Ondiri swamp, Naivasha Bridge, Muthangari Bridge and Outering Bridge, Ondiri bridge site with coordinates, S 010 15.005’ E 0360 39.741’ and altitude of 1999m is the source of Nairobi river. This was chosen as a suitable site to monitor chemical and biological changes that take place as the river meanders through residential and industrial activities downstream.

Naivasha Bridge site at S 010 16.396' E 0360 43.999' and altitude of 1791 m is the second site downstream Nairobi River and was chosen to capture information on the impact of floricultural and agricultural activities concentrated on the riparian land.

Muthangari bridge site at S 01018.48' E 0360 49.420’ and altitude of 1746m is situated on the Nairobi River after draining through Kangemi informal settlements. The water at this site has a lot of foam, solid wastes and is brown due to siltation. It captures sewer discharges from residential estates, sanitary wastes and runoff from riparian agricultural activities.

Outering bridge site at S 010 14.823'E 0360 52.725’and altitude of 1601m represents the last sampling site downstream Nairobi river. This site captures discharges from light industries within Jericho, Eastleigh, Kimathi estates as well as effects of encroachment of riparian land for urban agriculture. Fig 3.1 below shows the sampling sites along the Nairobi River.

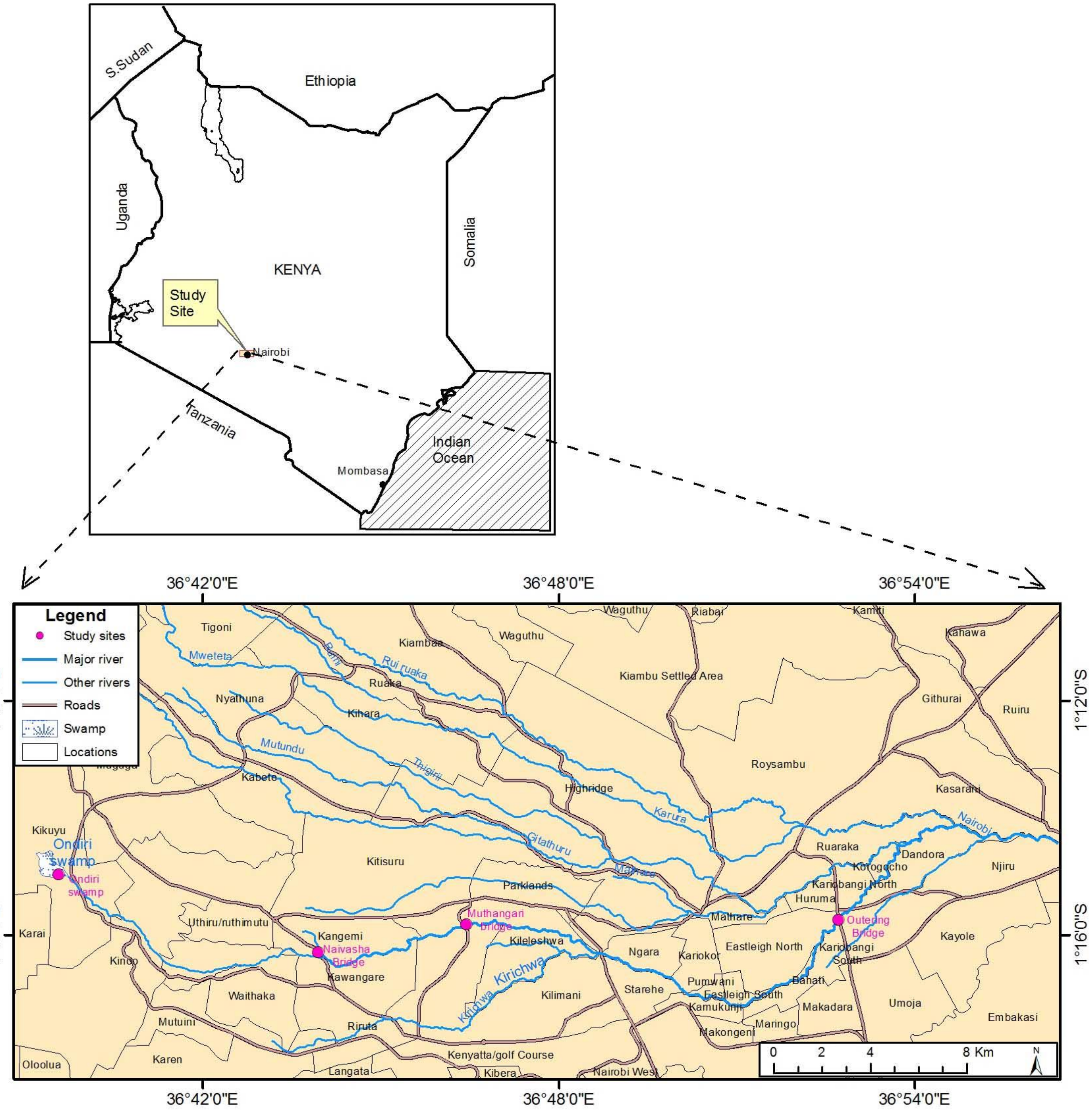

Figure 3.1: Map of the study area.

## 3.2 Chemicals and Reagents

General purpose grade acetone, dichloromethane, hexane, anhydrous sodium sulphate, analytical sodium chloride, mercuric chloride, silica and copper powder were all obtained from Scie Lab Chemical Ltd. HPLC grade 2-Octane and methanol were purchased from Fischer scientific Kenya Ltd.

Analytical grade (AR) disodium hydrogen phosphate and hydrochloric acid were purchased from Kobian Kenya Ltd. Florisil (Magnesium silicate 60-100 mesh size) was purchased from Pyrex E.A Ltd.

Helium gas (>99.999 purity) for Gas Chromatography Mass Spectrometry and White Spot Nitrogen (WSN) for sample concentration was purchased from British Oxygen Company (BOC) Kenya Ltd. The organochlorine pesticide mixture consisting of 16 pesticides was obtained from Ultra Scientific, North Kingstown, USA. The organophosphate pesticides were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Distilled water was used throughout where necessary.

## 3.3 Equipment and Apparatus

A soxhlet extractor composed of a heating mantle and condensers was used to extract sediment samples while 2.0 litre glass separatory funnel were used in solvent - solvent extraction of water samples, glass columns of length 60 cm and 2 cm id were used in cleanup procedures, whereas a LABCONCO rotary evaporator model RE300 MS, was used for concentrating sample extracts. The extracts were stored in refrigerator at $2^0$C before instrumental analysis.

Agilent GC-MS comprising of a 6890N GC, and 5975 MSD was used for analysis of organochlorine and organophosphate pesticides in water and sediment samples. Moisture in sediments was determined by heating sediments in a Binder E28#04-71528 oven and all glassware were dried in a Mammoth oven.

The pH, TDS, and Electrical conductivity experiments were carried out with ExStik® II meter. All weights were taken using a Fisher Scientific A-160 weighing balance.

Other apparatus used were nitrogen concentrator, beakers, autosampler vials, conical flasks, micro syringes, dessicator, measuring cylinders and surgical gloves.

## 3.4 Sampling

### 3.4.1 Field Sampling of Sediments

Sediment samples were collected in triplicate over a period of six months between March and September 2009 capturing the wet (March, April, June) and dry (July, August, September). seasons at four sites. Sediment samples were scooped using stainless steel shovels and about 500 g placed in an aluminum foil. The samples were packed in a self sealing bag, labeled and transported in a cooler box at 4 $^0$C to the laboratory. In the laboratory samples were stored in a deep freezer at -20 $^0$C prior to analyses.

### 3.4.2 Field sampling of water

Both water and sediment samples were collected from the same sampling points. Water samples were collected by grab method into 2.5 litre amber bottles prewashed with distilled water. Each water sample was labeled and treated with 1 g mercuric chloride to kill microorganisms that could degrade the pesticides. The samples were kept in cool boxes at 4 $^0$C and transported to the laboratory for analyses.

### 3.4.3 Preparation of Drying agents, column materials and Solvents

Anhydrous sodium sulphate ($Na_2SO_4$), analar grade (AR) was prepared by baking for 16 hours at 400 $^0$C in the oven to remove all the impurities. florisil (8 g per sample) was dried overnight at 200 $^0$C to activate. The performance of florisil was tested before it was used to clean up water and sediment extracts.

General purpose grade acetone, hexane and dichloromethane were each triple distilled to analytical grade level.

## 3.5 Extraction of sediments and water.

### 3.5.1 Extraction of sediment samples

EPA method 3540-soxhlet extraction method was used. The sediment samples were removed from the freezer and allowed to thaw for 4 hours prior to extraction. Triplicates of 20 g sediment samples were dried with 60 g of with baked out anhydrous sodium sulphate. The samples were allowed to stand for about 6 hours before being transferred to soxhlet thimbles. 100 µl of 1 ppm PCB 155 solution was added to the samples as recovery standard. This was soxhlet extracted with 130 ml of hexane: acetone (3:1v/v) in a round bottomed flask for 16 hours. The extract was concentrated using a LABCONCO rotary evaporator. The extracts were then transferred quantitatively to 10 ml volumetric flasks using isooctane and stored in fridge prior to clean up at 2 $^0$C.

### 3.5.2 Extraction of Water Samples

For the water samples EPA method, 3510 was used. One litre of the aqueous sample was transferred into a 2 litre separating funnel. pH was adjusted to neutral by adding 50ml of 0.2M disodium hydrogen phosphate buffer. 100µl of 1ppm PCB 155 solution was added as recovery standard and the neutral solution was treated with 100g of sodium chloride to aid in salting out of pesticides from the aqueous phase. 60ml of triple distilled dichloromethane was added and shaken for two minutes while releasing pressure and the water was allowed to settle to enhance separation of the phases. The organic layer was transferred to a 250 ml Erlenmeyer flask. The extractions were repeated twice using 60 ml portions of dichloromethane. The extracts were combined and then passed through anhydrous sodium sulphate to dry prior to concentration to 2 ml isooctane using a rotary evaporator. The extracts were transferred into glass vials and stored in fridge prior to clean up.

### 3.6 Clean up of the Water and Sediment Extracts

A chromatographic column 60 cm long x 2 cm id was filled with hexane (HPLC grade) and gently packed with 8 g Florisil (magnesium silicate 60-100 mesh).The Florisil was topped with 2 g anhydrous sodium sulphate and hexane was left to drain and discarded. The sample extract was introduced into the column and the sample vial rinsed four times with 1ml portions of hexane quantitatively.

The column was eluted with 200 mls of a solvent mixture comprising of HPLC grade, dichloromethane hexane and acetonitrile in the ratio of 50:48.5:1.5 respectively. The eluate was collected in a 500 mls round bottomed flask then concentrated to 2 mls in isooctane using a rotary evaporator. The extract was transferred into a clean pre weighed vial and concentrated to 0.5 ml under a gentle stream of Nitrogen.

To correct for variability due to injection conditions 100 µl of 1ppm PCB 198 was added to the extract as an injection check standard. The extracts were transferred quantitatively into GC vials for GC-MS analysis. The GC-MS was calibrated using two standards mixtures, containing 16 organochlorine pesticides and 14 organophosphorous pesticides.

### 3.7 Sulphur Removal from Sediment samples

EPA method 3660B was used. Sulphur was removed by addition of small amounts of activated copper powder to clean up sediment extracts. The copper needed for a particular day was activated by mixing it with concentrated hydrochloric acid that had been diluted by a factor of 3 with distilled water. Methanol was used to remove excess acid before drying the copper powder by placing in a water bath set at 30 $^0$C and passing through it a stream of white spot nitrogen (WSN).

### 3.8 GC-MS analysis and Pesticide Quantification

Organochlorine and organophosphate pesticides residues were identified and quantified using a GC-MS; Agilent Technologies 6890N GC, and 5975 MSD. A fused silica capillary column 5% phenyl methylsiloxane fused silica capillary column (DB -5 MS, 30 m x 0.25 mm id ) with film thickness of 0.1 µm produced by Agilent Technologies was used to separate analytes. Helium (99.9995%) was used as a carrier gas at a constant flow of 2 ml/min. The injection volume was 2 µl using a Split Splitless Injector operated in split less mode. The temperature programme was 90$^o$C (Hold 2 min), ramped at 15$^o$C to 165$^o$C (0 min hold) and finally ramped at 2$^o$C to 250$^o$C (Hold 1min). A maximum ionization time of 25,000µs was applied with ionization energy of 70 eV (Energy Volt). Mass spectra were acquired in both full scan from m/z 35 to m/z 550 at 1 scan/s and Select Ion Modes (SIM). A solvent delay for data acquisition of 4 minutes was used to avoid disturbances in the mass detection system.

The GC MS was calibrated using a multipoint internal standard calibration with 9 calibration levels Separate mixtures of analytical standards comprising of 16 OC and 14 OP pesticides were used. A calibration for each analyte was drawn and used in quantification of the pesticides and data processing was done using MS Excel.

For the interpretation of the complex chromatograms and mass spectra, the ADMIS software package was applied for deconvolution and background correction, the mass spectra was compared with NIST 05 and RTL Pest mass spectral databases.

### 3.9 Moisture Content Determination

Moisture content in sediments was determined by heating 10 g of sediment samples in triplicates in a memmert oven at $105^0$C for 24 hours. The weight of each glass vial while empty and with contents was determined before and after heating .The weight difference was used for calculating the moisture content of the samples at the time of extraction (UNEP, 1982).

### 3.10 Total Suspended Solids (TSS)

A well mixed water sample was filtered through a pre weighed whatman filter, 70 mm id under vacuum and filtration apparatus. The residues retained on the filter paper were dried to constant weight at 105 $^0$C. The weight difference was used for calculating the TSS in the water samples.

### 3.11 pH, Conductivity TDS Determination

pH, conductivity and Total Dissolved Solids (TDS) measurements were carried out using a calibrated portable meter model Exstik R II. Calibration of the meter was done using buffer solutions with pH 4, 7 and 10 for pH measurements. Calibration standards of conductivity 84 µS, 1413µS and 12880 µS were used for conductivity and TDS measurements. Sample measurements were taken by dipping the electrode into a sample solution, swirling and waiting up to 1 minute to obtain a steady reading. The electrodes were thoroughly rinsed with distilled water and carefully wiped with tissue before changing to another sample. All readings were taken and recorded.

### 3.12 Temperature

Temperature readings were made at the sampling sites using a digital thermometer by directly dipping the thermometer in the river. The temperature was read in degree Celsius and reported to one decimal place.

### 3.13 Quality Control and Quality Assurance

The performance of the analytical methods was verified before sample extraction and involved analysis of reagent blanks using the same procedures as used for the field samples, this was done to determine the presence of interferents in dichloromethane, anhydrous sodium Sulphate, hexane, acetone, distilled water, sodium chloride and florisil.

Recovery studies which involved spiking of blank matrices with known pesticide concentrations were used to determine extraction efficiencies. The spiked samples were then analysed using the same analytical procedures as field samples. The field sample results were not corrected for recoveries.

Analysis of field samples was carried out in triplicate, and OC and OP pesticides standards were injected before sample runs. This was used to check column performance, resolution, detector response and linearity. In the sample run sequence quality control was performed by regular analyses of solvent blanks and random injection of standards.

OC and OP pesticides were identified by comparing the retention times with those of the prepared standard mixtures; additional confirmation was carried out by searching the identified pesticides in the GC MS mass spectral libraries. Separate GC MS methods were run for OC and OP pesticides in both SIM and SCAN modes and compounds were assigned unique target and qualifier ionic masses.

### 3.14 Limit of detection.

The Limit of Detection (LOD) is the lowest amount of analyte in a sample that can be detected but not necessarily quantitated as an exact value.

The LOD of OC and OP pesticides were expressed as the analyte concentration required to produce a signal greater than three times the standard deviation of the noise level. It was determined by empirical approach consisting of measuring progressively more dilute concentrations of analyte and employing the following relationship:

$$\text{LOD} = \frac{\text{3x Noise peak area x concentration of standard injected (ng/ml)}}{\text{Analyte response in the lowest calibration point}}$$

### 3.15 Recoveries

Recoveries were determined for both sediment and water matrices by spiking with known pesticide concentrations of OC and OP pesticides prior to extraction. Mean recoveries for pesticides were calculated for both sediments and water samples.

### 3.15 Pearsons correlation

Correlation of pesticide residues and physicochemical parameters was done using Pearsons correlation from SPSS tool. Pearson, r is a measure of linear dependence between two variables X and Y giving a value of +1 and -1 inclusive. Where 1 is a total positive correlation, 0 is no correlation and -1 is negative correlation. Positive value indicates that the changes are in the same direction while negative values indicate inverse variation relationships. Correlation coefficients above 0.5 are considered strong while below 0.5 are considered to be weak. The significant of correlations is indicated by the P value. Correlations are significant if $p<0.05$ and are not significant if $p>0.05$(APA, 2001).

# RESULTS AND DISCUSSIONS

## 4.1. Identification and Quantification of OC and OP pesticides

A total of 144 samples comprising of 72 sediment and 72 water samples were analysed using GC-MS. Data from the GC-MS software was collected and analysed for 14 OP and 16 OC pesticides in the samples. The calibration curves for OC and OP pesticides were plotted in the concentration ranges of 0.003-0.564 µg/ml and 0.023-1.807 µg/ml, respectively.

The calibration curves of the standards were the best line of fit obtained by plotting the relative response factor (ratio of instrument response normalised with PCB 198 peak area) against pesticide concentration. Sample analyte concentrations were obtained by interpolation from the graphs. Samples which had analyte concentrations outside the calibration curves were diluted and re injected. Examples of multilevel calibration curves for a-HCH are shown in fig 4.1 below. Quality control data collected for OC and OP pesticides included linear correlations, recoveries, LOD and MS qualifier ions as shown below in tables 4.1a and 4.1b below.

All pesticides gave a correlation factor above 0.95, indicating a high correlation between instrument responses and analyte concentrations.

The limit of detection ranged from 0.0004-0.0138 ng/ml and 0.0008-0.0084 ng/ml for OC and OP pesticides, respectively. Any other values detected below LOD were considered as noise and hence reported as below detection limit (BDL).

Mean recoveries ranged between 69.98% to 119.45% for OC and 69.87% to 120.33% for OP pesticides, respectively. These values were within the recommended range of 70-120% and hence the results were not corrected for recoveries

Table 4.1a: OP pesticide Recoveries, $R^2$, LODs and MS ions.

| Pesticide | $R^2$ | LOD(ng/ml) | Recovery | Target and Q ions |
|---|---|---|---|---|
| **Dichlorvos** | 0.999 | 0.0019 | 78 | 109.00,184.90 |
| **Mevinphos** | 0.992 | 0.0018 | 80 | 127.00,192,00 |
| **Ethoprophos** | 0.996 | 0.0020 | 113 | 157.90,43.10 |
| **Cadusafos** | 0.999 | 0.0017 | 120 | 158.90,157.90 |
| **Dimethoate** | 0.990 | 0.0061 | 98 | 87.00,93.00 |
| **Diazinon** | 0.998 | 0.0012 | 76 | 179.10,137.00 |
| **Dichlorofenthion** | 0.999 | 0.0008 | 103 | 279.00,222.90 |
| **Chlorpyrifos methyl** | 0.999 | 0.0008 | 70 | 285.90,124.90 |
| **Pirimiphos methyl** | 0.999 | 0.0008 | 99 | 290.00,276.00 |
| **Malathion** | 0.996 | 0.0036 | 103 | 124.90,107.70 |
| **Chlorpyrifos** | 0.999 | 0.0023 | 77 | 196.90,96.90 |
| **Methidathion** | 0.989 | 0.0084 | 81 | 145.00,85.00 |
| **Ethion** | 0.996 | 0.0015 | 100 | 230.90,96.90 |
| **Triazophos** | 0.995 | 0.0057 | 70 | 161.00,77.00 |

Table 4.1b: OC pesticide Recoveries, $R^2$, LODs and MS ions.

| Pesticide | $R^2$ | LOD(ng/ml) | Recovery | Target and Q ions |
|---|---|---|---|---|
| **a-HCH** | 0.998 | 0.0032 | 119 | 182.90,216.90 |
| **b-HCH** | 0.999 | 0.0025 | 70 | 180.90,108.90 |
| **g-HCH** | 0.999 | 0.0072 | 87 | 180.90,218.90 |
| **d-HCH** | 0.989 | 0.0052 | 103 | 218.90,109.00 |
| **Heptachlor** | 0.995 | 0.0018 | 101 | 99.90.271.80 |
| **Aldrin** | 0.997 | 0.0005 | 117 | 66.00,262.80 |
| **Heptachlor epoxide** | 0.990 | 0.0006 | 105 | 81.00,152.90 |
| **o,p’-DDE** | 0.978 | 0.0138 | 76 | 246.00,317.90 |
| **Alpha endosulfan** | 0.998 | 0.0004 | 96 | 240.90,238.80 |
| **p,p’-DDE** | 0.999 | 0.0004 | 106 | 246.00,247.90 |
| **Endrin** | 0.995 | 0.0096 | 118 | 81.00,79.10 |
| **beta endosulfan** | 0.998 | 0.0013 | 75 | 194.80,240.90 |
| **o,p’-DDD** | 0.998 | 0.0006 | 102 | 235.00,237.00 |
| **Endosulfan sulphate** | 0.994 | 0.0016 | 116 | 386.80,271.80 |
| **p,p’-DDT** | 0.999 | 0.0031 | 117 | 164.90,236.00 |
| **Methoxychlor** | 0.999 | 0.0012 | 114 | 227.10,228,10 |

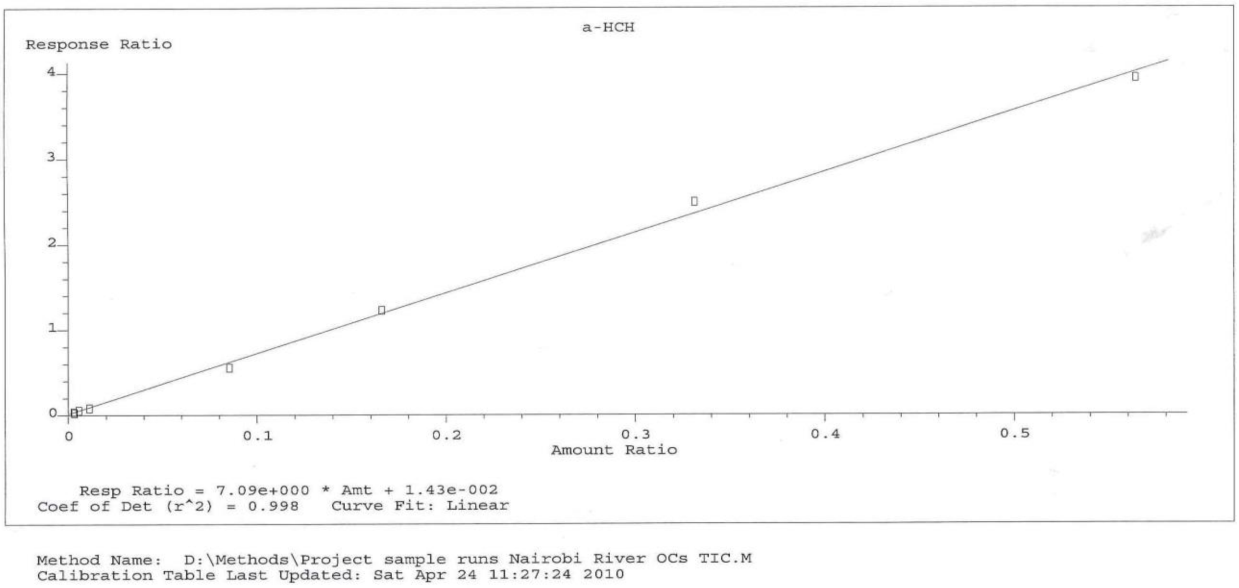

Figure 4.1 Multilevel calibration curve for a-HCH

## 4.2. Pesticides in sediment samples from Nairobi River

A total of 30 pesticides were measured in sediment samples collected from 4 sampling site along the Nairobi River. They included 16 OC pesticides (a-HCH, b-HCH, g-HCH, d-HCH, Heptachlor, Aldrin, Heptachlor epoxide, o,p’ DDE, Alpha endosulfan, p,p’ DDE, Endrin, beta endosulfan, o,p’ DDD, Endosulfan sulphate, p,p’ DDT, Methoxychlor) and 14 OP pesticides (Dichlorvos, Mevinphos, Ethoprophos, Cadusafos, Dimethoate, Diazinon, Dichlorofenthion, Chlorpyrifos methyl, Pirimiphos methyl, Malathion, Chlorpyrifos, Methidathion, Ethion and Triazophos).The samples were collected during the Wet season (March, April, June) and Dry season (July, August, September). The average levels of OC and OP pesticide concentrations are summarised in tables 4a and 4b as shown below.

Amongst the OC pesticides, a-HCH recorded the highest concentration of 1385±73.80µg/kg at Muthangari Bridge during the dry season while the lowest average concentration recorded was Methoxychlor, 0.88±53 µg/kg at Ondiri during the wet season. However, p,p’-DDT was pre dominant at most sites by having the highest average concentration recorded during the wet and dry seasons, average concentration at all sites was 638.07±313.59 µg/kg. Muthangari had the highest ∑ OC concentration amongst all the sites at 5025.47±393.82 µg/kg during the dry season. Pesticides concentrations in sediments during the wet and dry seasons ranged from 0.68 µg/kg to 1269.46 µg/kg**.**

The highest occurrences in the 14 OP pesticides across the 4 sites was observed for Chlorpyrifos, Malathion and Diazinon at frequencies of 38%, 26.7% and 10.1%, respectively Dichlorofenthion and Chlorpyrifos methyl had the lowest occurrence at 0.5% and 0.2%, respectively. Muthangari Bridge had the highest concentration of OP pesticides recorded during the wet season while the lowest levels were recorded at Ondiri site. Generally higher concentrations of OP pesticides were recorded during the dry season compared to the wet season, Malathion and Chlorpyrifos had the highest concentrations at Muthangari and Naivasha Road bridge sites, respectively. Seasonal variations of OC and OP pesticides in sediments at the respective sites are discussed below in sections 4.2.1 to 4.2.4.

Table 4a. Levels of OC Pesticides in Nairobi River Sediments in µg/kg ± SD

| **Pesticides** | **Ondiri swamp µg/kg** | | **Naivasha Bridge µg/kg** | | **Muthangari Bridge µg/kg** | | **Outering Bridge µg/kg** | | **Average (Wet+Dry) µg/kg** |
|---|---|---|---|---|---|---|---|---|---|
| | **Wet** | **Dry** | **Wet** | **Dry** | **Wet** | **Dry** | **Wet** | **Dry** | |
| **a-HCH** | 9.40±4.19 | 233.17±158.65 | 31.98±10.08 | 15.07±2.10 | 106.29±90.04 | 1385.89±73.80 | 333.48±51.45 | 181.63±160.89 | 287.11±458.63 |
| **b-HCH** | 41.87±0.10 | 249.22±18.49 | 240.68±53.14 | 35.24±4.47 | 107.69±1.00 | 316.15±17.87 | 553.61±346.93 | 246.46±134.84 | 223.87±169.40 |
| **g-HCH** | 29.57±18.19 | 71.35±11.99 | 321.01±90.68 | 69.76±20.41 | 221.87±18.91 | 254.17±19.31 | 299.30±63.43 | 590.55±170.00 | 232.20±183.11 |
| **d-HCH** | 5.82±1.90 | 85.26±9.07 | 21.97±11.78 | 16.25±2.99 | 18.88±6.30 | 83.37±11.55 | 71.12±19.44 | 45.95±7.17 | 43.58±32.37 |
| **Heptachlor** | 46.28±50.65 | 148.47±48.13 | 117.83±35.99 | 117.66±8.56 | 130.29±5.14 | 205.25±63.19 | 407.04±75.16 | 38.12±2.71 | 151.37±116.41 |
| **Aldrin** | 49.69±64.91 | 44.48±10.64 | 18.95±5.60 | 17.25±2.12 | 21.42±16.75 | 24.3±73.79 | 83.42±56.67 | 35.29±7.83 | 36.86±22.34 |
| **Heptachlor epoxide** | 26.39±9.58 | 304.90±88.06 | 97.68±34.11 | 128.93±94.75 | 40.03±11.28 | 1000.02±0.70 | 252.35±147.56 | 73.39±3.40 | 240.46±322.48 |
| **o,p'-DDE** | 33.08±32.74 | 287.90±50.27 | 184.02±53.26 | 116.66±3.33 | 137.50±8.42 | 356.25±97.31 | 514.82±176.59 | 224.09±7.43 | 231.79±152.46 |
| **Alpha endosulfan** | 18.93±4.12 | 122.35±1.86 | 44.03±24.27 | 70.69±9.32 | 79.70±18.36 | 42.59±24.37 | 177.12±110.95 | 71.98±16.66 | 78.42±50.40 |
| **p,p'-DDE** | 3.90±1.37 | 20.54±2.82 | 12.35±2.44 | 15.27±2.08 | 11.58±0.78 | 143.78±38.93 | 24.25±14.58 | 18.38±6.69 | 31.26±45.89 |
| **Endrin** | 35.30±5.61 | 420.35±70.10 | 234.18±33.99 | 285.81±60.52 | 94.08±7.80 | 491.78±269.88 | 204.34±13.68 | 337.26±74.04 | 262.89±154.82 |
| **beta endosulfan** | 13.61±1.27 | 121.97±30.64 | 1.94±4.12 | 29.70±5.55 | 11.53±24.47 | 22.96±48.70 | 23.38±49.60 | 88.231±87.16 | 39.17±42.54 |
| **o,p'-DDD** | 2.36±2.38 | 19.57±3.30 | 5.11±2.19 | 7.50±1.86 | 20.84±2.40 | 15.49±2.87 | 24.55±5.00 | 11.05±5.35 | 13.31±8.05 |
| **Endosulfan sulphate** | 3.19±2.40 | 15.09±1.28 | 3.89±3.37 | 11.06±1.18 | 6.47±0.73 | 68.83±0.94 | 8.39±3.77 | 5.31±1.52 | 15.28±21.99 |
| **p,p'-DDT** | 419.06±283.33 | 547.25±82.09 | 1009.70±433.51 | 1028.94±407.78 | 259.81±59.70 | 610.85±58.14 | 301.16±112.93 | 927.76±160.87 | 638.07±313.59 |
| **Methoxychlor** | 0.88±1.53 | 8.05±0.31 | 1.08±1.52 | 5.16±0.74 | 4.59±2.68 | 3.71±0.17 | 9.76±3.81 | 11.87±0.28 | 5.64±3.97 |
| **∑ 16 OCPs** | 793.33±100.8 | 2699.91±159.21 | 2346.40±251.99 | 1970.95±252.31 | 1272.59±78.60 | 5025.47±393.82 | 3288.09±183.25 | 2907.30±253.34 | 2531.26±165.14 |

N=3

Table 4b. Levels of OP Pesticides in Nairobi River Sediments in µg/kg ± SD

| **Pesticides** | **Ondiri swamp µg/kg** | | **Naivasha Bridge µg/kg** | | **Muthangari Bridge µg/kg** | | **Outering Bridge µg/kg** | | **Average (Wet+Dry) µg/kg** |
|---|---|---|---|---|---|---|---|---|---|
| | **Wet** | **Dry** | **Wet** | **Dry** | **Wet** | **Dry** | **Wet** | **D ry** | |
| **Dichlorvos** | 1.61±2.78 | 51.81±8.29 | 6.96±1.38 | 15.17±2.02 | 19.19±7.26 | 169.31±1.58 | 31.71±2.94 | 20.54±3.10 | 39.54±54.67 |
| **Mevinphos** | 2.85±4.94 | 54.49±6.61 | 9.40±7.03 | 32.76±4.67 | 23.43±1.81 | 146.70±13.03 | 55.79±8.12 | 76.82±39.16 | 50.28±46.29 |
| **Ethoprophos** | 4.80±8.32 | 76.27±37.98 | 17.89±12.48 | 42.01±7.15 | 87.56±15.45 | 374.95±40.16 | 189.45±42.12 | 127.19±1.75 | 115.01±120.96 |
| **Cadusafos** | 11.31±19.59 | 180.60±28.45 | 16.4±41.35 | 66.32±9.53 | 116.54±5.49 | 344.16±128.41 | 175.41±3.60 | 117.31±18.22 | 128.51±108.13 |
| **Dimethoate** | 15.49±26.82 | 65.02±11.93 | 11.79±3.91 | 24.07±2.49 | 44.61±14.85 | 61.37±10.04 | 29.04±2.52 | 27.08±8.23 | 34.81±20.09 |
| **Diazinon** | 122.95±1.74 | 142.00±53.73 | 273.53±6.30 | 283.30±152.27 | 45.36±5.36 | 341.50±118.20 | 368.49±161.39 | 299.58±0.54 | 234.59±116.08 |
| **Dichlorofenthion** | 0.68±0.12 | 23.50±9.80 | 3.69±0.77 | 10.47±0.73 | 19.37±3.36 | 15.848.03 | 6.13±0.49 | 4.59±0.21 | 10.53±8.22 |
| **Chlorpyrifos methyl** | 1.54±0.56 | 9.13±3.46 | 2.16±0.37 | 4.37±0.95 | 5.26±1.01 | 5.17±0.22 | 4.85±0.49 | 3.11±0.01 | 4.45±2.35 |
| **Pirimiphos methyl** | 1.69±1.12 | 23.23±3.96 | 6.30±1.44 | 20.73±4.36 | 35.39±0.03 | 18.29±0.03 | 47.65±19.21 | 32.51±0.85 | 23.22±15.17 |
| **Malathion** | 66.23±10.82 | 673.19±32.65 | 77.67±45.33 | 537.81±384.71 | 1308.26±439.09 | 1268.38±901.77 | 541.95±111.65 | 490.88±90.29 | 620.55±467.09 |
| **Chlorpyrifos** | 94.43±88.28 | 449.96±44.56 | 424.69±210.20 | 1269.46±7.03 | 1984.03±45.76 | 644.11±135.08 | 1181.946±37.33 | 1019.833±60.87 | 883.56±603.11 |
| **Methidathion** | 6.61±11.44 | 148.81±3.54 | 9.71±4.90 | 37.63±8.76 | 48.74±8.27 | 94.87±25.39 | 50.55±7.34 | 50.08±5.31 | 55.88±46.54 |
| **Ethion** | 2.87±4.98 | 65.98±22.72 | 9.51±1.92 | 39.20±14.04 | 139.30±0.79 | 63.73±55.25 | 41.79±18.36 | 70.88±41.34 | 54.16±42.70 |
| **Triazophos** | 10.03±17.36 | 164.40±30.30 | 17.08±5.63 | 44.04±5.83 | 122.71±2.63 | 63.59±15.87 | 88.75±31.66 | 64.52±7.49 | 71.89±52.31 |
| **∑ 14 OPPs** | 343.08±39.78 | 2128.40±187.14 | 886.79±126.02 | 2427.34±347.92 | 3999.77±592.90 | 3611.96±344.08 | 2813.51±321.92 | 2404.90±278.38 | 2326.97±260.32 |

N=3

### 4.2.1 Seasonal variation of OC and OP pesticides residues in sediment samples at Ondiri swamp

Figure 4.2 below shows the seasonal variation of OC pesticides residues in sediment samples at Ondiri swamp. OC pesticides concentrations ranged between 0.88-547.25µg/kg and the highest concentration of OC pesticide recorded was p,p'-DDT during the dry season while methoxychlor had the lowest concentration at 0.88±1.53 µg/kg during the wet season.

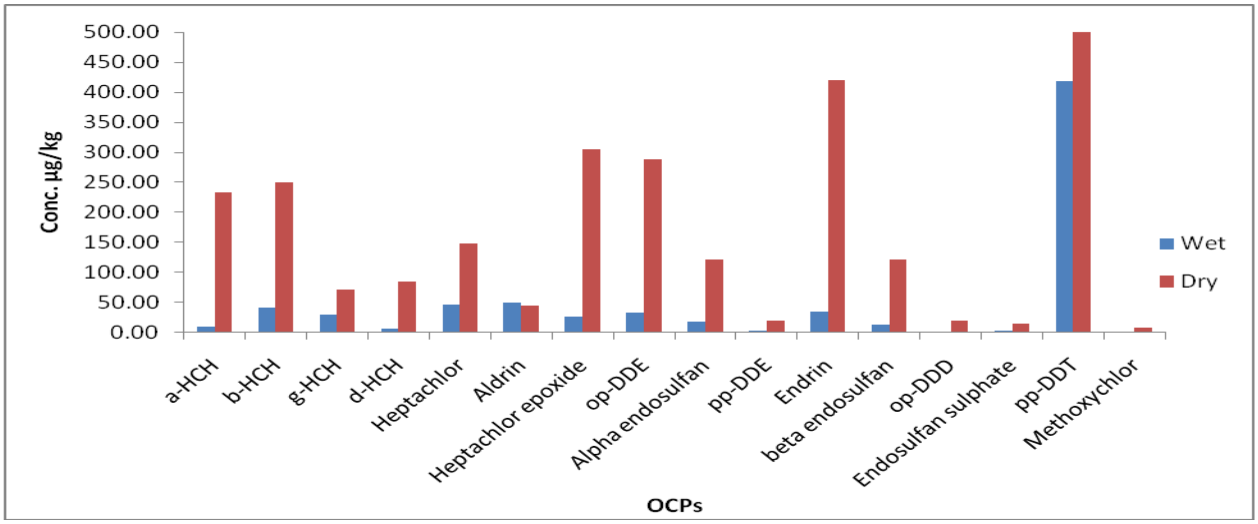

Figure 4.2: Seasonal variation of OC Pesticides residues in sediments from Ondiri swamp.

Figure 4.3 below shows OP pesticide residues recorded at this sampling site during the wet and dry seasons. The mean concentrations ranged between 0.68 to 122.95µg/kg and 9.13 to 449.96µg/kg during the wet and dry season, respectively.

Amongst the studied OP pesticides the highest pesticide concentrations recorded were Diazinon, 122.95±1.74 µg/kg, accounting for 35.8% of the total OPPs during the wet season. During the dry season, Malathion, dominated with a mean of 673.19±32.65 µg/kg followed by Chlorpyrifos, 449.96±44.56 µg/kg. The two accounted for 31.6% and 21.1% of the total OPPs during the dry season.

The high levels of OP pesticide residues may be attributed to riparian agricultural activities that include growing of tomatoes, kales, cabbages, onions and maize, where some of the detected pesticides are commonly used.

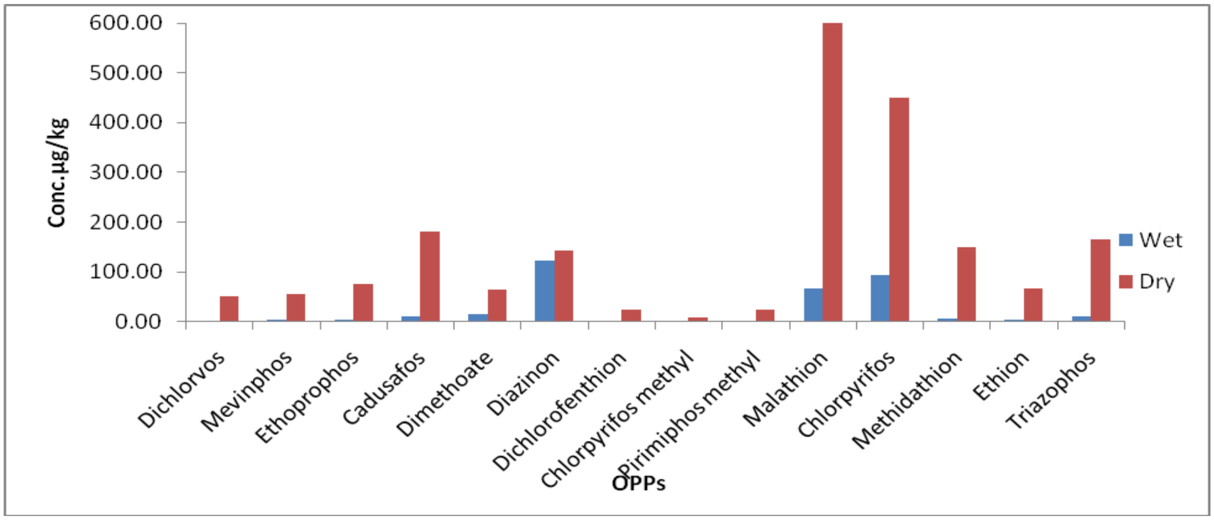

Figure 4.3: Seasonal variations of OP pesticides in sediments from Ondiri swamp

### 4.2.2 Seasonal variation in OC and OP pesticide residues in sediment samples at Naivasha Bridge

Figure 4.4 below shows the seasonal variations of OC pesticide residues at Naivasha Bridge. OC pesticides ranged from means of 1.08 to 1009.70µg/kg and 5.16 to 1028.94µg/kg during the wet and dry seasons respectively.

During the wet season p,p'-DDT recorded the highest concentration at 1009.70±433.51 µg/kg followed by g-HCH, 321.01±90.68 µg/kg and b-HCH, 240.68±53.14 µg/kg. The same trend in concentrations was evident during the dry season with p,p'-DDT having the highest concentration of 1028.94±40.78 µg/kg followed by Endrin and g-HCH with mean concentrations of 285.81±60.52 µg/kg and 69.76±20.41 µg/kg respectively.

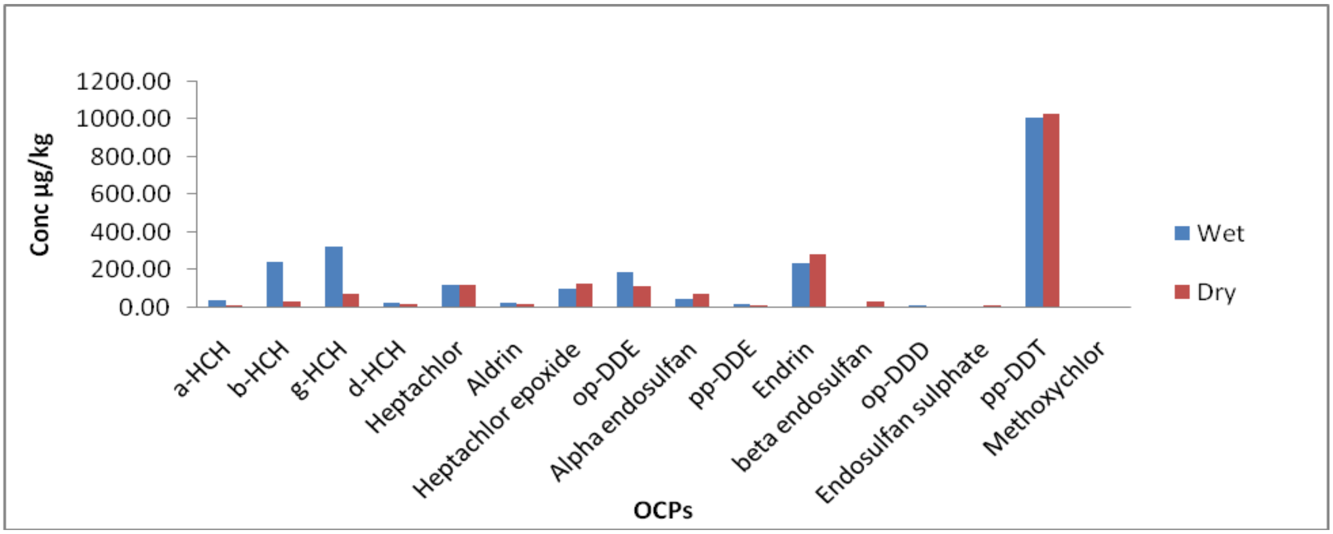

Figure 4.4: Seasonal variation of OC Pesticides in sediments from Naivasha Road Bridge

As shown in figure 4.5 below Chlorpyrifos recorded the highest mean concentrations at 424.69±21.02 µg/kg and 1269.46±7.03 µg/kg during the wet and dry season, respectively. This was followed by Malathion, 573.81±38.47 µg/kg and Diazinon, 283.30±15.27 µg/kg during the dry season. Generally high levels of OP pesticides were recorded during the dry season as compared to the wet season and this indicated high usage of OP, upstream the sampling site. There was substantial riparian agriculture as well as large scale flower farms which may have discharged the pesticides in to the river.

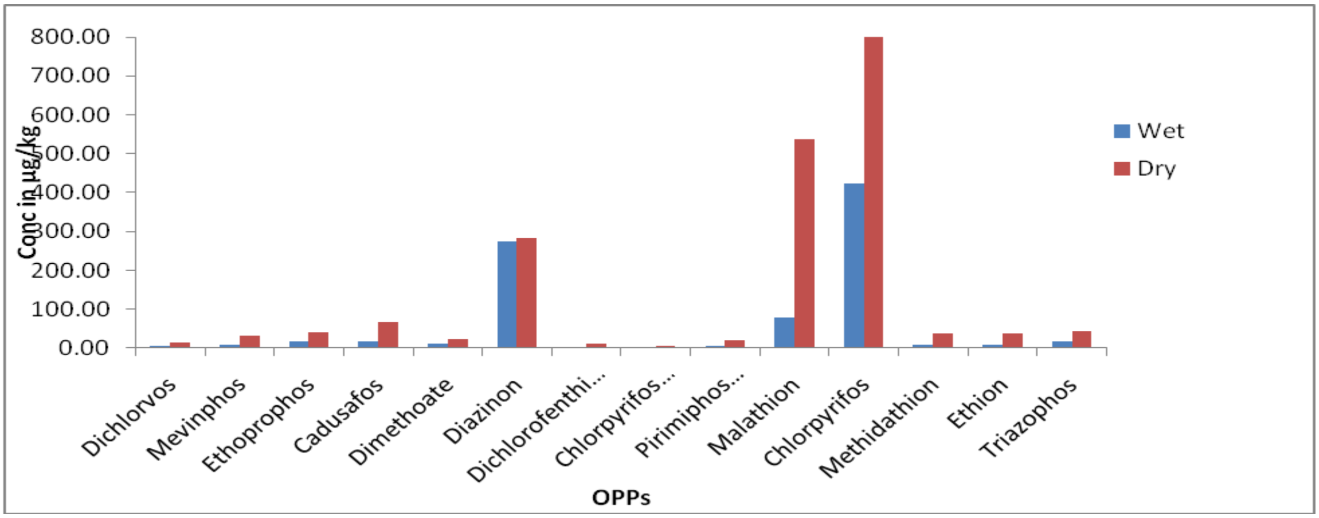

Figure 4.5: Seasonal variation of OP Pesticides in sediments from Naivasha Road Bridge.

### 4.2.3 Seasonal variation in OC and OC pesticide residues in sediment samples at Muthangari Bridge

Figure 4.6 shows seasonal variations of OC pesticides at Muthangari Bridge during the study period. The mean concentrations of pesticides for the wet and dry seasons ranged between 4.59 to 221.87 µg/kg and 3.71 to 1385.89 µg/kg respectively, with the total 16 OC pesticides being higher during the dry seasons compared to wet season. This may be attributed to concentration of pollutants in the river during the dry season.

Amongst the OC pesticides a-HCH had the highest concentration, 1385.89±73.80 µg/kg. HCH is available into formulations: technical HCH and Lindane, technical HCH contains isomers in the following percentages: α 55-80%, β 5-14%, γ 8-15%, δ 2-16%, ε 3-5% (Nhan et al,2001;Fu et al, 2001) and Lindane contains above 90% of γ-HCH. In this study the source of a-HCH may be point source pollution from the agricultural activities upstream the sampling site.

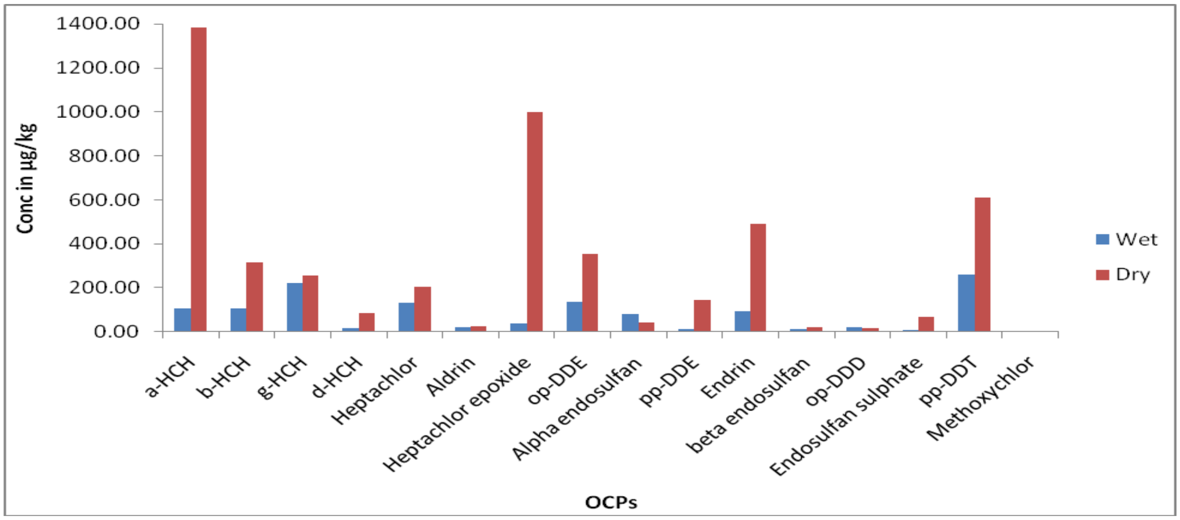

Figure 4.6: Seasonal variation of OC Pesticides in sediments from Muthangari Road Bridge.

Figure 4.7 below shows the seasonal variations of OP pesticide. The lowest concentration of pesticide recorded was Pirimiphos methyl, 5.17±0.22 µg/kg during the dry season with Chlorpyrifos recording the highest concentration of 1984.03±45.76 µg/kg followed by Malathion

1308.26±439.09 µg/kg during the wet season. The high levels of the two pesticides indicate high usage of pest control products mainly on kales, tomatoes, cabbages grown on riparian land on farms upstream this site. Higher pest prevalence during the wet season as compared to the dry season may explain the comparatively lower levels of Chlorpyrifos and Malathion at 1268.38±901.77 µg/kg and 644.11±135.08 µg/kg, respectively.

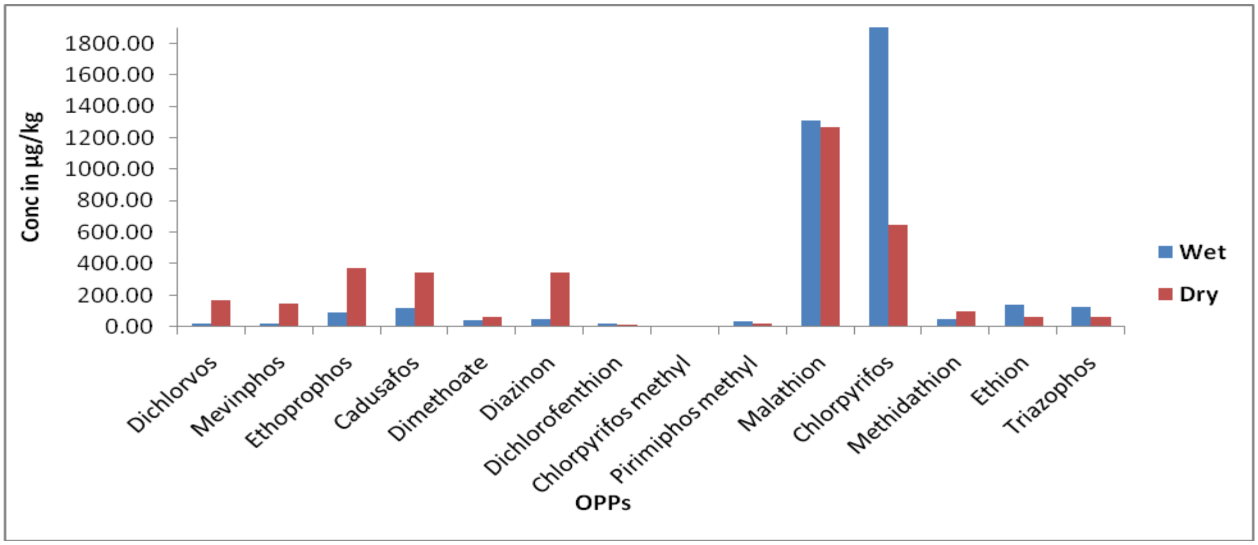

Figure 4.7: Seasonal variation of OP Pesticides in sediments from Muthangari Road Bridge.

### 4.2.4 Seasonal variation in OC and OP pesticide residues in sediment samples at Outering Bridge

At Outering road bridge the levels of OC pesticides showed p,p’-DDT having the highest average concentration of 927.76±16.07 µg/kg during the dry season. The concentration was the second highest recorded for p,p’-DDT after that at Naivasha road bridge. This site is characterised by dark murky water mostly from discharge of cottage industries, garages and residential areas. The elevated levels of OC pesticides suggests pollution from agrochemical industries upstream this site.

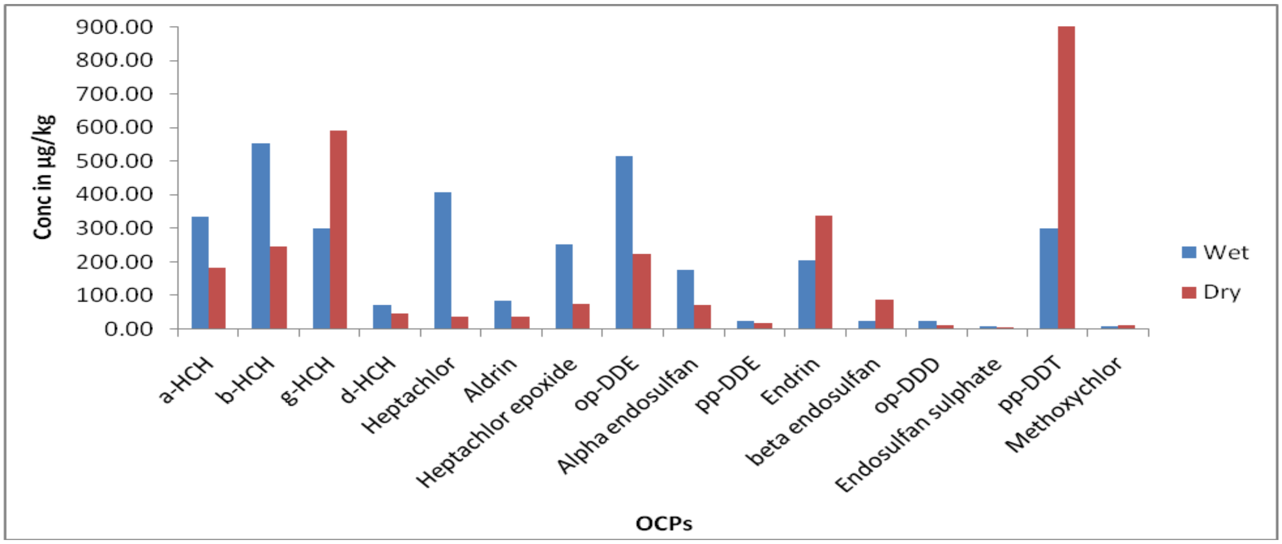

Figure 4.8: Seasonal variation of OC Pesticides in sediments from Outering Road Bridge.

OP pesticides at the Outering Road bridge exhibited the following descending order of concentrations, Chlorpyrifos>Malathion>Diazinon. The highest mean concentrations were recorded during the wet season. Runoff and discharge from surrounding cottage agrochemical industries can be attributed to the high pesticide levels.

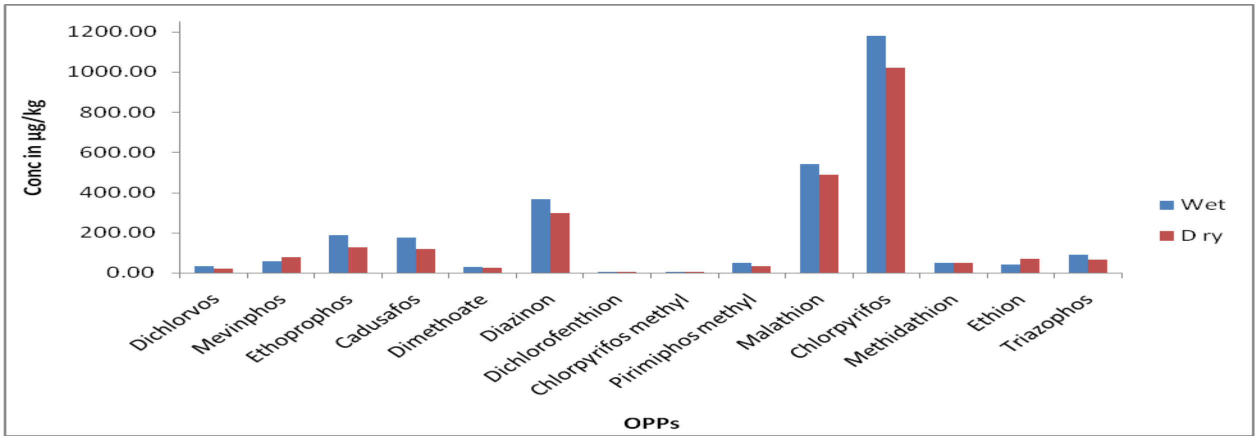

Figure 4.9: Seasonal variation of OP Pesticides in sediments from Outering Road Bridge

### 4.2.5 Spatial and seasonal variation of OC and OP pesticides in Nairobi river sediments

The seasonal variations of OC and OP pesticides are shown in Figure 4.10 below. The lowest concentration of ∑OCP and ∑OPP recorded was 739.33µg/kg and 343.08 µg/kg, respectively, during the wet months (March, April, and May) at Ondiri swamp, while the highest concentrations of ∑OCP and ∑OPP recorded were 5025.47 µg/kg and 3611.96 µg/kg,respectively at Muthangari Bridge during the dry months (July, August and September). Higher concentrations of pesticides were observed during the dry season compared to wet season at Ondiri, Naivasha and Muthangari sites, decreased river water flow leading to decrease in dilution effect during the dry season may have contributed to this trend.

However, the situation was the reverse at Outering Bridge site with higher concentrations of pesticides observed during the wet season, due to increase in the flow of river during the wet season, the pollution load may have been carried down-stream to Outering bridge site. On average higher concentrations of OC and OP pesticides were recorded during the dry season compared to the wet season, this can be explained by the dilution effect of pesticides in sediments during the wet season.

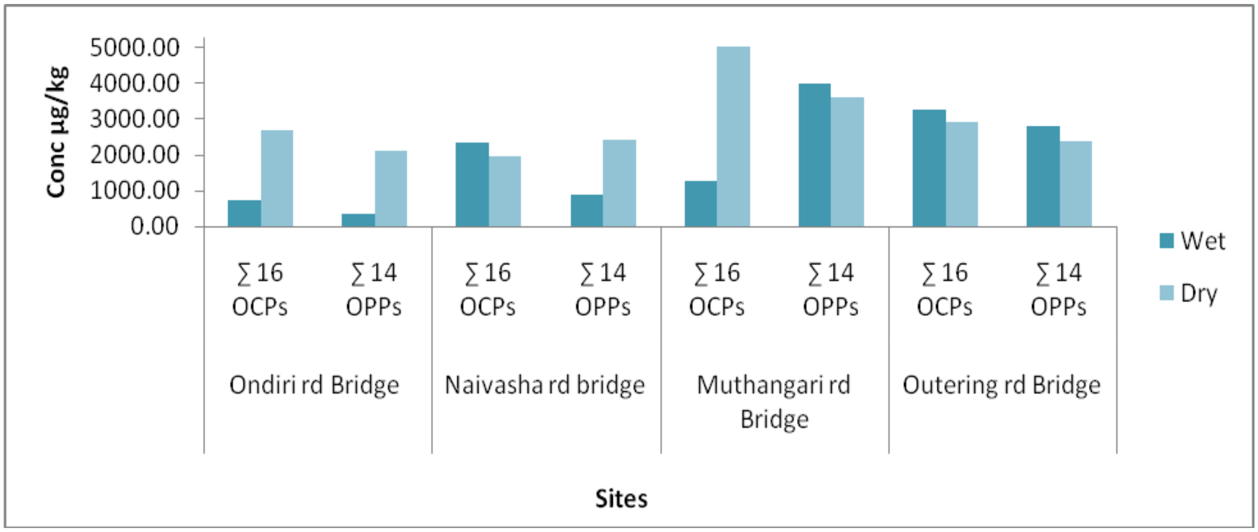

Figure 4.10: Seasonal variation of ∑OCP and ∑OPP in sediments

As shown in figure 4.11 below there was a general increase in OC and OP pesticide concentrations in sediments downstream Nairobi River with all the sampling sites reporting higher concentrations of OC compared to OP pesticides with the exception of Muthangari

Bridge. The increase in pesticide concentrations downstream may be contributed by intensive small scale riparian agriculture at Naivasha Road Bridge. Wash off of pesticide residues from large scale farms such as Magana flowers located up stream Muthangari Road Bridge could have resulted in enhanced pesticide concentrations at this site.

Considering the distribution of OC pesticides at the various sampling sites, p,p'-DDT had the highest average concentration of 638.07 µg/kg and dominated all the sites apart from Muthangari Bridge. This was followed in descending order by a-HCH, Endrin and Heptachlor at 287.11, 262.89 and 240.46 µg/kg respectively. Dominance of DDT in the sediments may be due to the slow degradation of DDT or recent input of DDT in the environment.

Chorpyrifos had the highest occurrence amongst the OP pesticides with an average concentration of 883.56 µg/kg, followed in descending order by Malathion and Diazinon at concentrations of 620.55, 234.59 µg/kg, respectively. Chlorpyrifos, a phosphorothiote broad spectrum moderately toxic insecticide remains one of the most widely used in agriculture and public health. Chlorpyrifos inhibits acetylcholinestrase (AChe) and alters haematological parameters (Ambali et al, 2010)

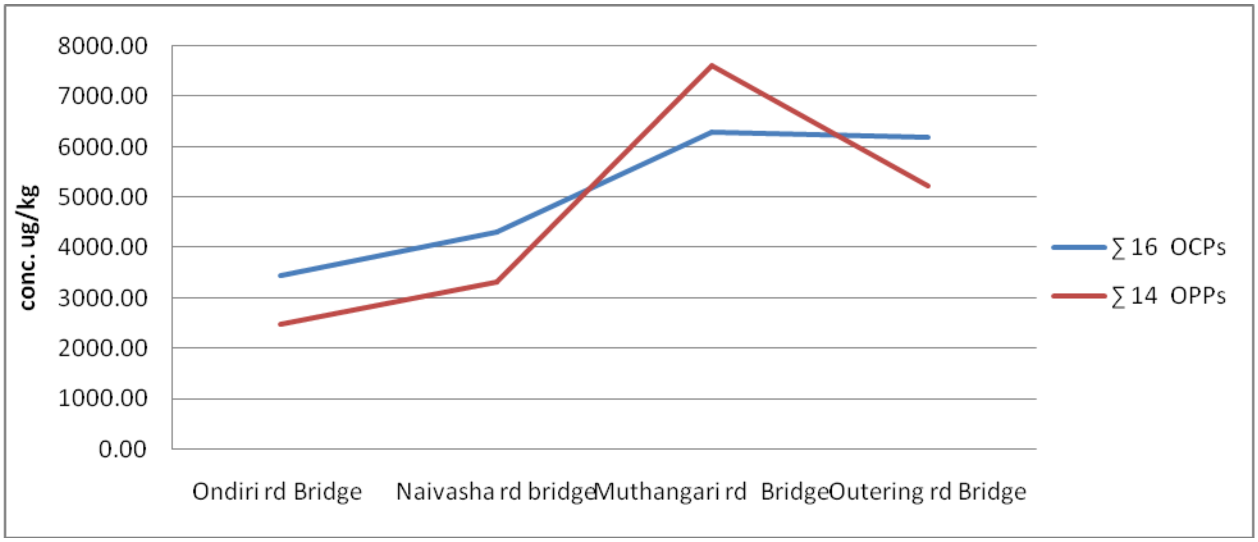

Figure 4.11: Spatial distribution of ∑OCP and ∑OPP in sediments.

### 4.3 Pesticides in water samples from Nairobi River.

The results of OC and OP pesticides in river water during the wet and dry seasons are tabulated in table 4c and 4d below. All the 16 OC pesticides were detected at all the four sites with concentrations ranging from 0.03-12.77 µg/l at Ondiri, 0.04-15.20 µg/l at Naivasha bridge, 0.02-5.29 µg/l at Muthangari bridge and 0.03-31.79 µg/l at Outering bridge site. p,p'-DDT had the highest occurrence of 28% with the highest concentration recorded at Outering Bridge during the dry season. This was followed by Endrin at a frequency of 27% also recording the highest concentration during the dry season at Outering Bridge. Endosulfan sulphate, Methoxychlor and o,p' DDD had the least frequencies at 0.3% for each pesticide. Generally higher pesticide concentrations were recorded in the dry season compared to wet season.

All 14 OP pesticides investigated at the 4 sites were detected with concentrations ranging from 0.04-11.65 µg/l at Ondiri, 0.02-17.05 µg/l at Naivasha Bridge, 0.03-44.99 µg/l at Muthangari Bridge and 0.05-38.55 µg/l at Outering Bridge. Ethoprophos, an organophosphate used against nematodes and soil insect pests had the highest concentration of 44.99 ±6.51 µg/l, recorded at Muthangari Bridge during the wet season. Ethoprophos, Malathion, Chlorpyrifos, Pirimiphos methyl and Diazinon were recorded in descending order of average concentrations at all the sampling sites with occurrences of 58.7%, 12.3%, 9.6% 4.4% and 5.5%, respectively. Higher concentrations of OP pesticides were recorded in the wet season compared to the dry season. Seasonal variations in OC and OP pesticide concentrations in the sampling sites are discussed in sections 4.3.1 to 4.3.4.

Table 4c: Levels of OC Pesticides in Nairobi River water in µg/L ± SD.

| **Pesticides** | **Ondiri swamp µg/l** | | **Naivasha Bridge µg/l** | | **Muthangari Bridge µg/l** | | **Outering Bridge µg/kg** | | **Average (Wet+Dry) µg/kg** |
|---|---|---|---|---|---|---|---|---|---|
| | **Wet** | **Dry** | **Wet** | **Dry** | **Wet** | **Dry** | **Wet** | **Dry** | |
| **a-HCH** | 0.37±0.12 | 0.10±0.07 | 1.72±0.23 | 0.28±0.10 | 0.70±0.57 | 0.35±0.27 | 0.21±0.20 | 2.25±1.05 | 0.75±0.79 |
| **b-HCH** | 1.22±0.75 | 0.28±0.24 | 1.57±0.24 | 0.44±0.42 | 2.03±1.75 | 0.35±0.28 | 0.75±0.68 | 6.33±0.73 | 1.62±2.00 |
| **g-HCH** | 0.66±0.52 | 0.23±0.22 | 0.62±0.43 | 0.51±0.42 | 0.86±0.81 | 0.65±0.13 | 0.66±0.30 | 5.02±3.64 | 1.15±1.57 |
| **d-HCH** | 0.82±0.66 | 0.26±0.22 | 0.75±0.11 | 0.18±0.15 | 0.20±0.19 | 0.64±0.58 | 0.34±0.23 | 0.99±0.41 | 0.52±0.31 |
| **Heptachlor** | 0.80±0.06 | 0.25±0.08 | 0.14±0.13 | 0.19±0.08 | 0.31±0.27 | 0.89±0.76 | 0.27±0.21 | 2.30±1.89 | 0.64±0.73 |
| **Aldrin** | 2.98±0.86 | 0.23±0.03 | 1.00±0.23 | 0.41±0.08 | 0.98±0.04 | 1.09±1.01 | 0.17±0.15 | 0.59±0.47 | 0.93±0.90 |
| **Heptachlor epoxide** | 3.81±1.61 | 0.43±0.20 | 3.01±2.29 | 0.73±0.03 | 0.67±0.07 | 0.78±0.66 | 0.28±0.27 | 4.42±3.68 | 1.77±1.69 |
| **o,p'-DDE** | 2.48±1.18 | 0.38±0.07 | 2.18±2.09 | 1.25±0.45 | 0.67±0.58 | 3.00±0.22 | 0.79±0.57 | 3.47±0.94 | 1.78±1.16 |
| **Alpha endosulfan** | 1.26±0.87 | 0.13±0.05 | 1.66±1.56 | 0.50±0.46 | 0.40±0.19 | 0.75±0.69 | 0.17±0.16 | 2.63±1.51 | 0.94±0.87 |
| **p,p'-DDE** | 0.26±0.05 | 0.05±0.02 | 0.14±0.23 | 0.10±0.10 | 0.09±0.01 | 0.20±0.03 | 0.05±0.04 | 19.06±3.18 | 2.49±6.70 |
| **Endrin** | 12.77±5.31 | 1.15±0.47 | 6.51±2.29 | 6.21±1.33 | 1.64±0.72 | 1.79±1.62 | 1.63±1.34 | 31.79±27.84 | 7.94±10.42 |
| **beta endosulfan** | 1.50±0.67 | 0.07±0.05 | 1.19±0.29 | 0.37±0.18 | 0.40±0.03 | 0.19±0.12 | 0.16±0.15 | 0.95±0.67 | 0.60±0.54 |
| **o,p'-DDD** | 0.13±0.10 | 0.03±0.01 | 0.16±0.12 | 0.06±0.05 | 0.06±0.06 | 0.08±0.07 | 0.04±0.04 | 0.27±0.19 | 0.10±0.08 |
| **Endosulfan sulphate** | 0.12±0.06 | 0.08±0.06 | 0.05±0.04 | 0.08±0.07 | 0.04±0.03 | 0.09±0.07 | 0.03±0.02 | 0.16±0.04 | 0.08±0.04 |
| **p,p'-DDT** | 9.26±2.15 | 1.80±0.84 | 15.20±4.20 | 4.83±1.08 | 2.85±0.49 | 5.29±4.53 | 2.14±0.11 | 26.11±19.27 | 8.44±8.42 |
| **Methoxychlor** | 0.23±0.06 | 0.04±0.01 | 0.13±0.08 | 0.04±0.04 | 0.02±0.01 | 0.05±0.05 | 0.03±0.02 | 0.11±0.06 | 0.08±0.07 |
| **∑ 16 OCPs** | 38.6±63.58 | 5.51±0.47 | 36.01±3.81 | 16.19±1.80 | 11.90±0.80 | 16.19±1.37 | 7.73±0.61 | 106.46±9.88 | 29.83±2.56 |

N=3

Table 4d. Levels of OP Pesticides in Nairobi River Sediments in µg/kg ± SD

| | **Ondiri swamp µg/l** | | **Naivasha Bridge µg/l** | | **Muthangari Bridge µg/l** | | **Outering Bridge µg/l** | | **Average (Wet+Dry) µg/kg** |
|---|---|---|---|---|---|---|---|---|---|
| **Pesticides** | **Wet** | **Dry** | **Wet** | **Dry** | **Wet** | **Dry** | **Wet** | **Dry** | |
| **Dichlorvos** | 0.11±0.09 | 0.15±0.15 | 0.05±0.05 | 0.13±0.11 | 0.17±0.04 | 0.26±0.14 | 0.14±0.13 | 0.17±0.17 | 0.15±0.06 |
| **Mevinphos** | 0.28±0.18 | 0.11±0.11 | 0.22±0.10 | 0.10±0.02 | 0.96±0.54 | 0.10±0.06 | 3.24±0.21 | 0.64±0.02 | 0.71±1.07 |
| **Ethoprophos** | 4.65±0.89 | 2.65±0.23 | 1.70±0.25 | 17.05±2.94 | 44.99±6.51 | 6.49±1.10 | 37.59±5.46 | 38.55±6.59 | 19.21±18.27 |
| **Cadusafos** | 0.59±0.01 | 0.26±0.03 | 0.27±0.14 | 0.33±0.06 | 0.85±0.27 | 0.83±0.43 | 1.11±1.03 | 1.60±0.74 | 0.73±0.47 |
| **Dimethoate** | 0.61±0.01 | 0. 46±0.39 | 0.11±0.08 | 0.12±0.11 | 0.34±0.18 | 0.56±0.09 | 1.27±1.00 | 0.83±0.36 | 0.54±0.38 |
| **Diazinon** | 0.22±0.13 | 0.81±0.13 | 1.62±0.74 | 0.09±0.01 | 2.07±0.26 | 0.22±0.05 | 0.48±0.19 | 5.92±1.02 | 1.43±1.95 |
| **Dichlorofenthion** | 0.01±0.02 | 0.05±0.01 | 0.02±0.02 | 0.02±0.02 | 0.03±0.04 | 0.06±0.02 | 0.05±0.04 | 0.05±0.02 | 0.05±0.03 |
| **Chlorpyrifos methyl** | 0.07±0.01 | 0.04±0.03 | 0.03±0.01 | 0.03±0.03 | 0.12±0.02 | 0.07±0.04 | 0.15±0.11 | 0.21±0.13 | 0.09±0.06 |
| **Pirimiphos methyl** | 0.27±0.05 | 0.06±0.06 | 0.05±0.04 | 0.05±0.02 | 0.10±0.09 | 0.06±0.02 | 13.69±2.36 | 0.07±0.06 | 1.79±4.81 |
| **Malathion** | 11.65±0.13 | 4.39±3.83 | 4.21±0.93 | 0.51±0.18 | 2.45±0.90 | 5.42±0.30 | 1.47±1.05 | 2.05±0.44 | 4.02±3.50 |
| **Chlorpyrifos** | 4.94±0.85 | 0.94±0.12 | 2.55±0.27 | 0.23±0.04 | 8.32±8.88 | 1.94±0.34 | 2.77±0.24 | 3.41±0.79 | 3.14±2.55 |
| **Methidathion** | 0.60±0.15 | 0.46±0.46 | 0.28±0.20 | 0.26±0.04 | 0.55±0.50 | 0.29±0.11 | 0.17±0.09 | 0.27±0.16 | 0.36±0.16 |
| **Ethion** | 0.16±2.13 | 0.15±3.83 | 0.09±0.69 | 0.13±0.08 | 0.11±0.90 | 0.31±0.30 | 0.12±0.65 | 0.34±0.44 | 0.17±0.10 |
| **Triazophos** | 0.62±0.35 | 0.40±0.33 | 0.19±0.13 | 0.40±0.06 | 0.34±0.30 | 0.43±0.17 | 0.19±0.15 | 0.27±0.17 | 0.35±0.14 |
| **∑ 14 OPPs** | 24.87±3.27 | 10.95±1.24 | 11.38±1.26 | 19.44±4.51 | 61.39±11.89 | 17.05±2.08 | 62.45±10.17 | 54.37±10.11 | 32.74±5.0 |

N=3

### 4.3.1 Seasonal variation in OC and OP pesticide residues in water samples at Ondiri Swamp.

OC pesticides at Ondiri swamp ranged from 0.03 µg/l to 12.77 µg/l as shown in Figure 4.12. Endrin recorded the highest concentration during the wet season followed by p,p'-DDT, 9.26±2.15 µg/l, also recorded during the wet months (March, April, June). o,p'-DDD, Methoxychlor, p,p'-DDE, Beta endosulfan and Endosulfan Sulphate had the least concentrations at 0.03±0.01 µg/l, 0.04±0.01 µg/l, 0.05±0.02 µg/l, 0.07±0.05 µg/l and 0.08±0.06 µg/l, respectively. Presence of p,p'-DDT at higher levels compared to its breakdown products (o,p'-DDD)indicates recent use of this pesticide. Endrin has been used as an agricultural insecticide on tobacco, apple trees, cotton, sugar cane and grain, as well as to control rodents and birds, thus its presence at the Ondiri swamp may be due to anthropogenic activities characterized by intensive vegetable farming at this site. In General, the water samples collected at Ondiri site showed higher organo chlorine pesticide residue concentrations in the wet than in dry season due to the strong wash-out of residues from surrounding agricultural activities undertaken at this site during the rainy season.

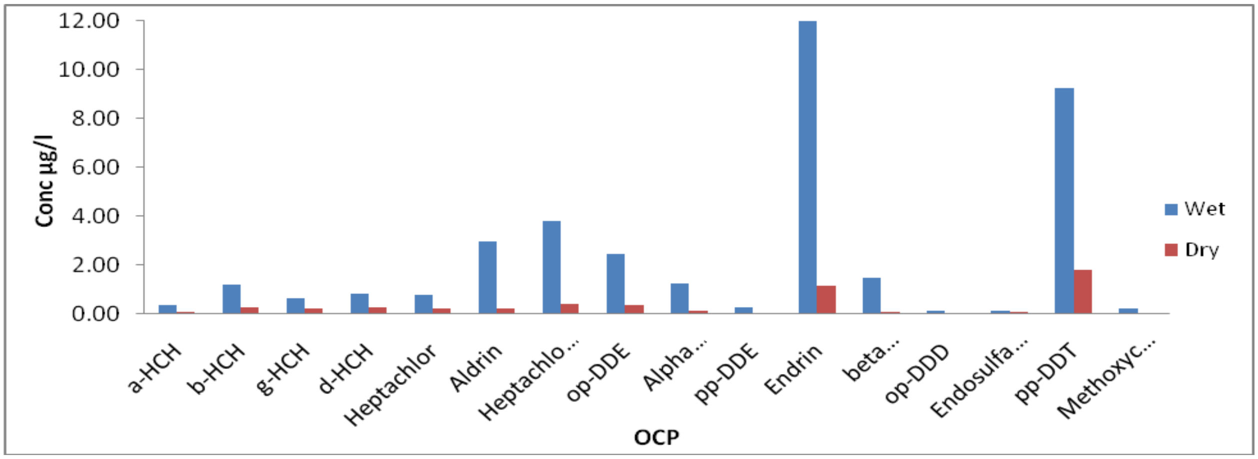

Figure 4.12: Seasonal variation of OC pesticides at Ondiri Swamp

All the 14 OP pesticides investigated during the period as shown in Figure 4.13 were detected with concentrations ranging from 0.01 µg/l to 11.45 µg/l. The OP pesticides detected in descending concentration were, Malathion> Ethoprophos> Chlorpyrifos> Dimethoate> Diazinon. Malathion is a broad spectrum organophosphate insecticide which combines contact, stomach and respiratory action for the control of pests like thrips, aphids, leaf miner, scales, and mealy bugs on vegetables, fruits and flower (PCPB, 2010). Ondiri swamp is characterized by small-scale horticultural activities which include growing of kale, tomatoes, cabbages, maize and onions and this may explain the high levels of Malathion in water detected at this site.

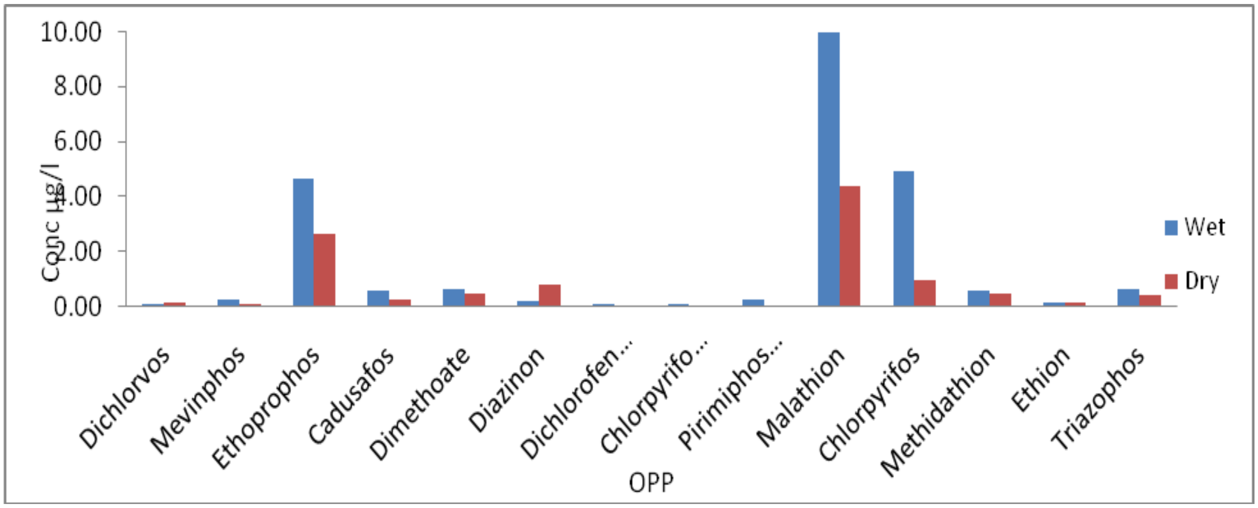

Figure 4.13: Seasonal variation of OP pesticides at Ondiri swamp**.**

### 4.3.2 Seasonal variation in OC and OP pesticide residues in water samples at Naivasha Bridge.

At this site all the 16 OC pesticides were detected as shown in Fig 4.14 and an elevation in concentrations was evident compared to Ondiri swamp, especially during the dry season. p,p'-DDT was dominant with a concentration of 15.20±4.20 µg/l with Endrin recording the second highest concentration of 6.51±2.29 µg/l. Naivasha Road Bridge is the second site from the source of Nairobi River and has floricultural and agricultural activities concentrated on the riparian land, notable farms includes Magana Flowers which is upstream this site. On average the ∑ 16 OCPs during the wet season was 2.1 times higher than during the dry season, an indication of pesticides wash-off from agricultural farms during the heavy rains in March, April and June.

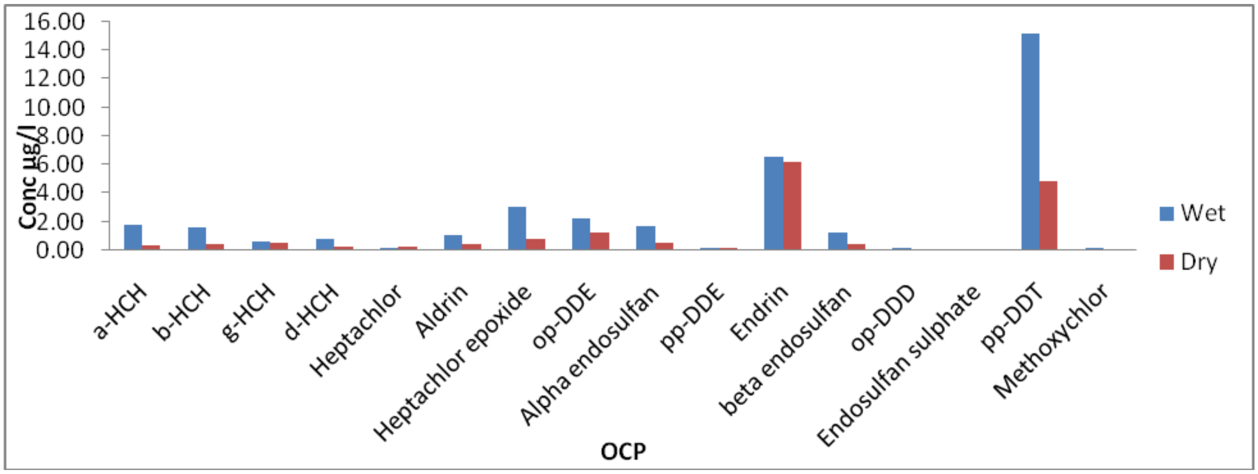

Figure 4.14: Seasonal variation of OC pesticides at Naivasha Road Bridge.

Ethoprophos as shown in Fig 4.15 had the highest concentration of 17.05±2.94 µg/l, amongst the OP pesticides at Naivasha Bridge during the dry season, followed by Malathion, Chlorpyrifos and Diazinon in descending order. The sharp increase in concentration of Ethoprophos, a nematicide may be attributed to release by farms upstream this site. The ∑ 14 OPPs during the dry season were higher compared to the wet season at this site.

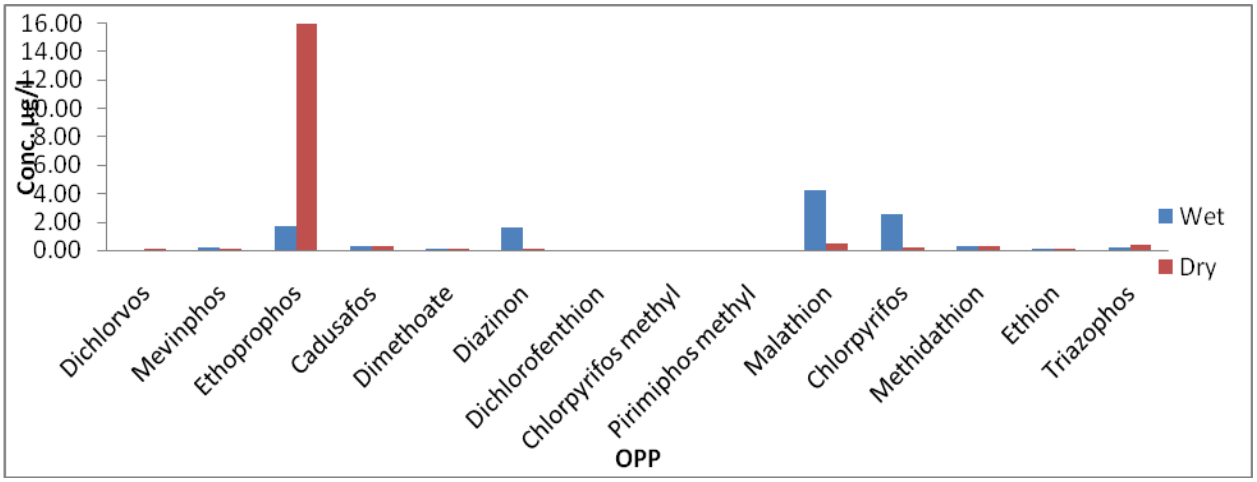

Figure 4.15: Seasonal variation of OP pesticide residues in water at Naivasha Road Bridge.

### 4.3.3 Seasonal variation in OC and OP pesticide residues in water samples at Muthangari Bridge.

The OC pesticides at Muthangari Bridge as shown in figure 4.16 ranged from 0.04 µg/l to 15.20 µg/l, with p,p'-DDT recording the highest concentration, p,p'-DDT and metabolites (o,p'-DDE, p,p'-DDE, o,p'-DDD) constituted 43 % of the ∑OCPS detected at this site. The high concentration of DDTs is indicative of recent use of this pesticide.

HCH is available in two formulations: technical HCH and Lindane. In this study amongst the HCHs, the following composition of HCH isomers was evident, a-HCH 18%, b-HCH 41%, g-HCH 26% and d-HCH 15%. b-HCH had the highest concentration of 0.86 µg/l recorded during the wet season. Recent use of Technical HCH and Lindane could not be ascertained from the results. At this site the ∑OCPS were higher during the dry season compared to the wet season.

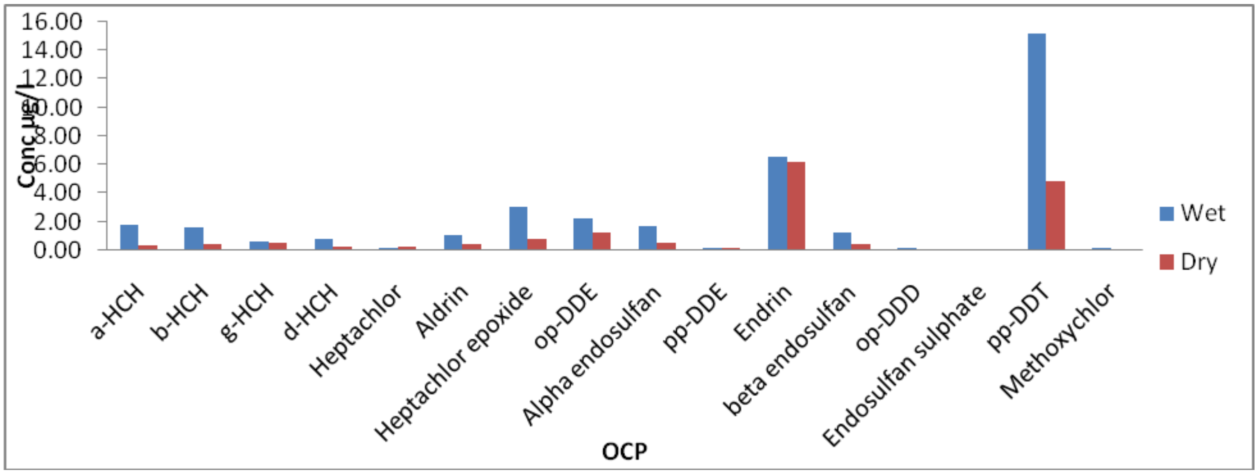

Figure 4.16 Seasonal variation of OC pesticides in water samples at Muthangari Road Bridge

All 14 OP pesticides were detected at this site as evident from Figure 4.17. The concentrations ranged from 0.06 µg/l to 44.99 µg/l. Ethoprophos had the highest occurrence constituting, 66% of the ∑ OPPs studied at this site during the period, followed by Chlorpyrifos 13% and Malathion 10%. Chlorpyrifos methyl, pirimiphos methyl, and dichlorofenthion had the least occurrences at 0.25%, 0.21% and 0.12%, respectively.

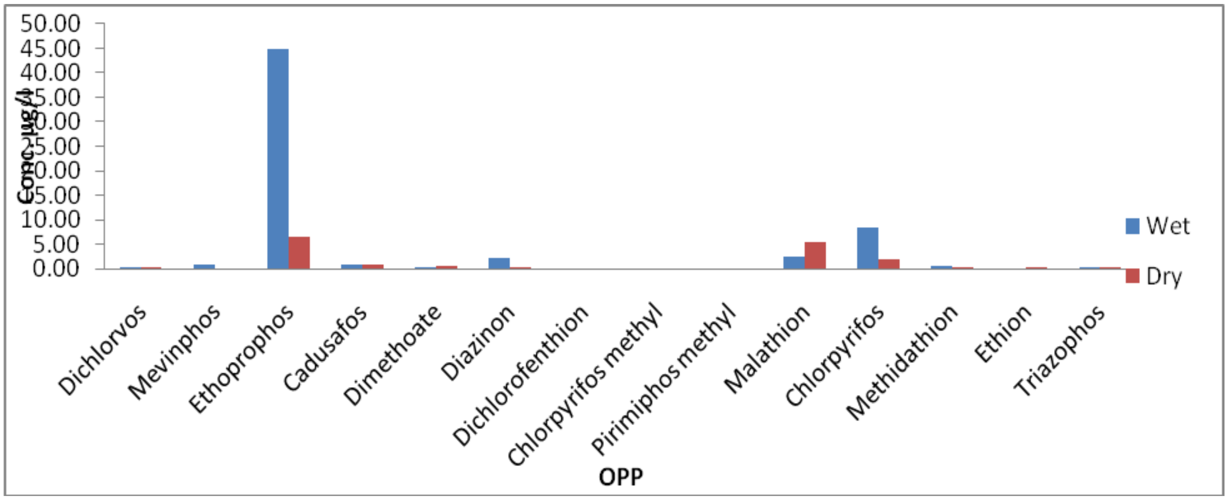

Figure 4.17: Seasonal variation of OP pesticides residues in water samples at Muthangari Road Bridge

### 4.3.4 Seasonal variation in OC and OP pesticide residues in water samples at Outering Bridge

All the 16 OC pesticides were detected at this site during the wet and dry season as shown in Figure 4.18. Endrin recorded the highest concentration, 31.79±27.84 µg/l followed by p,p’-DDT, p,p’-DDE and b-HCH having concentrations of 26.11±19.27 µg/l, 19.06±3.18 µg/l, and 6.33±0.73 µg/l, respectively. Significant concentrations of p,p’-DDT and its metabolite p,p’-DDE suggested recent use of this pesticide. Amongst the Hexachlorocyclohexanes (HCHs), b-HCH recorded the highest percentage composition representing 75% of the total HCHs. This can be attributed to the relative instability of g-HCH in the environment, which is easily metabolized to b-HCH (W. Qu, et al., 2010). Therefore, b-HCH is the main isomer determined in most water samples.

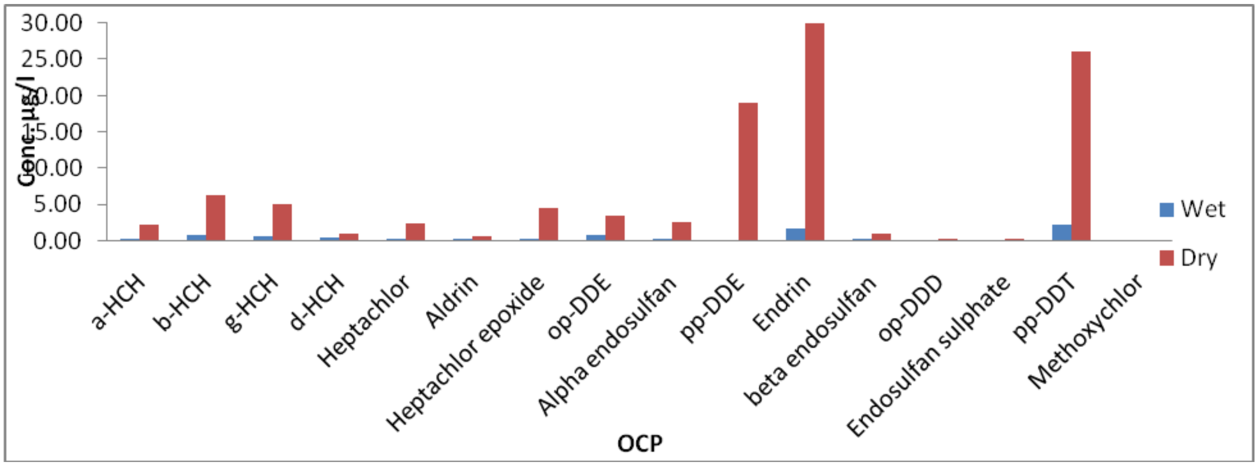

Figure 4.18: Seasonal variation of OC pesticides in water samples at Outering Road Bridge.

Amongst the 14 OP pesticides (figure 4.19), Ethoprophos recorded the highest concentrations during the wet and dry season at 37.59±5.46 µg/l and 38.55±6.59 µg/l, respectively. This was the highest level recorded at all the sites, signifying an increase in concentration downstream. In descending order of concentrations Pirimiphos methyl, Diazinon, Chlorpyrifos, and Malathion, were also recorded. The dry season recorded higher ∑ 14 OPPs concentrations compared to the wet season at 62.45±10.17 µg/l and 54.37±10.11 µg/l, respectively. The high levels were due to wash off of pesticides, from agricultural and industrial activities upstream this site.

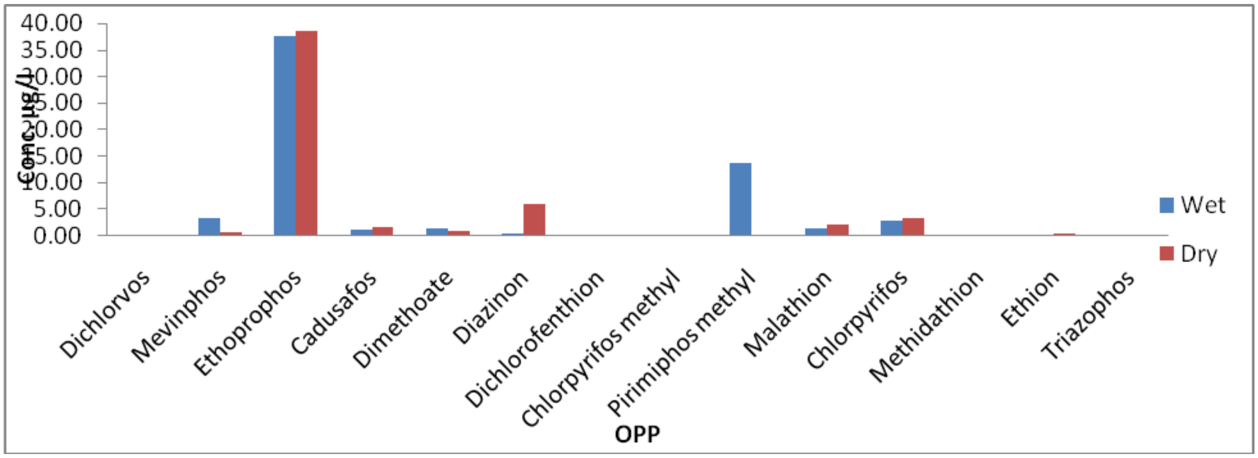

Figure 4.19: Seasonal variation of OP pesticide in water at Outering Road Bridge

### 4.3.5: Spatial variation of OC and OP pesticides in Nairobi River Water

All the 4 sampling sites recorded both OC and OP pesticides ranging in concentrations between 0.02-15.20 µg/l and 0.04-31.79 µg/l during the wet and dry seasons, respectively. The DDTs (p,p'-DDT, o,p'-DDE, o,p'-DDD, p,p'- DDE) recorded the highest occurrence of 43%, with p,p'-DDT having the highest concentration across all the sampling sites with an average concentration of 8.44±0.75 µg/l compared to the other pesticides. Aldrin and Endrin constituted 30% of pesticides detected during the study. Aldrin recorded relatively higher concentrations, at 7.94± 1.24 µg/l. 5% of the OC pesticides constituted the HCHs (a-HCH, b-HCH, g-HCH, and d-HCH); with b-HCH dominating with an average concentration of 1.62± 2.22 µg/l. Heptachlor and Heptachlor epoxide comprised 8% of the total OC pesticides. Elevated levels of p,p'-DDT especially during the wet season may be attributed to its use in mosquito malaria vector control as recommended by public health. Aldrin is used to control termite and it was detected in variable amounts in all the sites. Comparatively the concentrations of its breakdown product, Endrin were higher by 9 times and this indicated previous use of Aldrin at this locations. Dominance of b- HCH in this study is consistent with studies that indicate that it is the most persistent and bio accumulative amongst the other HCH isomers (Yang et al, 2005b). The least recorded OC pesticide residues were Endosulfan sulphate and methoxychlor with concentrations of 0.08± 0.05 µg/l and 0.08± 0.06 µg/l, respectively. There was steady increase in ∑OCPs downstream, as shown in Figure 4.20 and 4.21

Ethroprophos is a soil applied insecticide nematicide for use in bananas, maize, tobacco, ornamentals, potatoes, pyrethrum, sugarcane and vegetables. Ethoprophos dominated most sampling sites, recording an average concentration of 19.21± 18.20 µg/l., this represented 59% of ∑OPPs investigated in the study.

The relatively high level of leaching of Ethoprophos is consistent with its high solubility, 750 mg /l which is an important factor in the leachability of insecticides (Nicholls, 1988). Therefore, 30% of the applied Ethoprophos is likely to be removed by runoff to rivers depending upon the distance of the water body from the site of application.

Malathion and Chlorpyrifos recorded relatively higher levels amongst the OP pesticides. The average concentration of Malathion was 1.2 times higher than Chlorpyrifos. The compounds are registered in Kenya by PCPB as insecticides for use on a wide range of crops; agricultural and horticultural Chlorpyrifos is a priority pollutant in the European Water Framework Directive 2000/60/CE (Robles Molina et al 2012). Chlorpyrifos adsorbs to suspended solids and sediment and this makes it susceptible to movement to waterways via surface runoff (Wightwick and Allinson, 2007).

The study indicated chlorpyrifos levels ranged from 2.55 to 8.32 µg/l during the wet season and 0.23 to3.41 µg/l, during the dry season. The reported levels were lower compared to studies by Otieno et.al, (2012) in Lake Naivasha, with reported mean concentration of Chlorpyrifos ethyl in water in wet season ranging between 8.8 µg/l and 6.6µg/l and decreased to between below detection limit to 14.0µg/L in the dry season. Notably, levels of Chlorpyrifos were higher than the maximum allowable limits (0.1µg/L) recommended by European Union for drinking water and general water quality criterion for protection of freshwater water organisms (0.083µg/L). Generally OP concentrations increased downstream Nairobi River, with the wet season recording comparatively higher ∑OPPs concentrations than dry season at 40.02± 25.88 µg/L and 25.45± 19.60 µg/L, respectively. ∑OPPs recorded during the study in river water were 1.1 times higher than ∑OCPs, indicating significant contribution of pesticides load in water from riparian agricultural activities and effluent from agrochemical industries downstream Nairobi River.

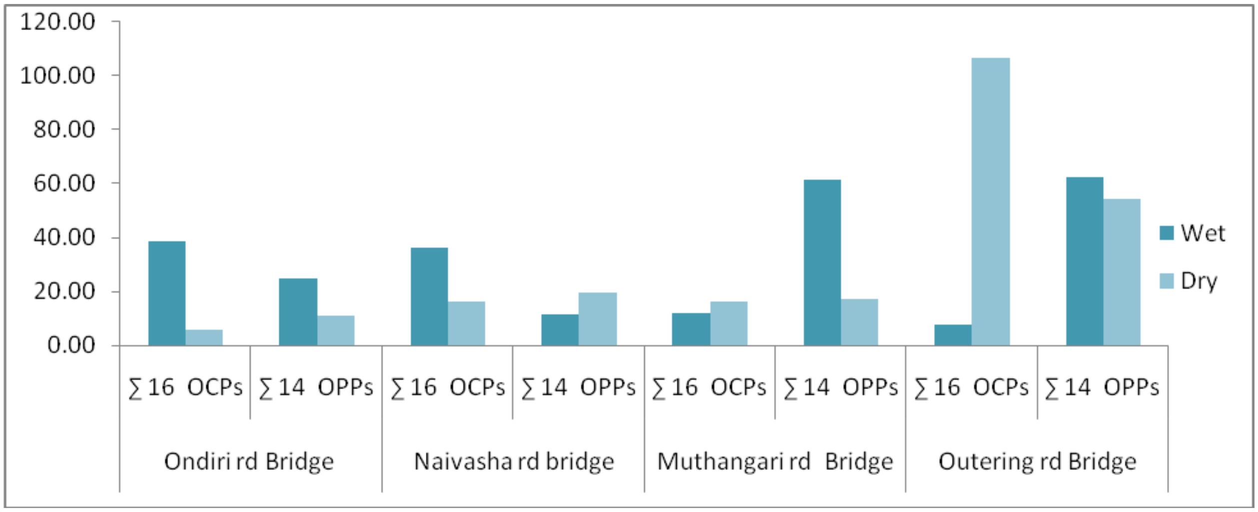

Fig 4.20: Seasonal distribution of ∑OCP and ∑ OPP in water.

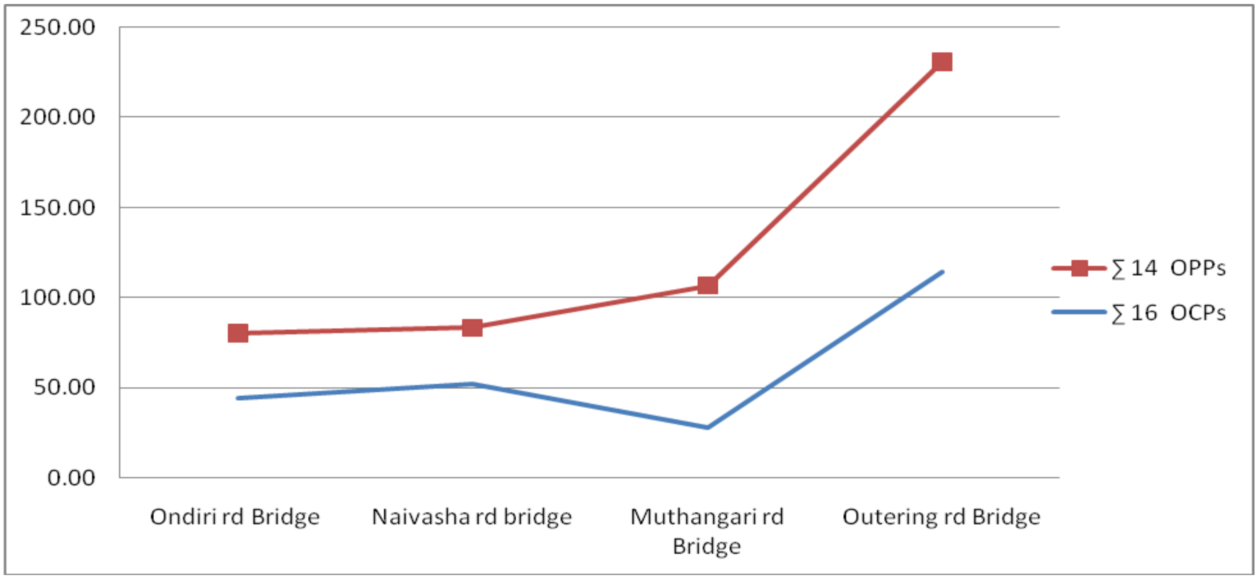

Figure 4.21: Spatial distribution of ∑OCP and ∑ OPP in water.

### 4.4. Physicochemical Parameters in Water and Sediments Samples

The parameters analysed in Nairobi river water and sediments included pH, Electro conductivity (EC), Total Suspended Solids (TSS) and Total Dissolved Solids (TDS). The samples represented 6 months of sampling which included both the wet (March, April, June) and dry (July August September) seasons. The results are as shown in Table 4.2.

Table 4.2: Physicochemical properties in sediments and water

| **Sites** | **Season** | **Water** | | | | **Sediments** |
|---|---|---|---|---|---|---|
| | | **TSS mg/l** | **pH** | **EC (µs/cm)** | **TDS(ppm)** | **TOC(%C)** |
| Ondiri | **Wet** | 30.9±22.6 | 7.6±0.3 | 432.5±193.3 | 289.8±129.5 | 3.0±2.0 |
| | **Dry** | 62.6±6.1 | 7.3±0.4 | 238.2±36.1 | 159.6±24.2 | 3.0±1.0 |
| Naivasha Bridge | **Wet** | 106.9±18.9 | 7.7±0.3 | 616.5±44.2 | 413.0±29.6 | 1.2±0.6 |
| | **Dry** | 251.1±42.4 | 7.4±0.5 | 603.9±5.6 | 404.6±3.8 | 1.9±0.2 |
| Muthangari Bridge | **Wet** | 62.8±6.9 | 7.6±0.4 | 777.1±41.3 | 520.6±27.7 | 1.7±0.8 |
| | **Dry** | 161.8±39.8 | 7.2±0.3 | 736.5±68.8 | 493.5±46.1 | 1.8±1.2 |
| Outering Bridge | **Wet** | 135.4±61.2 | 7.7±0.2 | 721.9±47.8 | 483.7±32.0 | 1.5±0.9 |
| | **Dry** | 141.5±25.7 | 7.1±0.2 | 967.1±50.0 | 647.9±33.5 | 1.3±1.3 |

N=3

### 4.4.1 pH of Nairobi River Water

The pH of Nairobi river water ranged between 7.1 and 7.6 as shown in fig 4.22. There was a slight decrease in the pH values from Ondiri swamp to Outering bridge sampling points. Naivasha Bridge and Outering recorded the highest average pH at 7.7 during the wet season while Outering Bridge, Muthangari Bridge and Ondiri swamp recorded the lowest average pH at 7.1, 7.2 and 7.3 respectively. In general higher pH values were recorded in the wet season compared to the dry season. However, the pH of Nairobi River was found to be within the EU permissible levels of 6.5-8.5 for drinking water in both wet and dry seasons

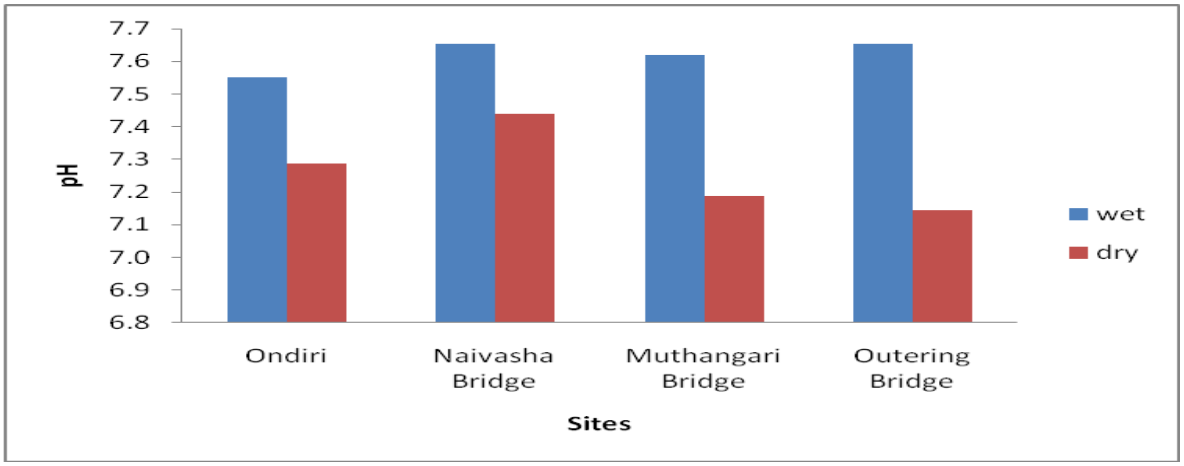

Figure 4.22: Average pH values of water from Nairobi River

### 4.4.2 Electrical Conductivity (EC) and Total Dissolved Solids (TDS) in water

The Electrical Conductivity values of water ranged from 432.5 to 771.1 µS/cm and 238.2 to 967.1 µS/cm during the wet and dry seasons.,The lowest average levels were recorded at Ondiri swamp and the highest at Outering bridge as shown in figure 4.23 as expected. The increasing concentrations downstream in both wet and dry seasons indicate that dissolved ions were being dicharged into the river through surface runoff from farming activities, surrounding industries and domestic effluents. This was evident during samples collection where unregulated broken sewer lines and drains discharged directly into Nairobi river. All sampling sites recorded EC values within EPA guidelines on drinking water quality (1000µS/cm).

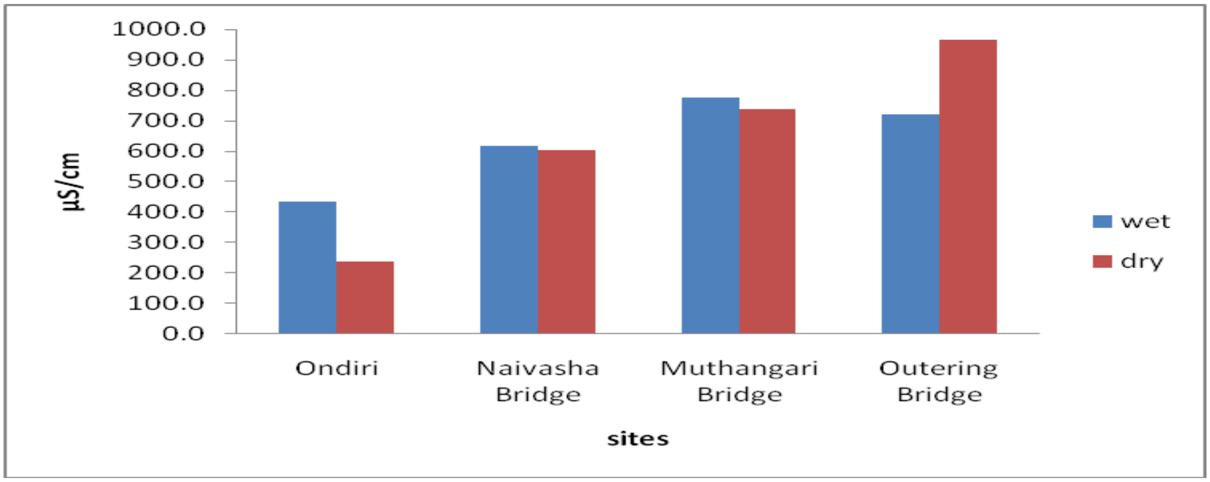

Figure 4.23: Average EC values of water samples from Nairobi River

On the other hand,total dissolved solids ranged from 289.8 to 520.6 ppm and 159.6 to 647.9 ppm during the wet and dry season, respectively as shown in fig 4.24. The lowest levels were recorded at Ondiri swamp and highest at Outering bridge. Most of the water samples had concentrations within the maximum WHO acceptable concentration of 600 ppm. However, Outering Bridge, during the dry season recorded average concentrations above the allowable limit. The high levels may be attributed to industrial discharge and concentration of wastes during the dry season (July, August and September).

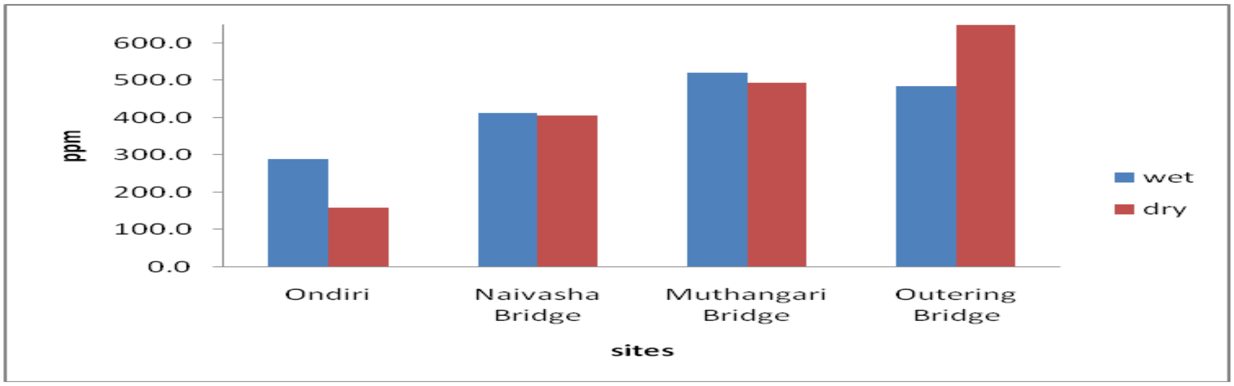

Figure: 4.24: Average TDS values of water samples from Nairobi River.

### 4.4.3 Total Suspended Solids (TSS)

The TSS values in water collected from the 4 sampling sites ranged from 30.9.to 135.4 mg/L and 62.6 to 251.1 mg/L during the wet and dry seasons,respectively.The TSS value were above the recommended limit of 30 mg/l as stipulated in Kenya environmental management and co-ordination (water quality) regulations, 2006. Ondiri swamp recorded the lowest average concentration during the wet season with Naivasha Bridge recording the highest concentration during the dry season as shown in figure 4.25. On average Naivasha bridge sampling site recorded comparatively high values of TSS, followed by Outering Bridge, Muthangari Bridge and Ondiri Bridge in descending order as shown in Fig 4.25.

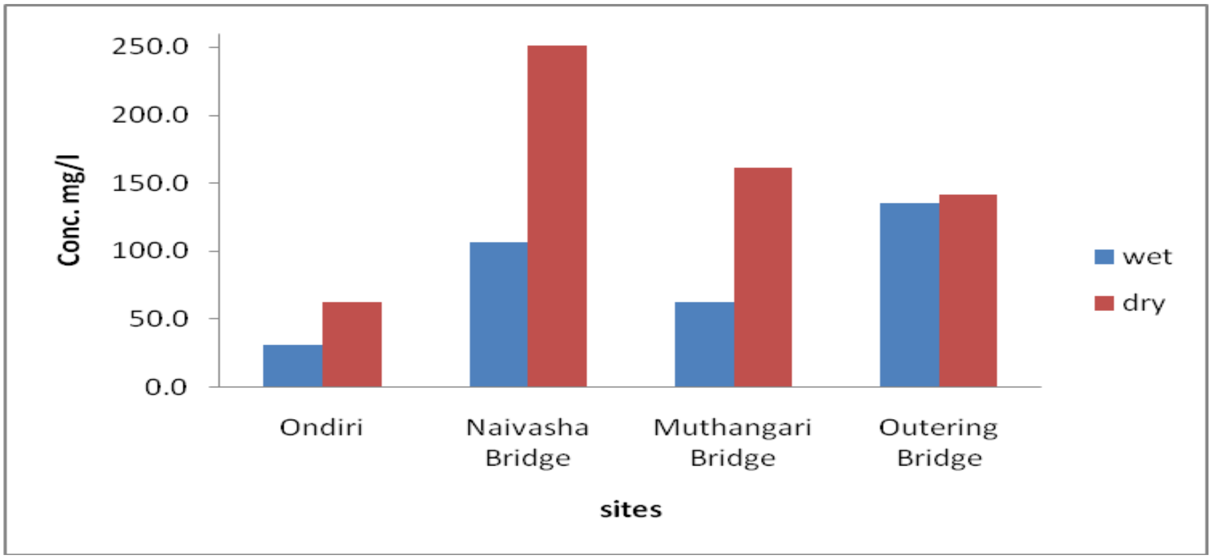

Figure 4.25: Average TSS Values in Water from Nairobi River (mg/l±SD)

### 4.4.4 Total Organic Carbon (TOC) in Sediments

The TOC values ranged from 1.3 to 3.0% and 1.2 to 3.0 % during the wet and dry seasons, respectively. The TOC concentrations in the 4 sites in descending order were Ondiri swamp 38%, Muthangari bridge 23%, Naivasha bridge 20% and Outering Bridge 19%. In general a decrease in TOC values was observed downstream the river and higher levels were recorded in the dry season compared to the wet season. Elevated TOC levels at Ondiri may be attributed to high content of organic matter from decaying detritus matter found in the swamp river channels.

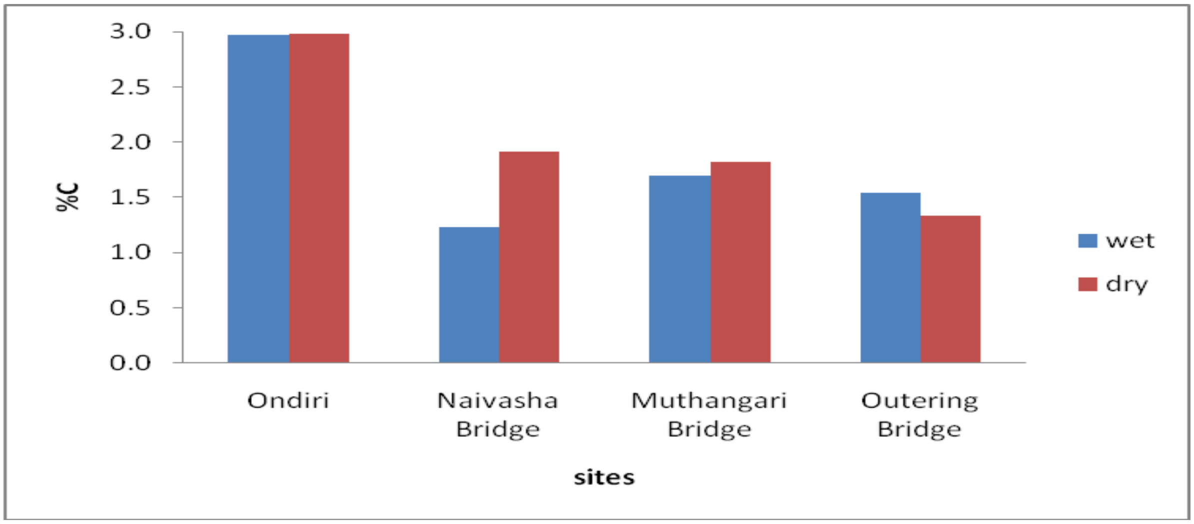

Figure 4.26: Average TOC values of sediments from Nairobi River.

### 4.5 Correlations of levels of pesticides in water and sediment

In this study OC and OP pesticides data in water and sediments was correlated with physicochemical properties namely TSS, TDS and TOC. Pearson's correlation values were computed, and temporal and spatial relationships derived between pesticides (∑17 OCPS, ∑ 14 OPPS), TDS and TSS in water samples. In sediment samples correlations were derived between pesticides (∑17 OCPS, ∑ 14 OPPS) and TOC. As shown in Appendix III table IVa, TDS in water gave the strongest correlation ($r=0.969$, $p<0.05$) with TSS having the weakest ($r=0.485$, $p>0.05$) across the 4 sampling sites. The positive r values indicates an increase in TDS downstream the river profile. Spatial correlations between ∑17 OCP, TDS and TSS were positive but weak at ($r=0.564,p>0.05$) and ($r=0.320$, $p>0.05$), respectively. Temporal correlations derived from ∑17

OCP, TDS and TSS during the 6 months sampling period were also positive but weak at ($r=0.485$, $p>0.05$) and ($r=0.424$, $p>0.05$) respectively as shown in table IVb.

Similar trends in p values were observed between ∑14 OPPS, TDS and TSS in water samples as shown in Appendix III,table IVc. TDS had a relatively stronger positive correlation ($r=0.818$, $p>0.05$) for ∑14 OPPS compared with similar comparison of ∑17 OCP ($r=0.485$, $p>0.05$). Some elements of TDS are pesticides and PCBs arising from surface runoff (Boyd, 1999) and the higher positive correlation between OP pesticides and TDS indicate higher relative solubility of OP pesticides in water compared to OC pesticides.

In sediments a strong positive correlation ($r=0.936$, $p>0.05$) was reported downstream the 4 sampling sites for ∑17 OCPS. A strong negative correlation ($r=-0,810$, $p>0.05$) for TOC indicated reduction in concentrations downstream the river as shown in table IVe. Correlation between ∑17 OCPS and TOC at the sampling sites indicates a strong indirect relationship ($p= -0.736$, $p>0.05$). However, a direct correlation ($r=0.586$, $p>0.05$) exists between temporal variations of ∑17 OCPS and TOC in sediment samples as given in table IVf. The same trend in correlation values was observed between ∑14 OPPS and TOC. However, weaker correlations in spatial and temporal values are reported for OP pesticides compared to OC pesticides as shown in table IVg and IVh respectively.

Inter matrix comparison of the pesticides (∑17 OCPS, ∑ 14 OPPS) in sediments and water indicated strong positive correlations between OC and OP pesticides in sediments ($r=0.905$, $p>0.05$) compared with equivalent values in water ($r=0.747$, $p>0.05$) as given in table IVi.

# CHAPTER FIVE

## CONCLUSIONS AND RECOMMENDATIONS

### 5.0 CONCLUSION

All the 16 OC pesticides and 14 OP pesticides consisting of a-HCH, b-HCH, g-HCH, d-HCH, Heptachlor, Aldrin, Heptachlor epoxide, o,p'-DDE, Alpa endosulfan, p,p'-DDE, Endrin, betaEndosulfan,o,p'-DDD,Endosulfansulphate,p,p'-DDT,Methoxychlor,Dichlorvos, Mevinphos, Ethoprophos Cadusafos, Dimethoate, Diazinon, Dichlorfenthion, Chlorpyrifos Methyl, Pirimiphos Methyl, Malathion, Chlorpyrifos, Methidathion, Ethion and Triazophos, were detected at varying concentrations in water and sediment samples in the 4 sampling sites. Seasonal variations in residues were also observed and this may have been attributed to the different chemical properties of the pesticides, point and non point sources of pesticides contamination including riparian agricultural activities along the river.

In sediments there was a general increase in concentrations downstream with Muthangari Bridge recording the highest pesticide concentrations. OC pesticides recorded 1.1 times higher average concentrations compared to OP pesticides and this may have been explained by the hydrophobic nature of OC pesticides which leads to higher affinity for sediment particles.

A similar trend of increase in pesticide concentration downstream was observed for water samples, however the relative quantities reversed with OP pesticides recording 1.1 times higher concentrations than OC pesticides, explaining the relatively higher solubility's of OP pesticides in water compared to OC pesticides.

Higher OP and OC pesticide concentrations were recorded during the wet season compared to the dry season in water samples but the trend reversed in sediment samples with higher concentrations being recorded in the dry season compared to the wet season. In general higher OC pesticides and OP pesticides concentrations were recorded in sediment compared to water samples. This is consistent with previous studies where Wandiga et al., [2002] has reported pesticides residues in sediments higher than those in water samples.

In sediments p,p’-DDT recorded t0he highest concentration amongst the OC pesticides followed in descending order by a-HCH, Endrin, Heptachlor epoxide, o,p’-DDE, g-HCH and b-HCH, Dominance of p,p’-DDT and Endrin residues may be explained by use of the products in public health and termite control, respectively. Chlorpyrifos was the dominant OP pesticide in sediments followed in descending order by Malathion and Diazinon. Chlorpyrifos has a lower solubility and high partition constant in organic carbon relative to Diazinon and Malathion (Panshin et al, 1998) and this explains its relatively higher abundance in sediment samples. These OP pesticides are relatively available and have a broad spectrum action for insect pests in a wide range of horticultural crops resulting in many small scale farmers using them, hence their high concentrations in sediment samples.

In water samples a similar trend was observed with p,p’-DDT being the dominant OC pesticide followed by Endrin. Ethoprophos had the highest concentration amongst the OP pesticides followed by Malathion and Chlorpyrifos. Dominance of Ethoprophos was attributed to its high solubility in water, 750 mg/l as compared to other OP pesticides. The high concentrations were attributed to agricultural activities up stream Nairobi River especially large flowers farms where Ethoprophos is used as a nematicide.

Some of the detected OC and OP pesticides during the study were above stipulated limits in drinking water of 0.5 µg/l (Total pesticides) and 0.1 µg/l (individual pesticides) as per EC directive 98/83/EC.

## 5.1 RECOMMENDATIONS

- The presence of OC and OP pesticides in the Nairobi river ecosystem indicates presence of point and non- point sources of pollution which may have adverse effects on humans and wildlife. Therefore, there is need for policy formulation to guide urban agricultural practices as well as industrial and domestic effluent management.
- A study on uptake of the pesticides detected in this study by plants should be explored; this will give the status of residues in food commodities from riparian agriculture and relative contributions of both direct and indirect applications of pesticides.
- There is need to conduct further studies on animal products including milk in the region to generate comparative pesticide residues data.
- Populations along the river may have high levels of pesticide contamination in their bodies resulting from the use of pesticides, drinking water, as well as consumption of contaminated produce. A study on these people is required to determine the levels of pesticide exposure and contamination.
- Further work on pesticide residues in water and sediments from Nairobi River should be conducted focusing on Ethoprophos, Diazinon, Malathion, Chlorpyrifos ,a-HCH, Endrin and pp-DDT. These pesticides were detected in significant amounts during the study.
- Remediation measures for cleaning and recycling surface water runoff and from agricultural farms and industrial establishments should be instituted before water is discharged to the river. There should be strict enforcement of laws and regulations on waste water treatments through use of soak pits and wetland construction, for industries and agricultural farms along the river profile.

- Policy framework should be instituted focussing on research and promotion on use of bio pesticides. Bio pesticides have strong specificity to target pests, safe to humans, animals and are pollution free.

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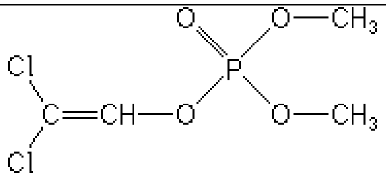
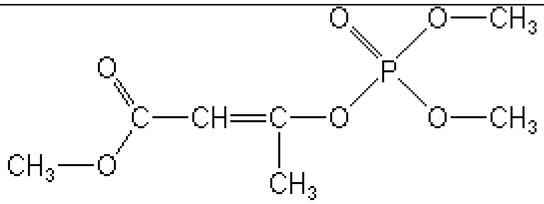
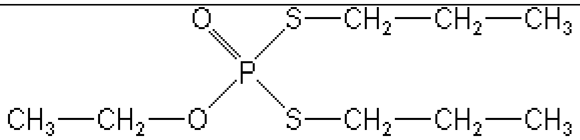
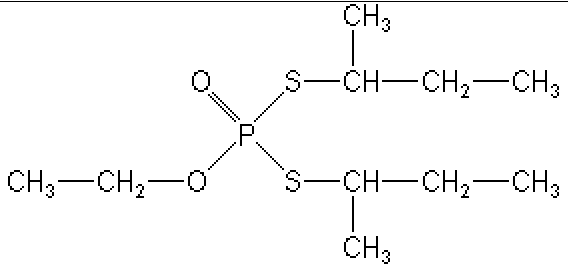
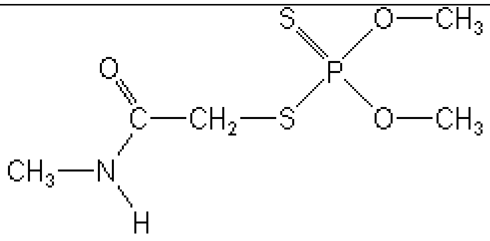
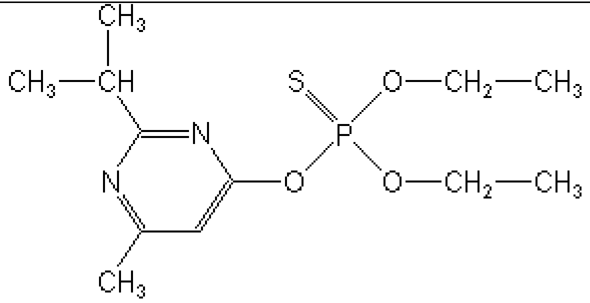
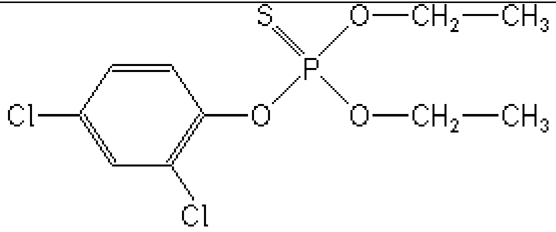
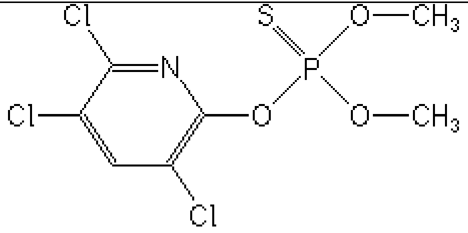
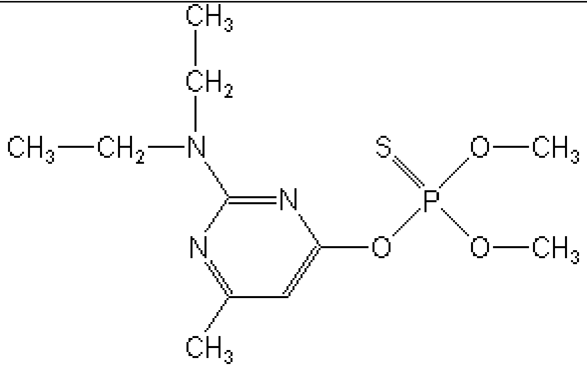
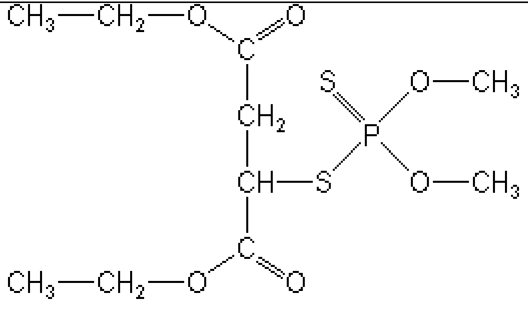
# APPENDICES

## Appendix I: Structures of pesticides

Table Ia: Structures of Organophosphates pesticides

| **Name** | **Structure** |
|---|---|
| **Dichlorvos** |  |
| **Mevinphos** |  |
| **Ethoprophos** |  |
| **Cadusafos** |  |
| **Dimethoate** |  |

| Name | Structure |
|---|---|
| **Diazinon** |  |
| **Dichlorofenthion** |  |
| **Chlorpyrifos methyl** |  |
| **Pirimiphos methyl** |  |
| **Malathion** |  |

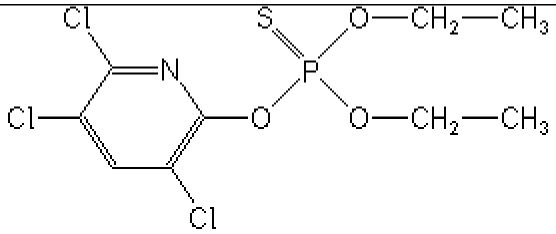
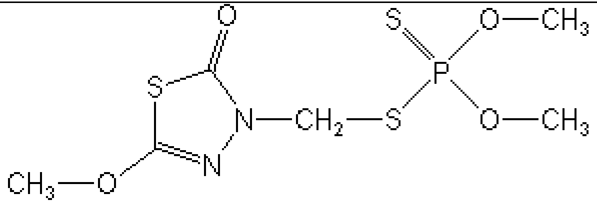
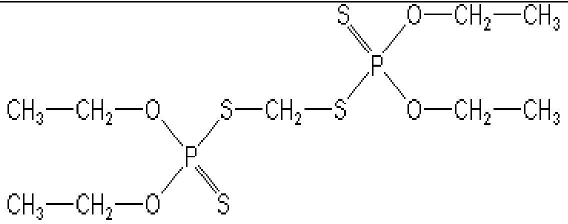
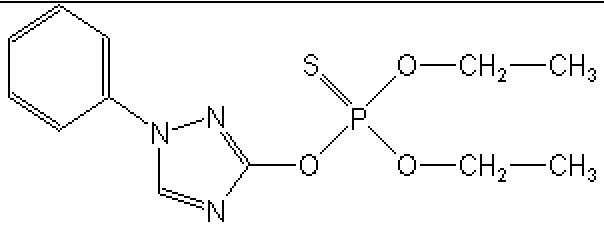
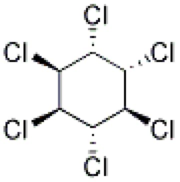
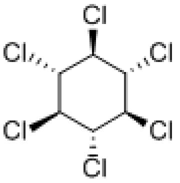
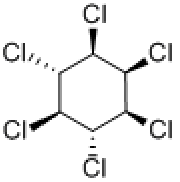
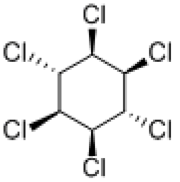
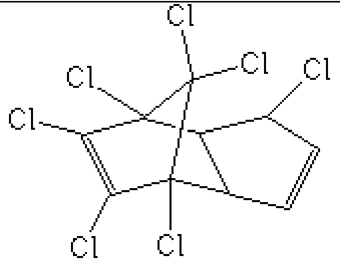
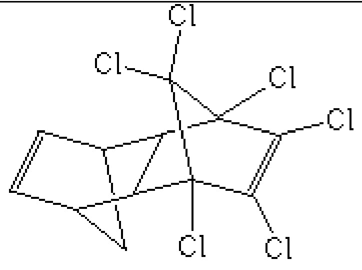
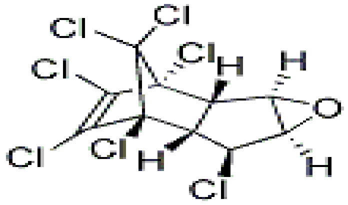
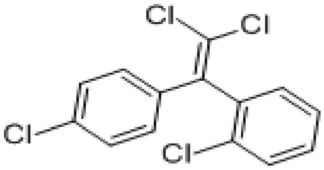
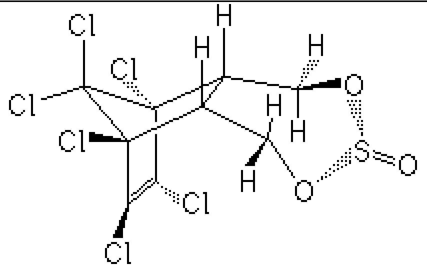
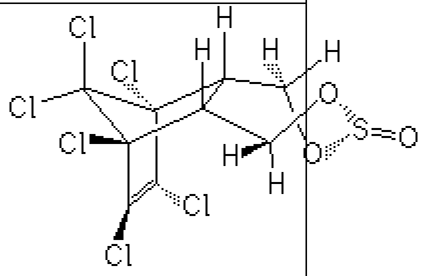
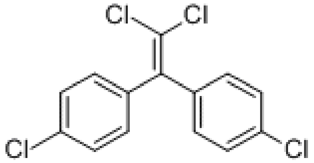
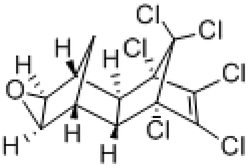
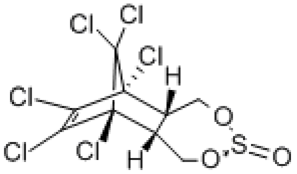
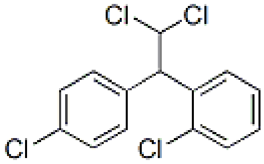
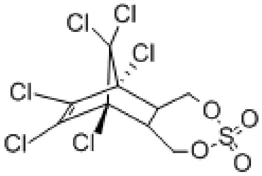
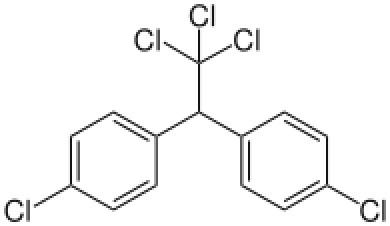
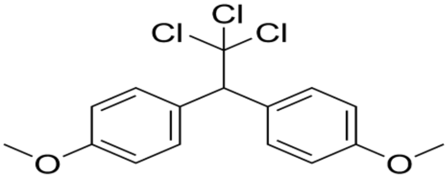
| Name | Structure |
|---|---|
| **Chlorpyrifos** |  |
| **Methidathion** |  |
| **Ethion** |  |
| **Triazophos** |  |

Table Ib: Structures of Organochlorine pesticides

| **Name** | **Structure** |
|---|---|
| **a-HCH**<br>(alpha–hexachlorocyclohexane) |  |
| **b-HCH**(beta–hexachlorocyclohexane) |  |
| **g-HCH**(gamma–hexachlorocyclohexane) |  |
| **d-HCH**(delta–hexachlorocyclohexane) |  |
| **Heptachlor** |  |
| **Aldrin** |  |

| | |
|---|---|
| **Heptachlor epoxide** |  |
| **o,p’-DDE**<br>1,1-dichloro-2(<br>o<br>-chlorophenyl)-2-(<br>p<br>-chlorophenyl)<br>Ethylene) |  |
| **Alpha endosulfan** |   |
| **pp DDE**<br>(1,1'Dichloroethenylidene)bis(4-<br>chlorobenzene) |  |
| **Endrin** |  |
| **beta Endosulfan** |  |

| | |
|---|---|
| **op DDD**<br>1,1-dichloro-2-(o-chlorophenyl) 2-<br>(p-chlorophenyl)ethane |  |
| **Endosulfan sulphate** |  |
| **p,p'-DDT**<br>1,1,1-trichloro-2,2-bis<br>(p-chlorophenyl)ethane |  |
| **Methoxychlor** |  |

# Appendix II: Standard chromatograms of 16OC and 14 OP pesticides

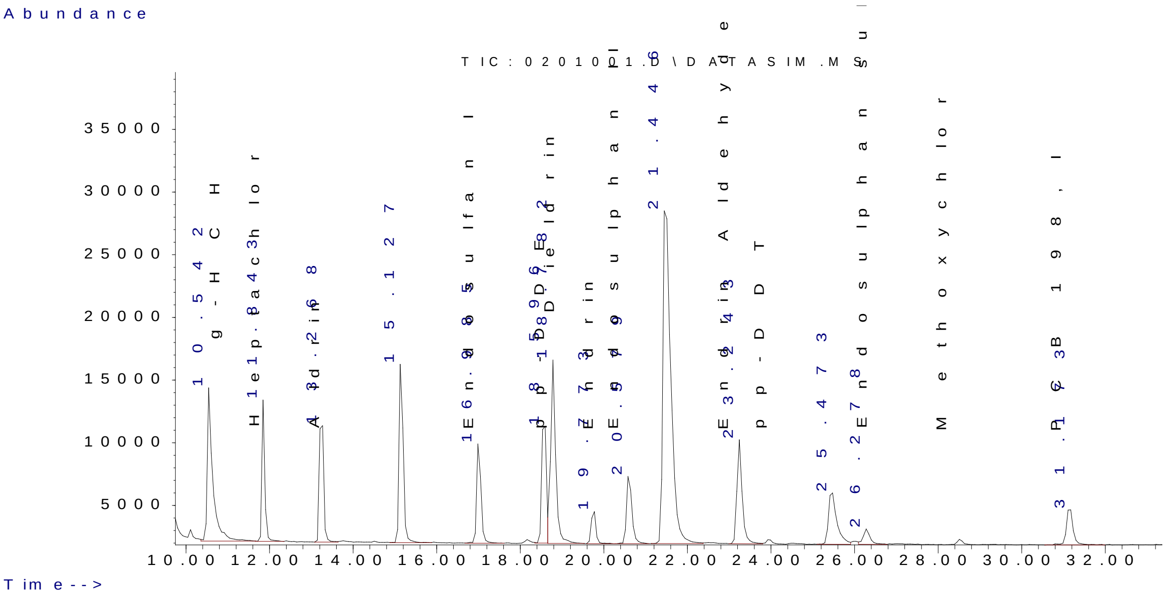


Figure Ia. Chromatogram of 16 OC pesticides

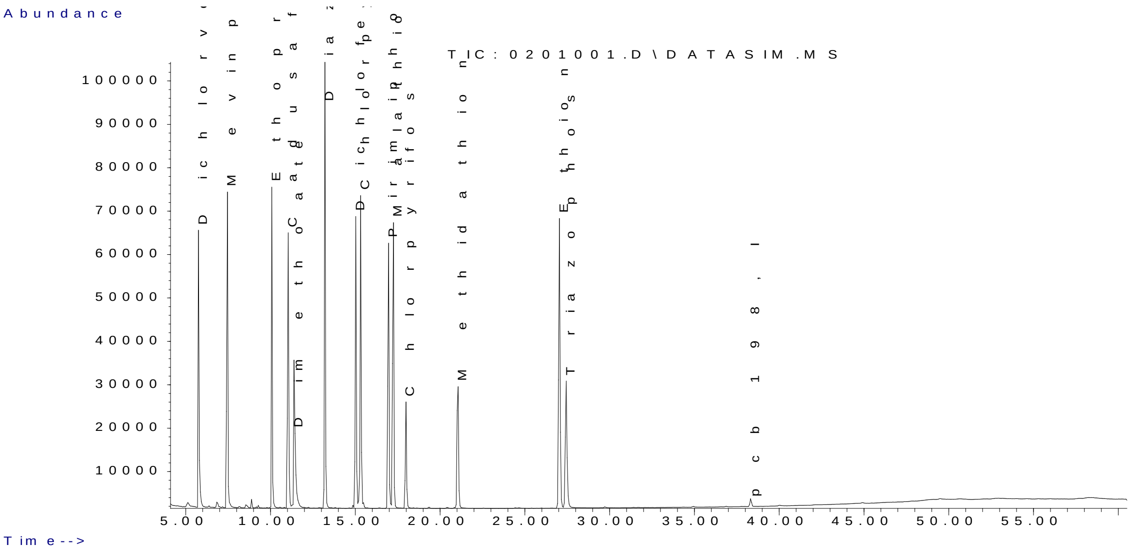


Figure Ib. Chromatogram of 14 OP pesticides

## Appendix III: Pearson's correlations between pesticides and physicochemical parameters.

Table IVa. Spatial correlations between ∑17 OCPS, TDS and TSS in water samples

Correlations

| | | SITENO | OCP | TDS | TSS |
|---|---|---|---|---|---|
| SITENO | Pearson Correlation | 1 | .705 | .969* | .485 |
| | Sig. (2-tailed) | | .295 | .031 | .515 |
| | N | 4 | 4 | 4 | 4 |
| OCP | Pearson Correlation | .705 | 1 | .564 | .320 |
| | Sig. (2-tailed) | .295 | | .436 | .680 |
| | N | 4 | 4 | 4 | 4 |
| TDS | Pearson Correlation | .969* | .564 | 1 | .631 |
| | Sig. (2-tailed) | .031 | .436 | | .369 |
| | N | 4 | 4 | 4 | 4 |
| TSS | Pearson Correlation | .485 | .320 | .631 | 1 |
| | Sig. (2-tailed) | .515 | .680 | .369 | |
| | N | 4 | 4 | 4 | 4 |

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

Table IVb: Temporal correlations between ∑17 OCPS, TDS and TSS in water samples

| | | OCP | TDS | TSS |
|---|---|---|---|---|
| OCP | Pearson Correlation | 1 | .485 | .424 |
| | Sig. (2-tailed) | | .329 | .402 |
| | N | 6 | 6 | 6 |
| TDS | Pearson Correlation | .485 | 1 | .487 |
| | Sig. (2-tailed) | .329 | | .328 |
| | N | 6 | 6 | 6 |
| TSS | Pearson Correlation | .424 | .487 | 1 |
| | Sig. (2-tailed) | .402 | .328 | |

| | | OCP | TDS | TSS |
|---|---|---|---|---|
| OCP | Pearson Correlation | 1 | .485 | .424 |
| | Sig. (2-tailed) | | .329 | .402 |
| | N | 6 | 6 | 6 |
| TDS | Pearson Correlation | .485 | 1 | .487 |
| | Sig. (2-tailed) | .329 | | .328 |
| | N | 6 | 6 | 6 |
| TSS | Pearson Correlation | .424 | .487 | 1 |
| | Sig. (2-tailed) | .402 | .328 | |
| | N | 6 | 6 | 6 |

Table IVc: Spatial correlations between ∑14 OPPS, TDS and TSS in water samples

**Correlations**

| | | SITENO | OPP | TDS | TSS |
|---|---|---|---|---|---|
| SITENO | Pearson Correlation | 1 | .930 | .969* | .485 |
| | Sig. (2-tailed) | | .070 | .031 | .515 |
| | N | 4 | 4 | 4 | 4 |
| OPP | Pearson Correlation | .930 | 1 | .818 | .145 |
| | Sig. (2-tailed) | .070 | | .182 | .855 |
| | N | 4 | 4 | 4 | 4 |
| TDS | Pearson Correlation | .969* | .818 | 1 | .631 |
| | Sig. (2-tailed) | .031 | .182 | | .369 |
| | N | 4 | 4 | 4 | 4 |
| TSS | Pearson Correlation | .485 | .145 | .631 | 1 |
| | Sig. (2-tailed) | .515 | .855 | .369 | |
| | N | 4 | 4 | 4 | 4 |

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

Table IVd: Temporal correlations between ∑14 OPPS, TDS and TSS in water samples

**Correlations**

| | | OPP | TDS | TSS |
|---|---|---|---|---|
| OPP | Pearson Correlation | 1 | .219 | -.042 |
| | Sig. (2-tailed) | | .677 | .937 |
| | N | 6 | 6 | 6 |
| TDS | Pearson Correlation | .219 | 1 | .487 |
| | Sig. (2-tailed) | .677 | | .328 |
| | N | 6 | 6 | 6 |
| TSS | Pearson Correlation | -.042 | .487 | 1 |
| | Sig. (2-tailed) | .937 | .328 | |
| | N | 6 | 6 | 6 |

Table IVe: Spatial correlations between ∑17 OCPS, and TOC in sediment samples

**Correlations**

| | | SITENO | OCP | TOC |
|---|---|---|---|---|
| SITENO | Pearson Correlation | 1 | .936 | -.810 |
| | Sig. (2-tailed) | | .064 | .190 |
| | N | 4 | 4 | 4 |
| OCP | Pearson Correlation | .936 | 1 | -.736 |
| | Sig. (2-tailed) | .064 | | .264 |
| | N | 4 | 4 | 4 |
| TOC | Pearson Correlation | -.810 | -.736 | 1 |
| | Sig. (2-tailed) | .190 | .264 | |
| | N | 4 | 4 | 4 |

Table IVf: Temporal correlations between ∑17 OCPS, and TOC in sediment samples

**Correlations**

| | | OCP | TOC |
|---|---|---|---|
| OCP | Pearson Correlation | 1 | .586 |
| | Sig. (2-tailed) | | .222 |
| | N | 6 | 6 |
| TOC | Pearson Correlation | .586 | 1 |
| | Sig. (2-tailed) | .222 | |
| | N | 6 | 6 |

Table IVg: Spatial correlations between ∑14 OPPS, and TOC in sediment samples

**Correlations**

| | | SITENO | OPP | TOC |
|---|---|---|---|---|
| SITENO | Pearson Correlation | 1 | .697 | -.810 |
| | Sig. (2-tailed) | | .303 | .190 |
| | N | 4 | 4 | 4 |
| OPP | Pearson Correlation | .697 | 1 | -.529 |
| | Sig. (2-tailed) | .303 | | .471 |
| | N | 4 | 4 | 4 |
| TOC | Pearson Correlation | -.810 | -.529 | 1 |
| | Sig. (2-tailed) | .190 | .471 | |
| | N | 4 | 4 | 4 |

Table IVh: Temporal correlations between ∑14 OPPS, and TOC in sediment samples

**Correlations**

| | | TOC | OPP |
|---|---|---|---|
| TOC | Pearson Correlation | 1 | .539 |
| | Sig. (2-tailed) | | .270 |
| | N | 6 | 6 |
| OPP | Pearson Correlation | .539 | 1 |
| | Sig. (2-tailed) | .270 | |
| | N | 6 | 6 |

Table IVi: Inter matrix correlation between ∑14 OPPS and ∑17 OCPS

**Correlations**

| | | SITENO | WATEROCP | WATEROPP | SEDIMENT OCP | SEDIMENT OPP |
|---|---|---|---|---|---|---|
| SITENO | Pearson Correlation | 1 | .705 | .930 | .936 | .697 |
| | Sig. (2-tailed) | | .295 | .070 | .064 | .303 |
| | N | 4 | 4 | 4 | 4 | 4 |
| WATEROCP | Pearson Correlation | .705 | 1 | .747 | .422 | .005 |
| | Sig. (2-tailed) | .295 | | .253 | .578 | .995 |
| | N | 4 | 4 | 4 | 4 | 4 |
| WATEROPP | Pearson Correlation | .930 | .747 | 1 | .865 | .632 |
| | Sig. (2-tailed) | .070 | .253 | | .135 | .368 |
| | N | 4 | 4 | 4 | 4 | 4 |
| SEDIMENTOCP | Pearson Correlation | .936 | .422 | .865 | 1 | .905 |
| | Sig. (2-tailed) | .064 | .578 | .135 | | .095 |
| | N | 4 | 4 | 4 | 4 | 4 |
| SEDIMENT OPP | Pearson Correlation | .697 | .005 | .632 | .905 | 1 |
| | Sig. (2-tailed) | .303 | .995 | .368 | .095 | |
| | N | 4 | 4 | 4 | 4 | 4 |

# Appendix IV: TIC Chromatograms for OC and OP pesticides.

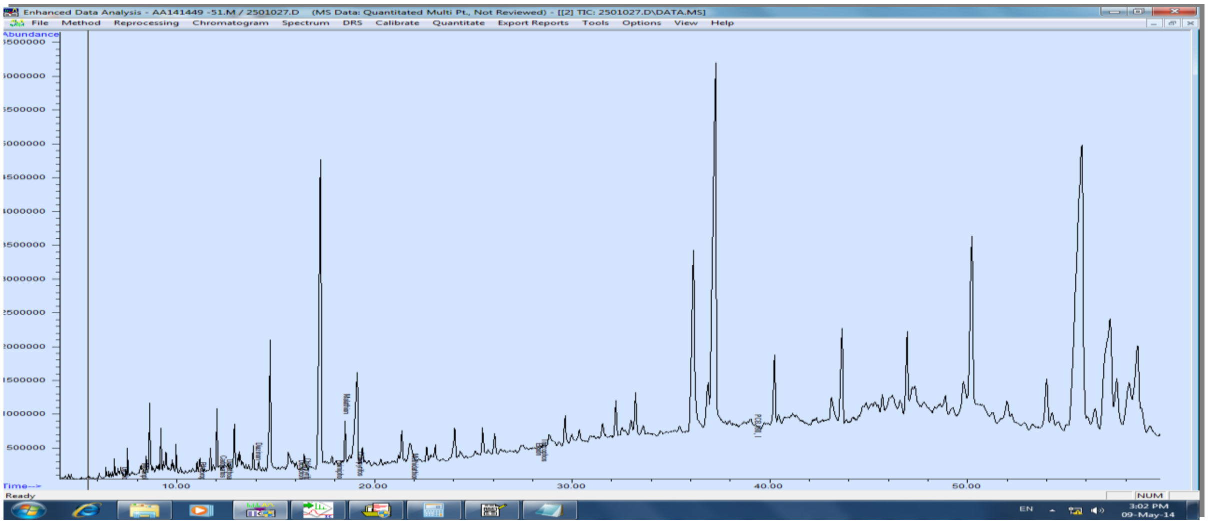


Figure Va. Standard of OC pesticides

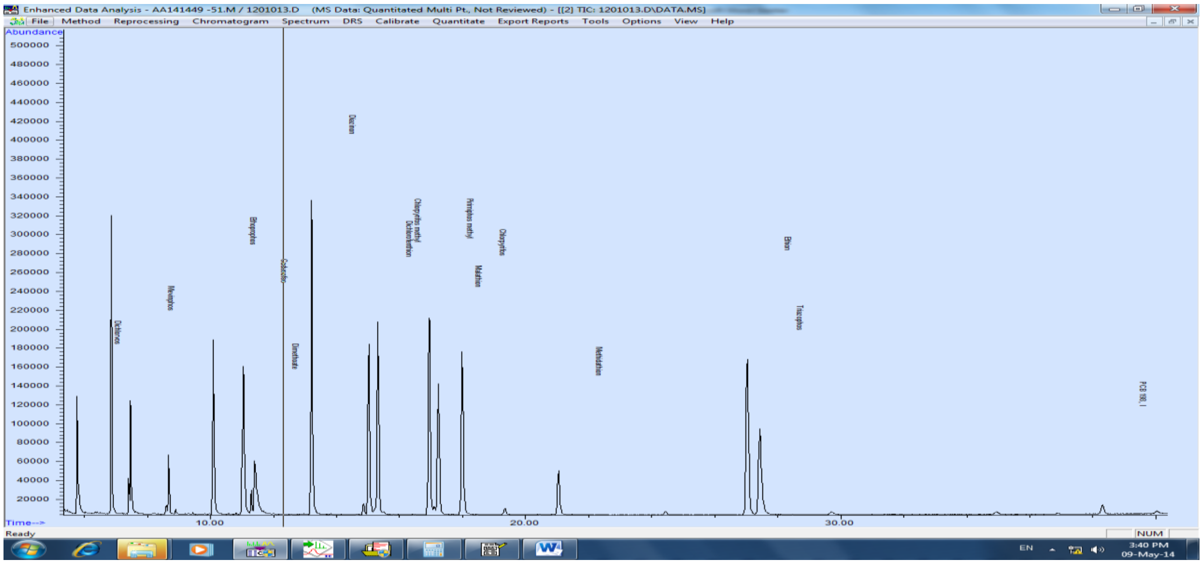


Figure Vb Mixed Standard of OP pesticides

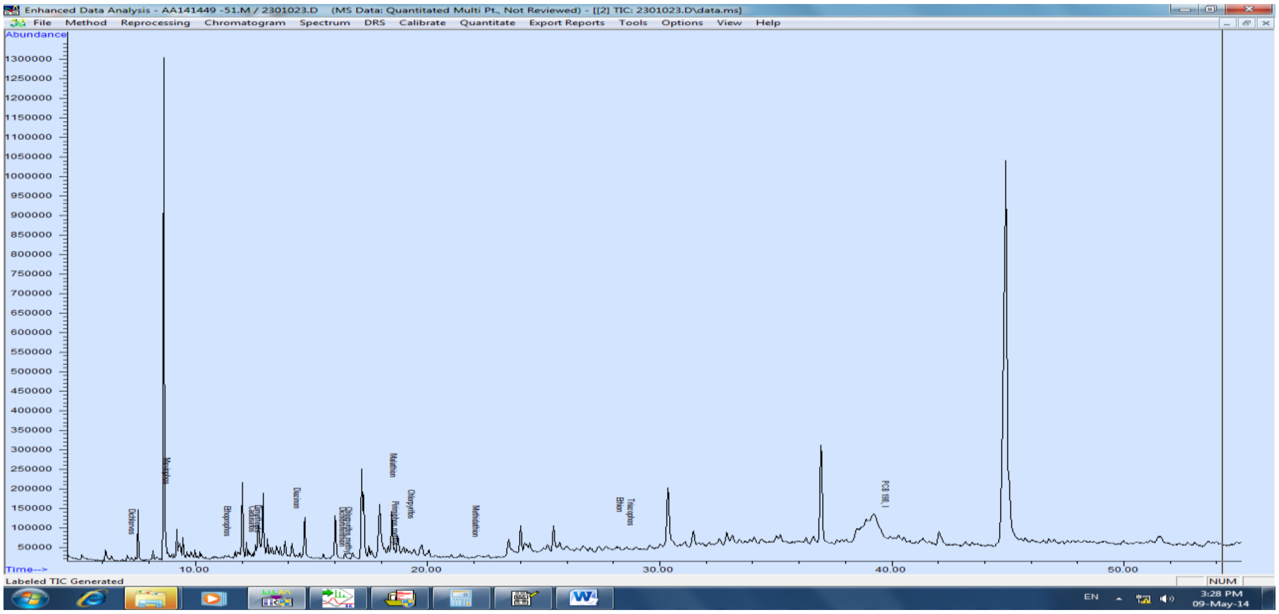


Figure Vc: OP pesticides in water sample

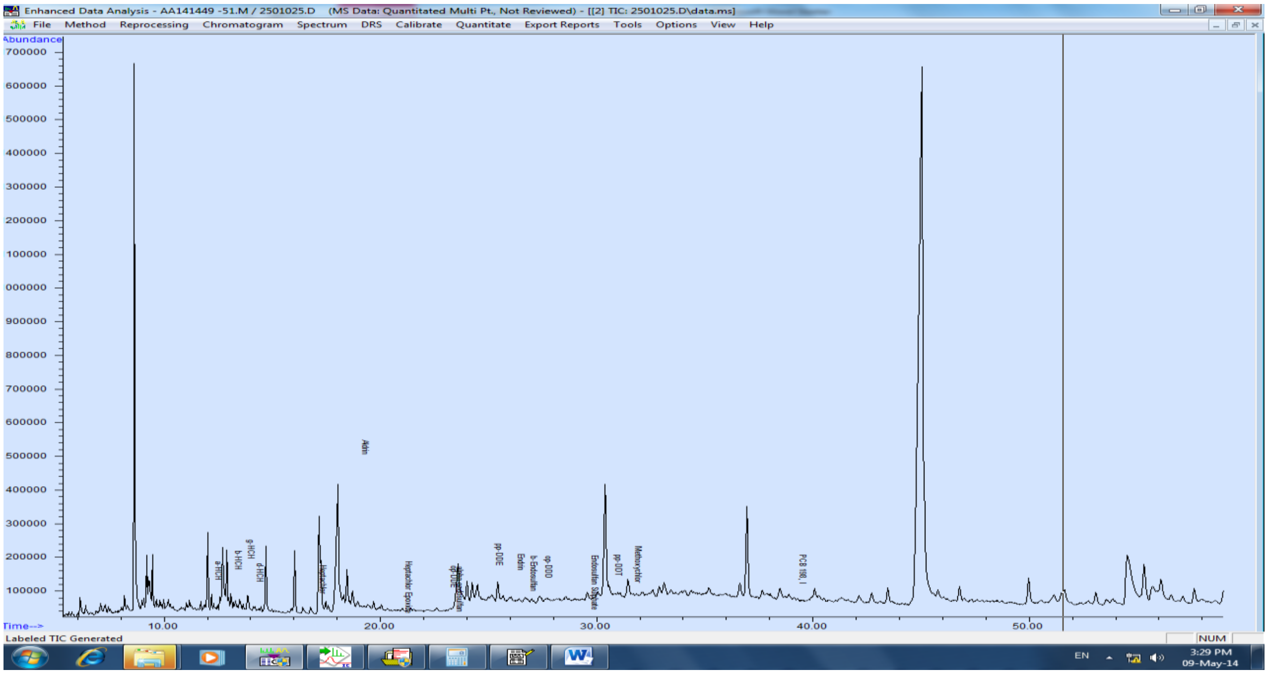


Figure Vd: OC pesticides in sediment sample.

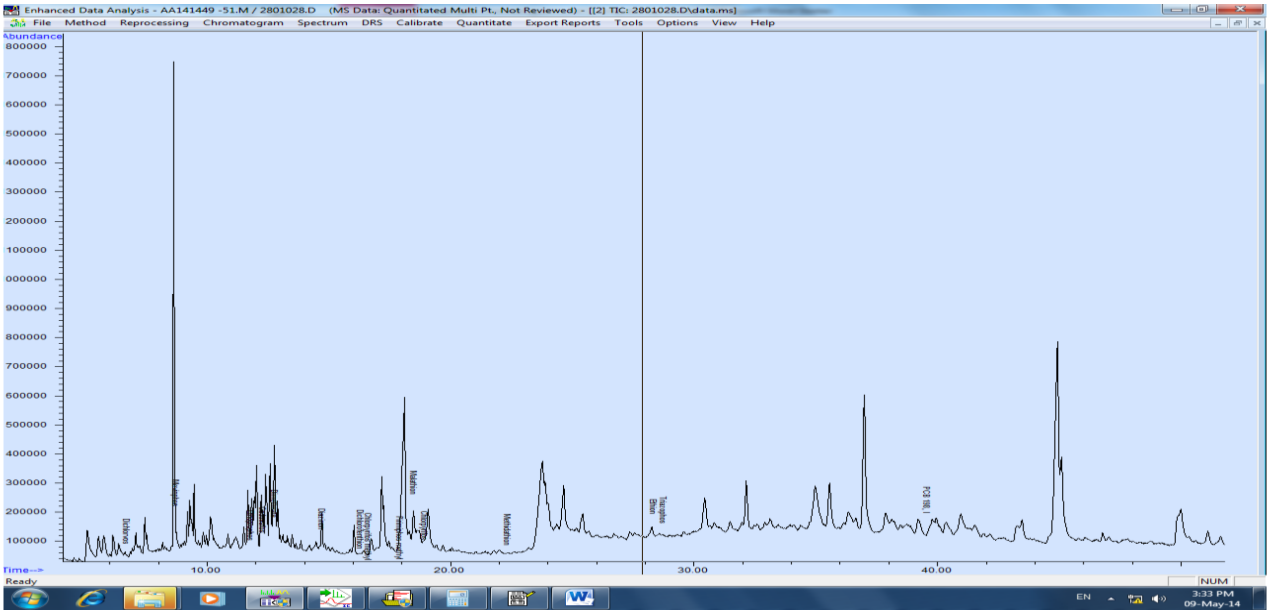


Figure Ve: OP pesticides in Sediment sample