"STUDIES ON DISTRIBUTION OF ORGANOCHLORINE PESTICIDE RESIDUES IN A TROPICAL MARINE ENVIRONMENT ALONG THE KENYAN COAST."

BY
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DECLARATION

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

MAURICE W. BARASA

This thesis has been submitted for examination with our approval as University Supervisors.

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DEDICATION

To my wife, Violet Wanyonyi and sons, Dancun Barasa and Doughlas Mulunda.

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ABSTRACT

A Study was conducted in which samples of seawater, seaweed, sediment and fish were collected from four sites: Sabaki, Kilifi, Ramisi and Mombasa along the Kenya coast between 1996 and 1997. The samples were subjected to liquid extraction and subsequent analysis of aldrin, lindane, endosulfan, dieldrin, and p,p'-DDT and its metabolites p,p'-DDD and p,p'-DDE using gas liquid chromatography with election capture detection. Identification was done by matching the retention times of the analytes with those of the standard compounds. The objectives of the work were to compare the concentrations of the chlorinated hydrocarbon insecticide residues both within and between sites in order to assess the contamination level of the coastal marine environment; and to establish their variation with season of sampling.

The DDT metabolites p,p'-DDT, p,p'-DDE and p,p'-DDD (0.072-0.30 ppb), dieldrin (0.144-0.50 ppb), endosulfan (0.17-0.30 ppb), and aldrin (0.02-0.054 ppb) were detected in all water samples at all sites. But p,p'-DDT and lindane were not detected in Mombasa although they reached concentrations of 0.37 and 0.53 ppb in Kilifi, respectively.

In Kilifi and Sabaki, lindane could not be detected in seaweed and sediment samples; but reached concentrations of 280 and 612 ppb in fish from Ramisi and Sabaki, respectively. By contrast, aldrin, dieldrin, endosulfan and the p,p'-DDT metabolites were detected in all samples at all sites, at concentrations ranging from 2.35-101, 5.85-48.5, 2.94-40.3, and 0.95-70.8 ppb, respectively. Concentrations of the residues were consistently high in fish samples from Sabaki and generally low in those from Ramisi.

The analysis of data for seasonal effects shows that samples obtained during the wet weather has relatively higher residue concentrations than those collected during the dry season, and the differences are particularly significant for seaweeds and sediments.

Comparison of the concentration in ppb of organochlorine pesticides with those for other global coastal waters shows, for example, that in 1995 dieldrin (1.88), endosulfan (2.98) and p,p'-DDT (7.02) recorded in waters from Kingston Harbour (Jamaica) were about four, ten and twenty times higher than the maximum range values obtained in this study. This suggests that the coastal marine environment in Kenya is relatively unpolluted. These data provide a baseline for future work in determining the concentrations of chlorinated cyclic pesticides in marine samples along the coast of Kenya.

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LIST OF ABBREVIATIONS

CRP - Coordinated Research Programme

FAO - Food and Agriculture Organization

IAEA - International Atomic Energy Agency

KEMRI - Kenya Medical Research Institute

KMFRI - Kenya Marine Fisheries and Research Institute

KNAS - Kenya National Academy of Sciences

MEL - Marine Environment Laboratory

PCPB - Pest Control Products Board

UNEP - United Nations Environment Programme

WHO - World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Categories of marine pollution sources

The principal causes of pollution along the Kenyan Coast can generally be categorized into land-based and maritime activities. Land-based sources comprise sewage and domestic waste discharge, outfalls of industrial waste, agricultural activities, river run-off and atmospheric transportation. The maritime-based sources include maritime and oil tanker traffic, sand and coral mining, coastal construction and dredging as well as ocean dumping. These sources give rise to four categories of pollution in addition to aesthetic impairment: physical, thermal, microbiological and chemical.

Obnoxious odours from anoxic coastal waters partly due to cooked plant residues and the littering of beaches, bays such as Malindi Bay, and the Sabaki River estuary with bottles, plastics, metal cans and old tyres constitute the aesthetic aspects and can lead to obstruction in the use of sea water.

Physical pollution entails soil erosion along the coastal strip and the transportation and deposition of silt and sediment load into the receiving waters. For instance, the global sediment load reaching oceans was estimated to amount to 13.5×10^3 Mt per year (UNEP, 1982). This can render the sea water turbid and create ecological stress on aquatic life.

Thermal pollution results from the discharge of hot industrial cooling waters from boilers into lagoons so that when temperatures exceed 30^0C - the maximum tolerable by tropical fishes, the natural behaviour of biota can be altered.

The presence of bacteriological constituents in the marine ecosystem from domestic and municipal sewage can cause infectious diseases which can lead to epidemic outbreaks such as typhoid and cholera.

Chemical pollution results from continued use of industrial chemicals including pesticides, heavy metals and their salts, and petroleum products; and may be aggravated by accidental spillage during transport and application as well as careless agricultural waste disposal.

1.2 Agricultural wastes

In the coastal region of Kenya, various cash crops are grown (Table 1.1). Nurseries for coconut palms are located in Kwale and Kilifi districts. Cashewnut is grown in large fields around Waa, Matuga and Msambweni in Kwale and some parts of Malindi. Cotton is mainly grown around Malindi. Sisal plantations are at Vipingo in Kilifi. The coast also produces a variety of fruits like mangoes and pineapples while the main subsistence crops include maize and rice. Crop yields are given in the appendix. Livestock is also practised especially in Kwale district.

Table 1.1: Sale of some major crops to marketing boards, 1992-1996.

Crop	Unit	1992	1993	1994	1995	1996
Maize	,000 tonnes	324.1	241.3	316.0	401.0	295.5
Wheat	"	125.1	93.1	105.2	125.5	130.0
Rice paddy	"	14.2	11.4	13.5	14.6	15.9
Cotton	"	2.8	2.5	1.8	0.2	0.5
Coffee	"	88.4	77.8	81.5	95.8	103.2
Tea	"	188.1	211.1	209.5	244.5	257.2
Sisal	"	34.1	35.1	33.9	27.5	28.1
Sugarcane	Mn. tonnes	3.7	3.8	3.3	4.0	4.1
Pyrethrum	tonnes	211.6	220.5	172.2	122.8	93.0

Source: Economic Survey (Kenya), May 1997.

Agricultural activities involve using inputs such as pesticides and fertilizers to protect and optimize crop yields as well as improve productivity. Organochlorine pesticides such as DDT, lindane, dieldrin, aldrin, thiodan, and toxaphene are used in varying quantities for a number of

applications. DDT is used extensively for aerial spraying of cotton fields around Margarini in Malindi, for disinfection of the Kilindini Harbour and for control of stalkborer in growing maize. Formulations containing DDT and dieldrin have been used for spraying tsetse-infested areas north of Malindi, while 2,4-D and 2,4,5,-T which contain the highly toxic by-product tetrachlodibenzodioxin (TCDD) are used on certain plantations especially sugarcane to control weeds.

Since some pesticides are generally not easily biodegradable, they can persist for a long time in the tropical environment (Lalah, 1993). They can also be absorbed into living organisms, enter and bioaccumulate in food chains and pose a threat to the health of marine life (fishes, birds, seagrass, plankton, etc). Humans may be exposed to these toxic chemicals through ingestion of contaminated fish or drinking water in those areas where these chemicals are heavily used.

1.3 The Pesticide Industry

Pesticide chemicals have played an important role in the improvement of human welfare all over the world (Hassall, 1990)). Pesticides are used in public health to control vector-borne diseases by combating veterinary and human pest related woes, and in agriculture to produce high quality crops and minimize the input of energy and labour (Mathews, 1979).

Pesticides occupy a unique position among chemicals used since they are inevitably introduced into the environment. The replacement of the first generation of inorganic pesticides (arsenicals, mercurials, etc) by the second generation synthetic organic pesticides (organochlorines, organophosphates, carbamates and pyrethroids) between 1939 and 1966 was extremely rapid (Hassall, 1982) but has helped double the world's food production every twenty years and saved millions of lives each year by controlling vectors. They have however posed serious economic, technological, ecological and environmental dilemma to the world because of problems related to their persistence.

Depending on their intended use, pesticides are grouped as acaricides, avicides, fungicides,

herbicides, molluscicides, nematocides and rodenticides, when used against ticks and mites, birds, plant fungal diseases, weeds, molluscs, nematodes and rodents respectively (Hodgson *et al.*, 1991). Their modes of action however vary. Organochlorines cause excitability of neurons; they initially act on peripheral sensory fibers and motor units, and the peripheral nervous system (Hassall, 1990). The nerve action has been attributed to a delayed shut-off of sodium gates during the action potential. This blockage causes hyperactivity followed by convulsions and death in insects. By contrast, the organophosphates act by inhibiting the enzyme cholinesterase which leads to a build-up of acetylcholine. The net effect is the paralysis of striated respiratory muscles. But they have higher acute toxicity than organochlorines, and therefore require more careful handling. A recent development has been the introduction of new synthetic insecticides which has led to an increase in pesticide use.

In Kenya, agriculture has been the mainstay of the economy. The use of pesticides in the past half a century has therefore been widespread since lindane was introduced in Kenya in 1949, toxaphene in 1950, DDT in 1956 and dieldrin in 1961 (Kaine, 1976). According to Foxall (1983) the percentage pesticides used in Kenya annually at that time consisted of fungicides (50%), insecticides (20%) and herbicides (20%). Nematocides, rodenticides, molluscicides and acaricides all accounted for only 10% of the total. Recent reports indicate that about 70 tonnes of DDT have been used annually for agricultural pest control on maize and cotton while lindane, aldrin and dieldrin have been used for seed-dressing in varying quantities (Munga, 1985). However, records available show that DDT was last imported into Kenya in 1985, and aldrin and dieldrin in 1992, while the endosulfun, alpha- and gamma-BHC and alochlor and other selected organochlorines continue to enjoy legal importation (PCPB, 1996).

Since 1985, however, Kenya has had a negative growth from food sufficiency to food deficiency status. To reverse the situation intensive agricultural undertakings involving use of large quantities of fertilizers and pesticides have been on the increase. For instance in 1995, Kenya imported a total annual average of 5,107.9 tonnes worth KShs 776.4 million compared to 2,6448 tonnes worth KShs 580.1 million realized previously in 1986 (PCPB, 1996). If the current food policy is to be implemented to achieve the goal of self sufficiency, then even large amounts of pesticides will have to be imported in the future.

The rising Kenyan population will continue to demand increased food productivity which in turn will depend on the availability of good soil, water and effective control of pests and

weeds which cause high crop losses estimated at about 40% in most developing countries (Wandiga, 1996).

While emphasis is made on the benefits derived from the use of pesticides, caution must be exercised so that use is only made of those pesticides that are not detrimental to human and animal health as well as the general environment. In order to eliminate undesirable products, the Pest Control Products Board of Kenya has either banned or restricted the use of some pesticides (PCPB, 1987).

The environmental hazards associated with pesticide use include: (a) the increased pesticide residues in agricultural products and in natural ecosystems, (b) the contamination of surface and ground water aquifers and (c) the breakdown of natural ecosystems. To monitor these hazards, it has been necessary to investigate the persistence, bioaccumulation and/or transformation of pesticides in different environments in both developed and developing countries.

1.4 Objectives

The objectives of the project whose results are presented in this thesis were:

1. To determine the concentrations of organochlorine pesticide residues in marine sediments, fish, water and seaweeds sampled from a range of lagoon and estuarine sites along the Kenya Coast.

2. To establish how the distribution of the residues are likely to be influenced by seasonal variations and sampling site characteristics.

Exact knowledge of residues would help to preserve the biodiversity of aquatic life and reduce adverse effects on human health. Furthermore, such knowledge would furnish sufficient information on the tropical marine environmental chemistry of organochlorine pesticide residues.

1.5 The Study Area

Kenya is located in East Africa (Fig. 1.1) between latitudes $5^0$40'N and $4^0$4'S and between longitudes $33^0$50'W and $41^0$45'S with a coastline of 640 km (UNEP, 1984) which is characterized by fringing reefs and a shallow narrow lagoon system linking it to the mainland.

The extensive reef system is critical to activities such as fishing, agriculture and tourism. Winds, tides, waves and currents predominate which help in erosion, transportation and deposition of marine biota and abiota.

Intensive and extensive agricultural activities are practiced at the upper and middle sections of river watersheds resulting in transport of a number of contaminants such as pesticides to the ocean (UNEP, 1982). The terrestrial ecosystems include coastal forests and comprise high-grass bush and grasslands. The agricultural production comprises sugarcane, mangoes, cotton as well as livestock farming (Ogallo and Mwangi, 1996). Industrial activities also prevail.

The mean annual rainfall at the coast of Kenya is about 1090 mm whereby 40% is received during the warm and wet long rains (March-June), 20% in warm and wet short rains (October-December) and the remaining 40% is received during the onset of monsoons (Ogallo and Mwangi, 1996). Relative humidity averages 75% while evaporation is about 170 mm. Sunshine is approximately 8.65 hours, radiation (449 Langleys) and surface winds (4.5 m/s).

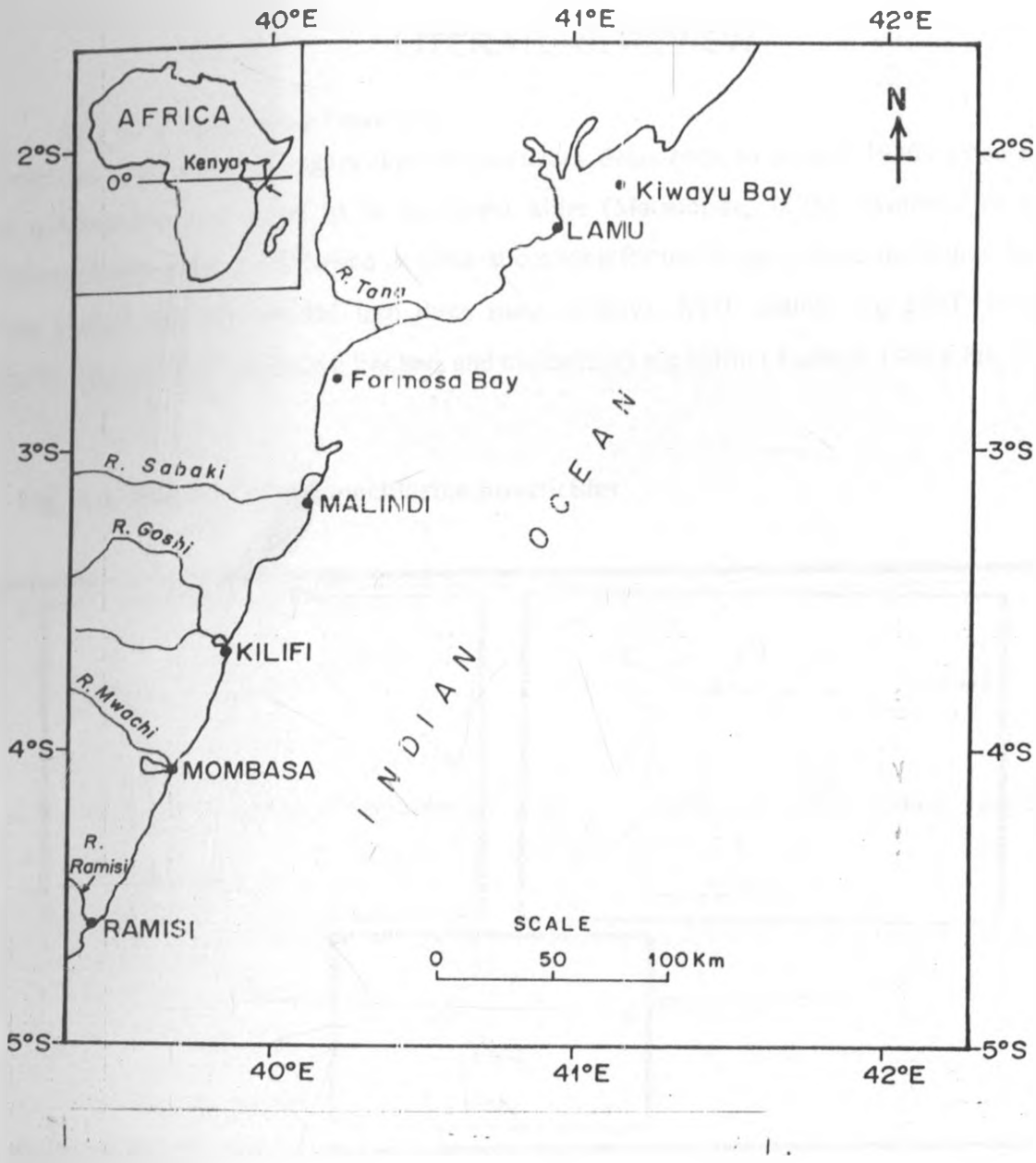


Fig.1.1: The study area of Kenya.

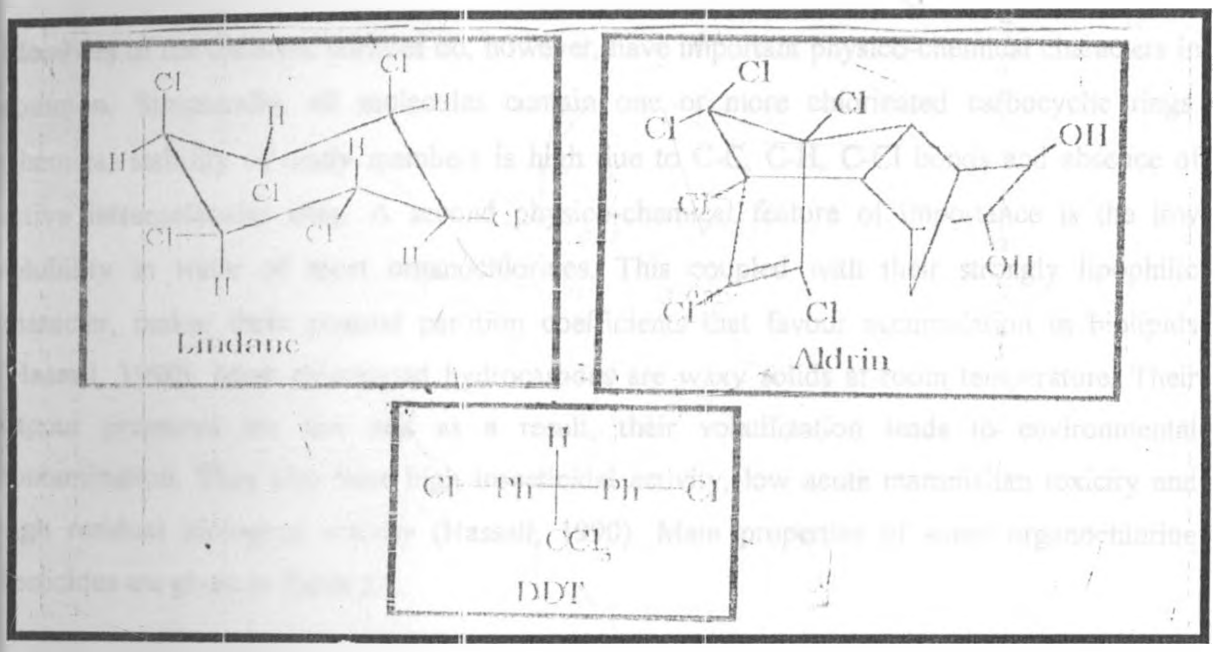
CHAPTER TWO

LITERATURE REVIEW

2.1 The Organochlorine Pesticides

Worldwide application of organochlorine pesticides dates back to around 1940s when DDT was accidentally discovered to be an insect killer (Matsumura, 1975). Synthesis of other chlorinated hydrocarbons followed in quick succession for use in agriculture and public health. These compounds are divided into three main families: DDT analogs e.g DDT, benzene hexachloride (BHC) isomers e g lindane, and cyclodienes e.g aldrin (Hassall, 1990)(Fig. 2.1).

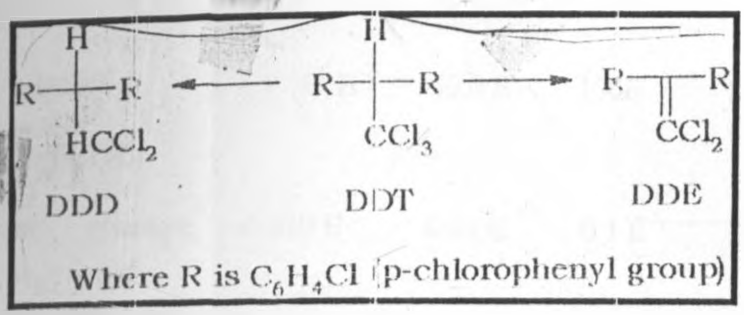
Fig. 2.1: Families of organochlorine insecticides



DDT was first synthesized by Zeidler in 1894 by the condensation of chlorobenzene with chloral in the presence of sulphuric acid. It undergoes dehydrochlorination to give DDE. Reductive dechlorination of DDT gives DDD (Fig. 2.2). Cyclodienes are prepared using the Dieis-Alder reaction with hexachlorocyclopentadiene (HCCP) acting as the diene in most

cases. Organochlorine chemicals have been used in insect control, soil fumigants, crop protection and in control of household pests and in mosquito eradication, locust control and in wood preservation. Hexachlorocyclohexane, commonly called gamma-HCH or lindane was reported to have insecticidal activity in 1935. Lindane is used for seed dressing, in soil treatment, for application on fruit and nut trees, vegetables and ornamentals, and for timber and wood preservation against pests.

Fig.2.2: Degradation pathways of DDT.



Members of the different families do, however, have important physico-chemical characters in common. Structurally, all molecules contain one or more chlorinated carbocyclic rings. Chemical stability of many members is high due to C-C, C-H, C-Cl bonds and absence of active intramolecular sites. A second physico-chemical feature of importance is the low solubility in water of most organochlorines. This coupled with their strongly lipophilic character, makes them possess partition coefficients that favour accumulation in biolipids (Hassall, 1990). Most chlorinated hydrocarbons are waxy solids at room temperature. Their vapour pressures are low and as a result, their volatilization leads to environmental contamination. They also have high insecticidal activity, low acute mammalian toxicity and high residual biological activity (Hassall, 1990). Main properties of some organochlorine pesticides are given in Table 2.1.

Table 2.1: Main properties of selected organochlorine crop protection chemicals in the tropics

Property	p,p'-DDT	p,p'-DDE	p,p'-DDD	Lindane	Aldrin	Dieldrin (I)
Solubility (mg/l)	0.0055	0.1 E	0.02	7	0.027	0.2
Half life Days	2000 E	1000E	1000E	400	365	1000 E
Soil sorption (Koc mg/g OC)	2×10^6 E	50.0 E	100E	1.100	5.00 E	12.0 E
Vapour pressure (mm Hg) $\times 10^{-5}$	0.019 E	0.65 E	0.1 E	3.3	6.6	0.3
LD_{50} (mg/kg) (rats)	113	880	113	79	39	46

E - Existing data diverse, value assigned on scientific judgement; Source: Tavares (1997).

(I) - Stereo-isomers

LD50 - Lethal dose for half the population

Little is known about the possibility of human chronic poisoning by the organochlorine pesticides. However, it is believed that members of the three families are neurotoxic thus they act by disturbing the sodium balance of the nervous membrane in insects (Hill, 1978). Captan was tested for genotoxicity in a range of assays, which demonstrated that it was mutagenic and clastogenic *in vitro* but not *in vivo* (FAO/WHO, 1995). The *in vitro* responses were reduced by the presence of liver homogenates, serum, and glutathione. Studies of the genotoxicity of captan in mouse duodenum indicated that it did not bind covalently to DNA and nuclear abberations were not induced. The US National Academy of Sciences ruled out that chlordane was carcinogenic to certain strains of mice but there was evidence that it could act as a promoter rather than an initiator of carcinogenesis.

There has been the tendency of DDT and other organochlorine pesticides to particularly persist in the environment. Their half-lives of 7 to 14 years established in temperate regions (Stickel, 1974) implies that they have the ability to accumulate in animal adipose and other tissues and organs occassionally disrupting equilibrium in a variety of animal species. Consequently, most organochlorine compounds have been banned in most countries although some are still available in many developing countries for designated purposes. Unfortunately in some cases, and in defiance of regulations, farmers use organochlorine compounds for non-designated purposes and crops since they are competitively priced compared to other new insecticides, particularly the organophosphates.

2.2 Occurrence of Organochlorines in Tropical Aquatic Ecosystems

The entry of pesticides into the environment is a direct consequence of their applications. Unknown but large quantities of pesticides enter drainage canals, rivers, lakes and oceans through spraying of water surfaces for control of mosquito larvae, accidental spillage of these chemicals into water, wash-out emanating from the cleaning of pesticide containers and subsequent release into waterways, discharge into waterways of industrial effluents containing pesticides used domestic, and from livestock dips. Erosion of contaminated soil by wind and water also contributes substantially since considerable quantities of insecticide residues find their way into the soils of large areas of cultivated land (Edwards, 1966).

The negative contribution of pesticides to organisms in water bodies results in inhibition of reproductive process in some species or extinction through death altogether. Generally, pesticides that enter water bodies are rapidly diluted, either by the large volumes of water in lakes and ponds or by the addition of stream and overland flow into oceanic systems. In addition, pesticides in aquatic ecosystems get adsorbed onto sediments or become degraded by micro-organisms, while others are metabolized by aquatic organisms (Miller, 1978).

Residues of organochlorine pesticides have been reported in water (Edwards, 1973). In aquatic environments these mainly occur adsorbed to particulate matter since the solubilities of pesticides in water are very low (Hassall, 1990). Physico-chemical properties of an ecosystem in which pesticides enter e.g the pH, mineral composition, organic matter and moisture content determine the behaviour of a particular insecticide and its ultimate fate in the environment

(Miller, 1978).

Over the years, data have accumulated from studies which give an indication of the extent of organochlorine pesticides contamination in both biotic and abiotic components of the aquatic environment in tropical countries. Organochlorines have been found strongly adsorbed onto the fine sediment and organic material in water (Miles, 1976). With DDT, dieldrin, endrin and lindane, adsorption on sediment has been found to be inversely correlated with solubility in water. Adsorption of pesticides onto sediment and detritus not only removes the pesticides from the water but also facilitates favourable conditions for biodegradation.

Sediments in lake Michigan averaged 0.014 ppm of DDT, DDE and TDE on a wet weight basis. From the same habitat, the amphipod *Pontoporeia affinis* averaged 0.14 ppm for DDT and its metabolites; various fish species had residues of 3.35 ppm (alewives), 4.52 ppm (Chub) and 5.5 ppm (Whitefish) showing biomagnification of pesticides along a food chain (Hickey *et al.*, 1966). Lipophilicity of persistent insecticides allows them to be deposited in an organic-lipid containing material.

Bottom sediments of Clear Lake, California contained noticeable amounts of DDD and DDE. The top 5 inches gave residue concentrations of 0.05-1.0 ppm on wet weight basis. A deep core sampling gave concentrations of 31 ppb in the top 6 inches and 12-18 inches deep gave 1.0 ppb. No residues were found in the 18-42 inches depth section (Rudd and Herman, 1972). A study carried out on the coastal and inland waters in Thailand indicated low levels of DDT and its metabolites DDE and DDD in the green mussel, bivalve molluscs, sediments and fish (Menasveta and Cheevaparanapiwat, 1981).

In 1983 analysis of liver sampled from a number of fish from Manila Bay showed presence of aldrin ranging from trace to 0.048 ng/g, while dieldrin and BHC levels ranged from 0.011-0.820 ng/g and 0.023-2.201 ng/g, respectively (Hingco, 1990). The aldrin levels were attributed to the presence of housing settlements near the tributaries where domestic use of this compound was inevitable.

From the field studies on the Pacific Coast of Mexico analytical results from samples collected in the lagoon provided crucial information on pesticides reaching the aquatic ecosystem. In sediments and biota collected in 1989, DDT residues were present at relatively low levels unlike its metabolites DDD and DDE (Mee *et al.*, 1991), suggesting decreased usage of DDT in the surrounding horticultural areas which later discharged into the lagoon.

Other studies dealing with the accumulation of pesticides in epibenthic (Shrimps and crabs) and the endobenthic (worms and bivalves) invertebrates from three intertidal mudflats along the coast of Malay peninsula indicated that among the DDT isomers. p,p'-DDE was present in the highest concentration, the levels varying with the biological species (Everaarts *et al.*, 1991). From the data obtained, it was inferred that p,p'-DDE in biota could be considered an indicator of environmental contamination.

Mansingh (1993) investigated the pesticide residues in rivers and coastal waters from adjacent coffee plantations in Jamaica and detected endosulfan and its metabolites in the water, sediment and fauna whose concentrations increased in that order of the aquatic compartments. Residues of dieldrin, and p,p'-DDE were undetected. The wide occurrence of endosulfan residues was attributed to its frequent use for the treatment of coffee berry borer in Jamaica.

Organochlorine residues in samples of marine biota have also been monitored along the Todo as Santos Bay, Bahia, Brazil (Tavares, 1994). Mussels and surface sediment samples collected on low tide at various points along the intertidal zones showed high DDE levels which were attributed to the use of DDT in upland areas for termite elimination.

In another investigation in Jamaica, samples of water collected from Kingston Harbour Bay as recent as 1992 revealed high mean concentrations of p,p'-DDT (7.02 ppb), endosulfan (2.98 ppb) and dieldrin (1.88 ppb) (Mansingh and Wilson, 1995). The concentration of these residues in marine ecosystem could be attributed to the Rio Cobre River load which drains through a rich agricultural valley where pesticides are heavily used.

Some work has been done to establish residual levels of organochlorine pesticides in aquatic environments in Kenya. Komen *et al.* (1972) found very low levels of residual DDT (0.001-0.064 mg/kg) in Lake Nakuru birds and fish. Later, Greichus *et al.* (1978) found slightly higher residue levels of DDE, DDD and dieldrin residues in the same lake. Lincer *et al.* (1981) found 0.4 mg/kg wet mass of p,p'-DDE in muscle tissue from a bottom feeding fish *Labeo cylindricus* in Lake Baringo. In L. Victoria study, a fish species *Lates nilotica* had 0.004 mg/kg wet mass of DDT (Foxall, 1983).

Levels of DDT and its metabolites as well as endosulfan and its metabolites were investigated in fish species from Hola irrigation scheme, in the lower Tana River basin (Munga, 1985). Both compounds have been applied by farmers on cotton fields by aerial spraying while DDT has been used on maize to control stalk borer infestation. The concentration of residues in fish samples varied with distance of the sampling site from the cotton fields. Fish samples from the closest site were the most contaminated. A bottom feeding fish species *Clarias mossambicus* showed the highest concentration of residues in muscle tissue.

In a recent study on organochlorine residues in sediment and macrobenthic organisms along the coast of Kenya, the DDT metabolite p,p'-DDE was quantified in sediment samples from two shallow coastal stations at the confluence of Sabaki River in a concentration range of 32.1 to 508.8 ng/g organic carbon (Everaarts *et al.*, 1996). Alpha-HCH was detected in increasing amounts across the continental shelves towards the deep sea while gamma-HCH had concentration range of 7.3 to 53.2 ng/g of organic carbon. Similarly, sediment samples had high dieldrin (37 ng/g of organic carbon) concentrations. p,p'-DDE was detected at levels ranging from 15-48 ng/g of lipid in bivalve and gastropod mulluscs.

2.3 Ecotoxicological Effects of Organochlorines on Non-Target Species

The environmental impact of a pesticide depends not only on its physiological selectivity, but also on its mobility and persistence in different matrices. Experience with OC insecticides shows that the usefulness of pesticides is currently marred by their adverse effects on non-target organisms whose extent depends on the type of pesticide used, the dose rate and the frequency of use, local circumstances such as the condition of soil and water, climate disturbance cycles (e g drought, floods), geomorphology ecosystem structure, presence of areas and species of recognized ecological value and the potential for recovery of affected species (Graham-Bryce, 1977).

In pest control only 1-3% of the applied dose actually contributes to the biological effect on target organisms (Graham-Bryce, 1977). The overall effects of pesticides on non-target species have been summarized as follows: (a) biological magnification, (b) disease susceptibility, (c) changes in food quality and quantity, (d) resistance, (e) growth changes, (f) altered reproduction, (g) change in behaviour, (h) alteration of habitats with species reduction and (i) reduction of species numbers (Ware, 1980).

2.3.1 Birds

Pesticides have a negative impact on the ecology of birds. Their residues and metabolites have been found in birds all over the world which can be passed from one generation to another (Stickel, 1974). At low levels of intake organochlorine pesticides are known to induce the production of hepatic enzymes in birds (Ware, 1980). These may cause metabolism of steroid hormones, such as oestrogen, resulting in a hormonal imbalance which affects the metabolism of calcium for eggshell formation and thus lowers reproduction success (Peakall, 1967). Evidence for this was noted in Britain and North America where a decline in numbers of the bald eagles, osprey, brown pelican, peregrine falcon, grey heron and other birds was revealed (Menzie, 1972; Hickey and Anderson, 1968). This was attributed to residues of DDT, PCBs, endrin and dieldrin which caused eggshell thinning and premature cracking of eggs.

2.3.2 Fish

Fish living in water are unable to escape from water contaminated with an insecticide. Consequently, they have to remain exposed to the pollutant until it is removed either by adsorption and sedimentation or by other mechanisms (Hansen, 1972). Thus the toxic effects

increase as the lethal concentration LC_{50} decreases with the duration of exposure.

About 5% of the mosquito fish that survived an exposure of aldrin above its threshold toxicity lay premature eggs (Boyd, 1964). Results of a study by Moye and Luckmann (1964) indicated that a single application of aldrin for insect control killed a large number of fish in a small exposed stream. A collection of fish seven months later, however, showed the usual diversity of fish species and size. Hence there appeared to be a rapid recovery of the fish population.

A spray of DDT (0.09 ppm) in water was used to treat a stream (Burden, 1956). Eight miles downstream from the treated area hundreds of fish were reported dying. The concentration of DDT at a point 10 miles downstream was 0.017 ppm. Fish specimens examined were found to have definitely died of poisoning. Sub-lethal levels of DDT between 0.008 and 0.2 µg/l caused a rise in locomotor activities of the bluegill sunfish which were symptoms of the onset of nerve poisoning (Ellgard *et al.*, 1977). Toxic effects of organochlorine insecticides on the nervous system result in uncoordinated movement, sluggishness alternating with hyperexcitability and difficulty in respiration. In another investigation, low concentrations of endrin (0.5 ppb) prevented reproduction in guppies and caused increased activity at lower dosages, possibly interrupting normal swarming and displacement behaviour (Mount, 1962).

Mathiessen *et al.* (1982) reported that accumulation of endosulfan and endosulfan sulphate occurred in several fish species and their predators during aerial spraying for tsetse fly control in the Okavango delta, Botswana. These insecticides not only led to fish mortality, but also affected the behaviour of the surviving fish, causing short-term hematological changes and damage to the brain and liver. The male fish experienced delayed breeding behaviour while some females tended to abort their unfertilized clutches when exposed to endosulfan (Mathiessen and Logan, 1984) leading to a reduction of fish counts.

Organochlorines are not water soluble. However, they are easily adsorbed to organic matter in water. Fish eat such organic matter as planktons. Small fish are eaten by big fish, which are in turn is eaten by birds, man and other animals. Thus the concentration of a pesticide is

magnified at each stage of the food chain. Because of this biomagnification, it has been found that some fish species like flaunder and trout are greatly affected by DDT in reduction of their reproduction.

2.3.3 Mammals

In the recent past, the side effects of insecticides and their degradation products on mammals were often related to the use of persistent organochlorine pesticides. However, less persistent pesticides may also cause side effects (Somerville and Walker, 1990). Release of toxic chemicals to the environment through spraying or by accidental spillage may cause acute mortality or long-term effects in mammalian populations. Insecticides are known to enter animal bodies through oral ingestion as residues in food and drinking water, and high doses are occasionally ingested unintentionally or in cases of suicide and homicide (Matsumura, 1975). Another significant route of entry is through the respiratory system due to the presence of alveolar tissues directly supplied with blood vessels and lined with thin moist membranes .

Organochlorine pesticides have been found in cow milk (Kituyi *et al.*, 1997), human milk (Wandiga and Mutere, 1978), fats of cattle (Maitho 1978) and adipose tissue of humans (Wasserman *et al.*, 1972). The Kenya Medical Research Institute (KEMRI) reports annual cases of acute pesticide poisoning in Kenya at 350,000 and an annual death toll of 700 (KEMRI, 1988). These and other hair-raising data warrant further studies into possible implications of continued exposure to pest control agents.

Other studies have established that the frequency of oestrus in one month old rats decreases significantly when they ingest 20 ppm of aldrin (Ball *et al.*, 1953). Guinea pigs, rats and rabbits given subcutaneous injections of arochlor at doses in the range of 17-1380 mg (Miller, 1944) resulted in liver damage and skin changes. Dieldrin was found to increase the number of trails required for the animals to relearn a visual discrimination task (Van Gelder *et al.*, 1969). Fish from Miramishi River in New Brunswick which were naturally contaminated with DDT were incorporated in a feed mixture and fed to mink (Gilbert, 1969). These animals developed high levels of DDT in their livers and adipose tissue. In the same study, females fed on the same mixture produced fewer young (4.8 kits) compared to the controls (5.2 kits), while embryonic losses after 24 hours post-birth was significantly greater

Accumulation of DDT in human is demonstrated by chronic diseases such as cancer carcinoma and hypertension. DDT affects human erythrocytes at concentrations of 10^{-6} to 10^{-5}M (O'Brien and Hilton, 1978). Lindane is considered to be a potent inducer of hepatic porphyria in humans (Tonkelaar, 1978). This is a pathological state characterized by abnormalities of porphyrin metabolism, excretion of excess porphyrins in the urine, and extreme sensitivity to light. Together with aldrin, DDE and DDT, lindane has been shown to act as an antagonist to pregnancy in humans (Saxena *et al.*, 1981).

Toxicological studies of lindane have shown carcinogenic effects in rats (Smith and Gabral, 1980) and degenerative ovarian changes in female rhesus monkeys (Iatrapoulos *et al.*, 1976).

2.3.4 Plants

Some insecticides have been known to cause phytotoxic effects on crops. For instance, MacPhee *et al.* (1960) showed that repeated applications of DDT among others for five years in a field experiment in Kentville, Nova Scotia, resulted in high residues in the soil. DDT residues decreased from 136 to 76 ppm on air dry weight basis. Consequently there was a decrease in yields of beans, carrots, tomatoes and peas. This could have come about as a result of the interference of DDT on the natural processes such as decomposition and mineralization of organic matter. Exposing phytoplankton communities in the laboratories for four hours to 1 ppm of dieldrin and endrin reduced the productivities of these communities (Butler, 1963).

2.4 Instrumentation techniques used in pesticide analysis

A good technique should be efficient, sensitive, highly selective and widely applicable. It should require small samples, may be non-destructive, and readily adapted to both quantitative and qualitative analysis. Techniques that meet these requirements for pesticide analysis include Infrared spectroscopy (IR), Ultraviolet spectroscopy (UV), Colorimetry, High Performance Liquid Chromatography (HPLC), Potentiometry and Gas Liquid Chromatography (GLC). Of these, IR, UV, HPLC and GLC techniques are the most commonly used for routine work. In this project, GLC was used and will therefore be described further.

2.4.1 Gas Liquid Chromatography

General principle

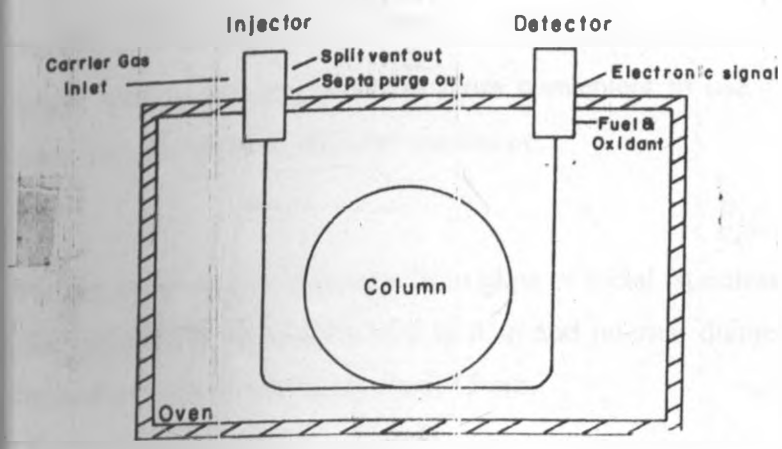
Gas liquid chromatography accomplishes the separation of components in a mixture by making use of their partition coefficients between a gaseous mobile phase and a liquid stationary phase

A sample containing two or more solutes is dissolved in a suitable solvent and injected into a heating block via the injection port where it is immediately vapourized and swept as a plug of vapour by the carrier gas stream into the inert column. Each solute travels at its own rate, influenced by differences in partition coefficients. The separate components emerge from the far end of the column at different times and pass through a detector which measures their concentrations. The detector output is fed into a recorder which registers each component as a peak whose area can be calculated either manually or by use of a microprocessor interfaced with the system. The retention-time is characteristic for each component under a specific set of operating conditions. Peak area is proportional to the concentration of the compound that passed through the detector. Furthermore, a direct comparison of the retention time of a sample component with that of the reference compound (standard) offers a qualitative identification of the unknown while quantitative analysis is possible by comparison of the peak area with that of the same compound (of known concentration) analyzed under the same set of conditions and sensitivity.

Basic Components of a Gas Chromatographic Assembly

Basic components of a GLC are shown in Fig. 2.3.

Fig. 2.3 : The GLC system.



(i) Carrier-Gas supply

Carrier gases, which must be chemically inert, include helium, argon, nitrogen and hydrogen. The choice of particular gas depends on the type of detector used. The carrier-gas is usually passed through a molecular sieve to remove water and other interfering impurities.

Flow-rates are controlled by a pressure regulator. Inlet pressures of 10-50 psi give flow-rates of 25-150 ml/min. Flow-rates are usually set by a soap-bubble meter attached to the inlet system.

(ii) Sample-Injection system

In order to avoid band broadening, the sample must be minute and be introduced rapidly as a plug of vapour. A calibrated micro-syringe is used to inject liquid samples via a septum into a heated sample port located at the end of the column. The port is ordinarily 50°C above the boiling point of the least volatile component of the sample so that flash vapourization occurs. Sample sizes vary from a few tenths of a microlitre to 20 μl. Gas samples are best introduced

by means of a sample valve whereas solid samples are first dissolved in a suitable solvent prior to injection.

(iii) Columns

Packed and capillary columns are widely used in GLC. Packed columns can accommodate a larger sample and are generally more convenient to use. Open capillary columns, however, have the advantage of efficient resolution.

Packed columns are fabricated from glass or metal (stainless steel, copper or aluminium) tubes that typically have lengths of 2 to 3 m and internal diameters of 2 to 4 mm. The tubes are formed as coils of diameters about 15 cm.

The efficiency of a GLC column increases with decreasing particle size of the stationery phase. Particles with diameters smaller than 150 μm cannot be accommodated because of the high pressures required to force the carrier gas and sample through such finely divided solids. As a result, typical packings are prepared from particle sizes ranging from 60, 80, or 100 mesh to 250, 170, or 149 μm respectively.

Two general types of packing are used in GLC. The first consists of an inorganic support material coated with an organic liquid held in place by either adsorption or chemical bonding. The second is filling the tube with a porous organic polymer that requires no additional coating.

Capillary columns are of three types: fused-silica, wall-coated and porous-layer columns. The inside of these columns is coated with a film of stationery liquid phase (as those used in packed columns) that varies in thickness from 0.1 to 1 μm.

The optimum column temperature in a thermostated oven depends upon the tolerance of column packing material, boiling point of the sample, and the degree of separation required. A temperature slightly above the average boiling point of the sample results in a reasonable elution time of 2 to 30 min. For samples with a broad boiling range, temperature programming

is desired. Optimum resolution is associated with minimum temperature although this results in an increase in elution time and therefore time required to complete an analysis.

Column optimization either reduces zone broadening or alters relative migration rates of components. Column resolution provides a quantitative measure of its ability to separate analytes which can be improved by lengthening the column. Reducing the particle of the column packing, column diameter, the thickness of liquid film, as well as flow rate of the mobile phase improves column performance.

(iv) GLC Detectors

A good GLC detector should have a high sensitivity (i.e high signal to concentration ratio) which results in a low level of detection. It should have good linearity and a wide linear working concentration range so that it is not easily overloaded. High sensitivity in detectors is important so that there is only response from the compounds of interest in the sample being analyzed. Detectors used for GLC include Flame Ionization Detector (FID), Thermal Conductivity Detector (TCD), Flame Photometric Detector (FPD), Nitrogen Phosphorous Detector (NPD) and Electron Capture Detector (ECD). The FID, TCD and ECD are the most commonly used detectors for routine work and are subsequently described in detail below.

(a) Flame Ionization Detector

Flame ionization detection is based on the principle that organic compounds when combusted in a hydrogen/air flame produce ions:

$$\text{Compound} + H_2 + O_2 \rightarrow CO_2 + H_2O + (\text{ions})^+ + (\text{ions})^-$$

Combination of the negatively charged species and electrons create a current flow. The ions are collected by a pair of polarized electrodes inside the detector to generate a current which is amplified into a measurable signal. The larger the amount of compound in a sample the higher the current and therefore the larger the signal. FID detectors have a linear working range of 10^{-9} - 10^{-2} g, and the detection limit to the order of 10^{-9} g (1 ng). The FID responds only to organic samples and gives little response to water and carbon disulphide. There is no response from fully oxidized carbons such as carboxyls and the response diminishes with increasing substitution of amino, hydroxyls and halogen groups.

(b) Thermal Conductivity Detector

The thermal conductivity detectors are based on the fact that the temperature and thus the resistance of a wire through which a current is flowing is dependent upon the thermal conductivity of the gas in which it is immersed. The thermal conductivity of a gas is a function of its compounds. The detector has two channels - (known as the reference and sample side) in which identical wires are used. These wires are connected to a Wheatstone bridge and heated by the passage of a current. The carrier gas flows through the reference side (before the sample is injected so that the reference side always contains gas of the same composition) and emerges through the sample side as it exits through the column, carrying the separated components. When there is no component exiting from the column, the gas compositions in the two sides are identical, and the Wheatstone bridge remains in balance since the wires are at the same temperature. As soon as a sample component is injected, the composition of the sample side differs from the reference side. This causes a change in temperature of the wire and an imbalance in the bridge. The circuit is designed to measure the extent of the imbalance and to feed this signal to a recorder. Since the degree of imbalance is a function of the concentration of the component in the carrier gas, the recorder presents the chromatographic separation in form of peaks. The limit of detection for TCD is in the order of 10^{-7} g. The TCD detector is universal, accommodates large sample sizes, is non-destructive and can be applied to the analysis of inorganic compounds. Its sensitivity is however lower than that of FID.

(c) Electron Capture Detector

An ECD detector has a beta-emitting source (e.g Ni-63 or tritium) in its housing chamber. Bombardment of the carrier gas with the beta radiation causes ionization of the gas to occur in which electrons are produced. With N_2 as carrier gas, the following reaction occurs:

$$N_2 + \text{ß-particle} \rightarrow N_2^{+} + e^{-}$$

When a potential between the source and anode is applied, a current is produced by aggregation of the electrons in the chamber. If an electrophilic compound is present in the chamber, a reaction can occur in which the collected electrons are captured. The capture of electrons is the

basis of ECD detection. The net process is the replacement of fast-moving electrons with slow-moving negative ions in the chamber. This process results in a change in standing current of the detector as the compound elutes. This change is measured and displayed on the chromatogram after appropriate amplification. The ECD is selective towards molecules containing electronegative atoms such as N, O, S and particularly halogens, hence organohalogen pesticides give excellent response. It requires clean laboratory environment to avoid contamination of the radioactive ionization source. It has a detection limit of 10^{-12} g and due to its high sensitivity, an ECD detector unless carefully handled is easily contaminated and is difficult to use and maintain.

Details of quantitative analysis

Quantitative analysis is based upon a comparison of either the height or area of the peak with that of one or more standards which vary linearly with comcentration under similar operating conditions. The peak height is obtained by connecting baselines on two sides of the peak by a straight line and measuring the perpendicular distance from this line to the peak. For a symmetrical peak with reasonable width, peak area is obtained by multiplying peak height by the width at one-half peak height. Electronic integrators connected to the system also provide precise measurements of peak areas.

Quantitative analyses also involve the preparation of a series of standard solutions that approximate the composition of unknowns. Peak heights or areas of standard chromatograms are plotted as a function of concentration yielding a straight line through the origin, and analyses based upon the plot. Alternatively, a measured quantity of an internal-standard substance is introduced into each standard and sample, and the ratio of analyte peak area (or height) to internal-standard peak area (or height) is the analytical parameter.

2.5 Statement of the Problem

While acknowledging that marine pollution arises from actions of man, this cannot be attributed solely to activities performed directly in the ocean (UNEP, 1990). Kenya has a coastline of 640 km (UNEP, 1984) with two major rivers (Tana and Athi) which drain into the

Indian Ocean. River Tana originates from highland areas in the central part of the country. River Tana, together with its numerous tributaries drains some of the most fertile lands where intensive and extensive agricultural activities prevail. Crops grown include rice, sorghum, beans, cotton, horticultural crops and maize so that every year substantial amounts of pesticides are applied through aerial sprays (Lalah, 1993). Marine life and tourism activities predominate at the coast while fishing occurs along rivers draining into the sea and coastal shores. Large amounts of pesticides are either applied directly to the water surface or reach it indirectly after application to target organisms.

For many years to come, pesticides will remain an important means of controlling pests afflicting man, his animals and food crops. Although the use of pesticides is beneficial, some of them are persistent and present toxic effects. This has raised serious concerns about environmental contamination. Due to the widespread use of pesticides, most human and animal populations receive chronic amounts in food and water.

Data on the fate of pesticides in tropical marine environments are very limited when compared with available literature for the temperate regions.

The negative effects of chemical contaminants on tropical marine ecosystems are of increasing concern as human populations expand adjacent to these communities. Estuaries and coastal lagoons are especially rich and provide optimal conditions for growth of aquatic organisms, which are important economic assets. Watershed streams and groundwater carry a variety of chemicals from agricultural, industrial and domestic activities, while currents and winds transport pollutants from atmospheric and oceanic sources of these coastal ecosystems. Information is lacking with regard to long-term recovery, indicator species and biomarkers for communities in the marine environment along the coast of Kenya. Critical areas that are beginning to be addressed include the development of appropriate benchmarkers for risk assessment, baseline monitoring criteria and effective management strategies to protect tropical marine ecosystems in the face of mounting anthropogenic disturbances.

From agricultural areas upstream of major rivers (Tana, Sabaki, Ramisi, Galana), there exists

poor farming practices, overgrazing and indiscriminate destruction of vegetation which contribute to rapid loss of top soil and eventual transport to the sea (UNEP, 1984). Recent studies reveal that there is a correlation between the type and amount of pesticide sprayed, time and frequency of application, seasonality of rainfall, and the frequency and concentration of pesticide residues detected. For instance, Foxall (1993) reported the presence of DDT, DDE and DDD in samples collected from Kenyan lakes while Everaart *et al.* (1996) showed presence of some organochlorine pesticides in sediments and macrobenthic invertebrates from the Kenyan coast.

Since marine life is an important source of protein in humans, birds and other higher organisms depending on their level of feeding in the food chain, it is necessary to continually monitor the level and fate of pesticide residues in marine ecosystems so as to provide suitable information for preservation and effective environmental management of coastal zone natural resources.

CHAPTER THREE

EXPERIMENTAL SECTION

3.1 Materials and Methods

3.1.1 Chemicals and Reagents

The solvents- hexane, acetone and methanol were obtained from J.T. Baker Inc. USA. They were distilled twice in an all-glass apparatus and stored in clean reagent bottles with aluminium-lined screw caps.

Pronalys grade anhydrous sodium sulphate (Na_2SO_4) was obtained from J.T. Baker Inc. USA. It was further purified as follows: 100 g portions were each soxhlet-extracted with 100 ml hexane for 8 hours, then baked in a muffle furnace at 400°C overnight, cooled and stored in a desiccator prior to subsequent use.

Florisil (Magnesia-silica gel 60-100 mesh) was purchased from Fisher Scientific. Each batch was extracted for 8 hours with hexane then baked in an oven at 130°C overnight, cooled and stored in a glass container before use in column clean-up operations.

Glasswool was soxhlet-extracted with hexane and stored in a desiccator before use.

To check the purity of each solvent distillate as well as the Na_2SO_4, Florisil and glasswool, procedural blanks were performed with each batch of samples (UNEP, 1982).

Certified A.C.S acetonitrile was obtained from J.T. Baker Inc. USA. It was used directly without further purification.

Whatman No. 42 filter papers were obtained from Whatman International Ltd. They were soxhlet-extracted with hexane before use either as extraction thimbles or for filtration purposes.

3.1.2 Pesticide standards

High purity (99%) p,p'-DDT, p,p'-DDE, p,p'-DDD, endosulfan, aldrin, dieldrin and gamma-BHC (lindane) were obtained from Aldrich Chemical Company Inc., USA. Stock solutions (200 ppm) were prepared every six months by dissolving appropriate amounts of each standard in 25 ml of hexane. Working standard solutions in the range 1-10 ppm were made weekly by serial dilution and transferred to Macartney bottles stoppered with screw tops lined with aluminium foil. The solutions were stored in a deep freezer when not in use.

3.1.3 Glassware

All glassware used for sample collection, extractions and analysis were thoroughly cleaned to eliminate all electron-capturing contaminants which would interfere with pesticide GLC detection (UNEP, 1982). The cleaning procedure involved thorough rinsing with tap water and then with distilled water, redistilled acetone and finally with pesticide-quality hexane. The glassware was then baked in an oven at 130°C overnight and then stored in a dust-free atmosphere. Just before use, the glassware was rinsed with the extracting solvent and checked randomly for contamination (Mansingh and Wilson, 1995).

3.2 Sampling

There were four sampling sites along the coast; namely, Funzi Lazy Lagoon next to the confluence of Ramisi River, Mombasa Old Town, Kilifi Creek at the confluence of Goshi River and at the confluence of Sabaki River near Malindi (Fig. 1.1).

Sampling of seaweed, sediment, seawater and fish was done twice in mid-January and early May 1997 corresponding to two seasons: the hot, dry northeast monsoon and the warm and wet long rains period, respectively (Ogallo and Mwangi).

Water samples were collected in hexane-rinsed 1L brown bottles with screw caps lined with hexane-rinsed aluminium foil. The sample bottles were lowered to fill against the sea tide at knee-height and labelled accordingly (Mansingh and Wilson, 1995).

Sediments were collected by lowering an augur and scooping up the 2 cm undisturbed layer. Samples were then wrapped in hexane-rinsed aluminium foil, fastened by the masking tape and placed in a labelled self-sealing polythene bag prior to storage in a deep freezer.

Five to 10 specimen samples of fresh, small fishes were taken from lots brought by fishermen on the shores of the ocean and wrapped in pre-cleaned aluminium foil. The fish species *Sardinella fimbrita* of length 19.23 cm weighed 27.04 g was from Sabaki, *Penaeus sp* 18.54 cm in length had 77.05 g from Kilifi, *Apolectus niger* with the length of 18.50 cm and weight of 62.66 g were collected from Mombasa and *Pampus argenteus* of length 15.34 cm and weight of 54.72 g were from Ramisi.The wrapped samples were sealed with a masking tape before placing in a labelled polythene bag (UNEP, 1991) and storing in a deep freezer.

Seaweed was harvested using a knife. Samples were washed with seawater, wrapped in aluminium foil and sealed with masking tape before placing in a labelled polythene bag. All the samples were collected in triplicate and within a distance of 100 m from the coastal shores. They were taken at a depth of 0-10 m above and below sea surface and immediately stored in an ice-box. The preserved samples were then transported to Nairobi and stored in a deep-freezer prior to analysis.

3.3 Sample Extraction

For seaweed, sediment and fish, about 30 g of sample was weighed in triplicate and each portion transferred to a mortar. 20 g of anhydrous sodium sulphate was added and the mixture thoroughly crushed using a pestle to ensure homogenity. The homogenate was then quantitatively transferred to a filter paper and sealed using a stapler. Samples were soxhlet-extracted for three hours at the rate of 6 cycles/hr, using 100 ml of a solvent system comprising 85% hexane, 10% acetone and 5% water.

For seawater, 1 litre of sample contained in a separating funnel was shaken with 100 ml of hexane for a period of 30 min. After standing for 10 min the hexane layer was collected in round-bottomed flasks and the extraction repeated twice on the aqueous phase using the same volume of solvent. The hexane extracts were then added together.

A blank extraction involving 20 g of Na_2SO_4 was carried out using the same procedure. All extracts were then evaporated to dryness on a rotary evaporator at reduced pressure. Each residue was reconstituted to 15 ml with hexane.

3.4 Clean-up of Extracts

The hexane concentrates were subjected to clean-up procedure in glass-wool pluged miniature columns each containing 4 g of Florisil (Holden and Marsden, 1969). The column internal diameter was such that when packed with Florisil, an active layer of 10 cm in height was obtained. Once packed, the Florisil was protected at the top from absorbing miosture with a 2 cm fill of anhydrous sodium sulphate and a layer of glass-wool.

For seawater, seaweed and sediment, a 5 ml aliquot of extract was transferred to the Florisil packed column and eluted first with 10 ml hexane, then 10 ml of 5% acetone in hexane, and finally with 10 ml of 10% acetone in hexane. The three fractions were pooled and the solvents expelled using a nitrogen purge on a hot waterbath at 50^0C. The residues were stored in a refrigerator at -5^0C prior to analysis.

The fish extracts in a sample bottle were concentrated by expelling the solvent on a hot water bath at 50^0C, leaving behind fats only. 0.5 g of fat residue was dissolved in 1 ml hexane and applied to the Florisil column. The column was then eluted first with 10 ml hexane, then with 10 ml of 1% acetone in hexane, and finally with 10 ml of 2% acetone in hexane. The eluates were combined and solvent completely expelled on a water bath at 50^0C using N_2 gas as a purging aid.

Each sample extract was reconstituted to 0.5 ml of hexane prior to GLC analysis.

3.5 Sample Analysis

3.5.1 pH of Sediment

All the pH readings were measured according to the procedure of Nderitu (1990) using a Pye Unicam Model 292 Mk2 pH meter. Fresh sample (20 g) was scooped and transferred into a 250 cm^3 conical flask. After attaining room temperature (about 22^0C), 50 cm^3 of distilled water was added to the conical flask and the mixture shaken for 30 min to give a 1:2.5 sediment: water suspension. The pH of the suspension was measured using glass electrodes.

3.5.2 Evaluation of Organic Carbon and Moisture Content of Samples

Portions of seaweed, sediment and fish were each pulverized to obtain coarse powder. 1.5 g of the powder was transferred to a pre-weighed crucible and contents placed in an oven. The temperature of the oven was raised gradually to, and maintained at 110^0C for 24 hr. The residue was re-weighed. The loss in weight was attributed to the moisture content of the sample.

The crucible plus sample were then transferred to a muffle furnace and the temperature raised gradually to, and maintained at 550^0C for 3 hr. The difference in weight was attributed to the organic matter of sample.

3.5.3 Determination of Fat Content in Fish

A gravimetric method was used to determine the fat content of extracted samples. The fish residue from the hexane extraction stage was quantitatively transferred to a pre-weighed Macartney sample bottle. The excess solvent from the residue was expelled by a nitrogen purge on a water bath at 50^0C. The sample bottle was then weighed and the weight of fat extracted determined to the nearest 0.1 mg. The percentage fat contents of samples were then calculated.

3.5.4 Gas Liquid Chromatographic Analysis

The identification and quantification of organochlorine pesticide residues were done using a Perkin-Elmer model 8500 Gas Chromatograph equipped with 63Ni-ECD and a Perkin-Elmer model GP-100 graphics printer. White Spot Nitrogen flowing at a rate of 2 ml/min was used as carrier gas. The stationary phase was an SE-54 capillary column of dimension 30 m x 0.25 mm i d x 0.25 μm film. Column and oven temperatures were set at 200^{0}C and 260^{0}C respectively using a ramp rate of 4^{0}C/min with a 17 min hold at 260^{0}C. Detector and injector temperatures were set at 350^{0}C and 270^{0}C respectively. An attenuation of 128 and chart speed of 5 mm/min were used.

An intercomparative analysis for the confirmation of pesticide residues was done by considering retention times of pesticide standards and those of unknown compounds in sample extracts using a Varian model 3400 Gas Chromatograph equipped with a 63Ni-ECD and a Phillips model 8220 chart recorder set at a speed of 5 mm/min. White spot nitrogen was used as carrier gas at a flow rate of 5 ml/min. The stationary phase was a DB-5 capillary column of dimension 15 m x 0.25 mm i.d x 0.25 μm film. The injector and detector temperatures were set at 230^{0}C and 250^{0}C, respectively while the column temperatures were programmed between 100^{0}C and 250^{0}C at a ramp rate of 5^0/min.

Each sample and blank extract was made to 0.5 ml with hexane and 1 μl of the solution injected into the GLC. For every few injections made, 1 μl of the chlorinated pesticide mixture (CPM) was injected to check on variations in detector response as well as stability of operating conditions. Results from duplicate samples were compared and their means calculated.

3.5.5 Limit of Detection

The limit of detection (LOD) was determined using each of the two GLC columns. In stage one, standard solutions of 0.01-0.10 ppm were prepared and 1 μl solution (10-100 pcg) injected into the SE-54 column. In the second stage, standard solutions of 0.02-0.6 ppm were also

prepared and 1 µl (20-600 pcg) injected into the DB-5 column.

To determine the minimum concentrations of the pesticides at which the detector could give response, peak heights for a series of standard dilutions were plotted against the quantities of standards injected. The plot gave a straight line through the origin and the concentration at the origin was taken as LOD at three times the noise level. Peak heights were also used for quantification of samples. The matrix effect was taken care of by running blanks using capillary columns SE-54 and DB-5.

3.5.6 Recovery studies

Recovery experiments were performed to estimate the losses of organochlorine pesticide residues during the extraction in the clean-up and concentration procedures.

The experiments were performed in two stages. In the first stage, the crude sample was analyzed directly in duplicate. In the second stage, the duplicate portions of the homogeneous crude extracts were spiked with known amounts of aldrin, lindane and p,p'-DDT standards and the contents subjected to the sample analysis procedures (extraction, clean-up and concentration) followed by GLC analysis.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1.1 GLC retention times

Retention times in minutes of the organochlorine pesticides varied with the type of column used (Table 4.1). There were also slight differences in values for standards and sample extracts but these were attributed to differences in matrix composition.

Table 4.1:Variation in GLC retention times with Column Type and Matrix Composition.

Pesticide	SE-54 Column		DB-5 Column	
	Standard	Sample	Standard	Sample
Lindane	15.90	15.93	3.41	3.46
Aldrin	19.89	19.92	5.56	5.55
Endosulfan	23.64	23.60	6.56	6.58
P,p'-DDE	24.29	24.31	6.88	6.85
Dieldrin	25.06	25.04	6.95	6.96
P,p'-DDD	27.40	27.38	7.34	7.32
P,p'-DDT	30.08	30.09	7.96	7.93

4.1.2 Limit of detection

The limit of detection (LOD) of pesticide standards (section 3.6.5) gave an indication of the sensitivity of the ECD detector. However, the minimum levels of pesticide residues from biota

and abiota marine samples which could be reliably detected and quantified could be influenced by the purity of solvents, and the reagents, as well as efficiency of the clean-up procedures but this effect was nullified by a parallel run of the blank.

As was the case with the RT values presented in the preceeding sections, the LOD (at twice the detector noise level) depended on the GLC column used. The SE-54 column generally gave lower LOD for aldrin, p,p'-DDE, p,p'-DDD and p,p'-DDT, than the DB-5 column, which was more sensitive for endosulfan but gave comparable values for lindane and dieldrin.

Table 4.2: Limit of detection

Pesticide	Limit of detection (pcg/uL)	
	SE-54 Column	DB-5 Column
Lindane	25.96	25.00
Aldrin	15.07	30.00
Endosulfan	89.71	50.00
P,p'-DDE	35.45	100.00
Dieldrin	97.78	100.00
P,p'-DDD	34.80	200.00
P,p'-DDT	96.42	500.00

4.1.3 Recoveries

Mean percentage recoveries of over 83% were obtained for aldrin, lindane and p,p'-DDT in all the marine samples analysed (Table 4.3). These recoveries were taken as good enough and therefore no adjustments in concentrations of organochlorine pesticide residues obtained in this current study were made.

Table 4.3: Recoveries of aldrin, lindane and p,p'-DDT in marine samples

Samples	Pesticides	Amount spiked (ng/g)	Amount recovered (ng/g)	Mean recovery (ng/g)
Seawater	Aldrin	10.00	8.36	83.60
	Lindane	10.00	8.81	88.10
	p,p-'DDT	15.00	13.10	87.33
Seaweed	Aldrin	10.00	8.63	86.30
	Lindane	10.00	8.54	85.40
	p,p'-DDT	15.00	13.41	89.40
Sediment	Aldrin	10.00	9.23	92.30
	Lindane	10.00	8.85	88.50
	p,p-'DDT	15.00	12.93	86.20
Fish	Aldrin	10.00	9.07	90.70
	Lindane	10.00	8.79	87.90
	p,p'-DDT	15.00	12.98	86.53

3 Samples analysed

4.2 Discussion of marine samples analyzed

4.2.1 Seaweeds

The results of moisture and organic contents of seaweeds determined at four sampling stations are presented in Table 4.4.

The moisture content of seaweeds was about 69.52% by weight compared to the organic content of 9.28%.

Table 4.4 Moisture and organic contents of seaweeds

Station	Percentage content	
	Moisture	Organic
Sabaki	71.29	8.23
Kilifi	74.12	13.25
Mombasa	77.21	12.05
Ramisi	55.45	3.60

4.2.2 Sediment composition and texture

The sediments along the Kenyan coast seem very heterogenous except for the pH and moisture content (M.C) which were similar at all the four sampling stations (Table 4.5).

Table 4.8: Some characteristics of sediments used in this study

Station	PH	Sand (%)	Silt (%)	Clay (%)	O.C (%)	M.C (%)	Texture
Sabaki	7.6	0.32	42.49	30.16	4.70	20.33	Silty clay
Kilifi	7.7	76.46	1.98	0.27	0.54	18.20	Sandy
Mombasa	7.6	69.14	2.46	1.62	0.56	17.00	Sandy
Ramisi	7.4	45.02	14.24	6.80	0.73	19.66	Sandy loam

O.C:- Organic Carbon M.C:- Moisture Content

Organic carbon (O.C) content was generally below 1% except for Sabaki station which showed a very high value probably due to the greater primary productivity of the river mouth. Similarly, Sabaki station had high values of silt and clay while the three other stations had high sand content in sediments.

Chemical and physical properties of an ecosystem in which pesticides enter e.g the pH, mineral composition, organic material and moisture content determine the behaviour of a particular

insecticide and its ultimate fate in the environment (Miller, 1978). Pesticides persist longer in soils with higher organic matter (which binds the residues tightly) than in mineral (sandy or clay) soils. Water causes residues to be displaced from the soil particles which then vapourize.

4.2.3 Marine fish

Fish characteristics were analyzed and the results are given in Table 4.6.

Table 4.6: Characteristics of fish samples analyzed

Station	Fish species	Mean weight(g)	Mean lenght(cm)	Moisture content (%)	Organic content (%)	Lipid content (%)
Sabaki	Sardinella fimbrita (sardine)	27.04	19.23	73.36	19.35	3.92
Kilifi	Penaeus sp (Prawn)	77.05	18.54	79.51	18.46	4.36
Mombasa	Apolectus niger (black pomfret)	62.66	18.50	74.27	21.54	3.25
Ramisi	Pampus argenteus (silver pomfret)	54.72	15.34	75.66	18.90	3.74

In the marine environment, moisture content in fish accounts for about three-quarters of its mass on wet weight basis, whereas the organic and lipid contents cater for the remaining weight comparable to results obtained by Nhan *et al.*(1997) at the Red River estuary in Vietnam.

Similarly, Munga (1985) found 3.62% lipid content of fish from Tana River while Everaarts *et al.*(1996) obtained 2.09% lipid content of fish from Formosa Bay adjacent to the confluence of Sabaki River.

Generally, the marine fish from different sampling sites under this study showed similar trends in composition of moisture, organic and lipid parameters. All the fishes analyzed were migratory and are well distributed along the coastal areas of Kenya at the depth of between 30 m to 210 m.

4.3 Organochlorine residues in marine samples

6 samples of seawater, and 6 samples each of seaweed, sediment and fish were analyzed for organochlorine residues each from four sites. All the results are expressed in parts per billion (ppb). The following main factors were considered important for discussion of the results in this investigation.

a) The distribution of organochlorine pesticide residues in marine samples from different sampling stations and

(b) Seasonal variations of the organochlorine residues along the Kenyan coastal marine environment.

4.3.1 Variation of organochlorine pesticide residue concentrations with sampling sites

4.3.1.1 Water samples

The mean residue concentrations of the seven organochlorines in seawater samples (Table 4.7) show that water from all the four sampling stations was contaminated.

Table 4.7 : Organochlorine pesticide residues detected in water samples at different sites.

Insecticide	Mean (±sd)* residues in water (ppb)			
	Sabaki	Kilifi	Mombasa	Ramisi
Lindane	0.241± 0.09	0.503±0.161	BDL	BDL
Aldrin	0.378±0.002	0.019±0.004	0.054±0.019	0.025±0.006
Endosulfan	0.166±0.015	0.239±0.142	0.397±0.223	0.155±0.057
p,p'-DDE	0.213±0.032	0.299±0.175	0.175±0.128	0.064±0.035
Dieldrin	0.251±0.006	0.160± 0.05	0.501±0.458	0.144±0.034
P,p'-DDD	0.295±0.231	0.177±0.146	0.072± 0.01	0.058±0.017
p,p'-DDT	0.168±0.067	0.370 ±0.01	BDL	0.194±0.073

sd:- Standard deviation BDL:- Below detection limit 6 samples per site

In the samples from the confluence of Sabaki River, which flows from the central highlands of the country with intensive agricultural and other human loads, all the pesticides were detected, the highest concentration being that of p,p'-DDD (0.295 ppb) of the DDT family, while the least concentration was aldrin (0.0378 ppb).

In Kilifi Creek, residues of all the seven insecticides were also detected with four at relatively higher levels than at Sabaki. Highest concentrations found were those of lindane (0.503 ppb) while aldrin (0.019 ppb) gave the lowest levels. Goshi River which rises from the Taita Hills is a possible carrier of pollutants including pesticides and enters the Indian ocean at the Kilifi Creek.

Of the compounds under investigation, concentrations of dieldrin were highest in Mombasa Old Town water samples (o.501 ppb) compared to those of aldrin (0.054 ppb) which were the lowest. However, lindane and p,p'-DDT were below the detection level. And among the DDT

metabolites, only p,p'-DDE and p,p'-DDD were detected at concentrations of 0.175 and 0.072 ppb, respectively. Of the cyclodiene compounds, endosulfan was detected at mean concentrations of 0.40 ppb.

Water samples from the confluence of Ramisi River had lindane below detection level as found in Mombasa station water but concentrations of the residues of other organochlorines detected were the lowest compared to those of the rest of the sampling sites. The p,p'-DDT mean concentrations (0.194 ppb) were the highest while those of aldrin (0.025 ppb) were the lowest. Ramisi area is fairly remote with few agricultural activities since the closure of Ramisi Sugar Factory. However, presence of dieldrin (an epoxide metabolite of aldrin), endosulfan and p,p'-DDT indicates recent use of insecticides in the areas.

Generally, the solubility of organochlorines in water is very low (Hassall, 1990). Therefore, low concentrations of residues are expected in contaminated water. In an experiment simulating a tropical marine environment (Mbuvi, 1997) the distribution of spiked DDT in water declined drastically within the first 24 hours, from 1.71 to 0.05 ppb but thereafter the decrease was almost negligible to the end of the experimental period. Therefore the levels detected could be the residual concentration of the initial concentrations.

The occurrence of the residues in coastal shallow waters at the four sampling stations is not surprising since endosulfan, lindane, dieldrin and DDT are still in restricted usage legally (PCPB, 1996). Besides the anthropogenic activities, tides have the potential to transport pollutants from one area to another and have contributed to the contamination in coastal surface waters globally (Everaarts *et al.*, 1996).

Samples from the sea coast of Portland in Jamaica had mean concentrations of endosulfan and p,p'-DDE at 0.042 and 0.83 ppb, respectively (Mansingh, 1993). Later, the concentration levels of dieldrin, endosulfan and p,p'-DDT were 1.88, 2.98 and 7.02 ppb, respectively in Kingston Harbour, Jamaica (Mansingh and Wilson, 1995). These coastal waters are relatively more polluted than those along the coast of Kenya.

By contrast, recent findings in coastal waters at the Bay of Bengal in India showed lindane at concentrations of 0.002 ppb (Matin *et al.*, 1997) which were less contaminated than those in the current study.

However, the observed variations in the residue levels along coastal regions of the world could be attributed to variations of physico-chemical properties of waters and biogenic matter influencing degradation of the pesticides.

4.3.1.2 Seaweed samples

Residues of seven organochlorine pesticides (lindane, aldrin, endosulfan, p,p'-DDE, dieldrin, p,p'-DDD and p,p'-DDT) were detected in measurable quantities in most seaweed samples collected from the four sampling stations (Table 4.8).

Table 4.8 : Organochlorine pesticide residues detected in seaweed samples at different sites.

Insecticide	Mean (±sd) residues in seaweeds (ppb)			
	Sabaki	Kilifi	Mombasa	Ramisi
Lindane	BDL	BDL	10.1 ± 0.08	34.6±1.87
Aldrin	5.27±1.43	5.37±0.63	9.51±8.60	2.35±0.656
Endosulfan	7.49±4.44	16.68±1.13	10.63±1.40	18.79±2.45
p,p'-DDE	6.38±7.15	5.11±2.87	6.18±6.25	1.66±0.715
Dieldrin	8.20±7.88	7.49±5.71	9.68±4.84	9.53 ± 0.03
p,p'-DDD	8.45±8.44	7.27±2.01	4.21±4.61	6.41±6.76
p,p'-DDT	7.56±1.77	34.26±25.7	5.27±0.013	BDL

sd:- Standard deviation BDL:- Below detection limit 6 samples per site

Mean organochlorine pesticide residue concentration in samples from Mombasa Old Town

was highest for endosulfan (10.4 ppb) but lowest for p,p'-DDD (4.21 ppb), while concentrations of dieldrin (9.68 ppb) and aldrin (9.51 ppb) were comparable in magnitude.

Samples from the confluence of Sabaki River had lindane at concentrations below the detection level. The DDT metabolite p,p'-DDD gave the highest residue concentration of 8.45 ppb and was present in all samples analyzed. Aldrin was detected in only 40% of samples at concentrations (5.27 ppb) slightly lower than its metabolite dieldrin (8.20 ppb).

Samples from Kilifi Creek had no detectable concentrations of lindane but p,p'-DDT was detected at levels of upto 34.26 ppb similar to samples from Sabaki, suggesting of a prevailing pollution source in the two sampling sites.

Concentrations of lindane were highest in all samples from the confluence of Ramisi River. Two members of the DDT family were present in very low concentrations: p,p'-DDE (1.66 ppb) and p,p'-DDD (6.41 ppb). The parent compound could not be detected while aldrin and endosulfan concentrations were twice those of p,p'-DDE and dieldrin, respectively.

Different species of macroalgae from the Venice Lagoon gave mean concentrations of lindane and DDTs of 1.33 and 2.05 ppb , respectively. But the variation in levels depended on the structure of fronds, the life length, the period of the year and the constituents of fronds (Maroli *et al.*, 1993). These levels were approximately seventeen times less than the highest concentration found in this study.

Seaweeds can therefore store micropollutants, by a mechanical and physico-chemical concentration process and disseminate them to surface sediments and/or to the water body through dispersion of fine materials into which they are transformed upon decomposition.

4.3.1.3 Sediment Samples

The data showed a striking difference in concentrations of various pesticides residues detected in sediment samples from the confluence of Sabaki River (Table 4.9).

Table 4.9 : Organochlorine pesticide residues detected in sediment samples at different sites

Insecticide	Mean (±sd) residues in sediment (ppb)			
	Sabaki	Kilifi	Mombasa	Ramisi
Lindane	BDL	BDL	7.55±7.50	13.4±3.72
Aldrin	4.38±2.63	6.76 ± 0.12	7.39±4.94	21.4±2.01
Endosulfan	2.94±0.386	6.77±0.443	7.34±6.04	8.71±4.30
p,p'-DDE	3.19±1.19	7.05±4.08	0.954 ± 0.25	3.85±2.33
Dieldrin	22.74±15.4	11.8±5.62	5.85±2.45	9.33±4.56
p,p'-DDD	4.94±4.85	10.5±7.40	2.82±1.31	6.13±2.58
p,p'-DDT	7.04±3.39	10.8±3.94	3.55±0.639	12.20±6.80

sd:- Standard deviation BDL:- Below detection limit 6 samples per site

Of the seven pesticide residues, dieldrin (22.7 ppb) had the highest mean concentration which was approximately 7 times greater than that of endosulfan (2.94 ppb). The concentrations of the metabolites p,p'-DDE and p,p'-DDD, and the parent p,p'-DDT were 3.19, 4.94 and 7.04 ppb, respectively. But aldrin had very low concentration while lindane had undetectable quantities.

Dieldrin concentrations in samples from the Kilifi Creek (11.8 ppb) were much lower than at the confluence of Sabaki River. Lindane was undetected while aldrin (6.76 ppb) gave the lowest concentration. Members of the DDT family were all detected and quantified with their concentrations in close range. These values are relatively much higher than those detected by

Prats *et al.* (1992) along the coast of Alicante, Spain which ranged between 0.002 to 0.230 ppb.

Residues detected in samples from Mombasa Old Town gave lindane, aldrin and endosulfan with relatively high mean concentrations. In Kenya, these compounds are legally in restricted use and their presence in marine sediments is not unexpected. Dieldrin and lindane at concentration levels of 5.85 and 7.55 ppb, respetively, showed the highest frequency of occurrence (80%) from samples analysed while p,p'-DDE (0.95 ppb) was the lowest.

Pesticide residues in sediment samples from the confluence of Ramisi River were present above their limit of detection. Aldrin had the highest mean concentration at approximately 2.4 times those for endosulfan and dieldrin. p,p'-DDT at mean concentrations of 12.2 ppb were higher than p,p'-DDD and p,p'-DDE by factors of 2 and 3.6, respectively.

In a recent study by Everaats *et al.*(1996), sediment samples from the shallowest point next to the Sabaki River had dieldrin at concentrations averaging 98.5 ppb, wet weight. The sharp drop in concentrations to over four times in this currnt study indicates that the use of dieldrin has been on the decrease in the area. p,p'-DDE was quantified at the same sites with concentrations ranging from 65.5 to 1038 ppb wet weight. But concentrations of lindane ranged from 31.5 to 137 ppb while those of p,p'-DDD were 185 ppb wet weight. At Gazi next to Ramisi, lindane concentration was 215 ppb.

The occurrence of dieldrin in sediment samples was relatively high at the confluence of Sabaki River and the Kilifi Creek suggesting a prevailing pollution source. The concentrations of aldrin was much higher than that of dieldrin for samples from Mombasa and Ramisi. Aldrin is rarely found in the environment (unlike dieldrin) as a result of its rapid transformation into dieldrin. Therefore detection of aldrin in sediment suggested the direct input of aldrin into the aquatic environment from nearby point sources, followed by rapid burial and preservation under anaerobic sediments (as for DDT). It is most likely that dieldrin was also released directly to the coastal waters in the industrial run-off in Mombasa and human habitation areas in Ramisi.

The predominance of p,p'-DDT in sediment samples from all the four sampling stations suggested that very little degradation had taken place and the compound was still in use. The observation that the concentration of DDD in sediments was always greater than that of DDE implied occurrence of anaerobic degradation of DDT. Any aerobic breakdown of DDT was limited since DDE was below 25% of total DDT. These results suggest that DDT entry to the oceans was from sources closer to the coastal aquatic environment and that DDT was retained under mostly anaerobic conditions within the sediment which acts as a sink.

Decomposition of large amounts of biomass enriches the surface sediments with organic carbon but redistribution of the organochlorines by bioturbation and/or the physical mixing of sediments probably moved the contaminants into lower levels of sediments. This process could lower the concentration of total organochlorines in the surface sediments since analysis was done for 2 cm layer depth.

Residue concentrations of pesticides in sediments along the west coast of India showed that dieldrin < aldrin < HCH < DDT with the highest values of total DDT ranging from 32 to 43 ppb wet wt (Zitko and Hanlon, 1991) while the east coast had the concentration ranges of aldrin: (20-530), lindane: (10-210), dieldrin: (50-510) and total DDT: (0.020-0.780), all in ppb wet weight (Sarkar and Gupta, 1988). These values are relatively higher than the ones obtained in this study.

In Kingston Harbour sediments, more than one residue was detected with the aldrin showing the highest concentrations of 36.7 ppb (Mansingh and Wilson, 1995) while the estuary of Palizada River in Mexico had lindane, p,p'-DDE and aldrin levels of 0.57, 17.67 and 9.02 ppb, respectively (Gold-Bouchot *et al.*, 1993). In this study, the highest values for lindane, p,p'-DDE and aldrin were 13.4, 7.05 and 21.4 ppb, respectively which illustrates usage of these pesticides globally.

4.3.1.4 Fish Samples

Data from the confluence of Sabaki River (Table 4.10) revealed that lindane (612.02 ppb) lipid

content) had the highest mean residue concentration as well as the frequency of occurrences (80%) in the number of fish samples analysed.

Table 4.10 : Organochlorine pesticide residues detected in fish samples at different sites

Insecticide	Mean (±sd) residues in fish (μg/kg fat)			
	Sabaki	Kilifi	Mombasa	Ramisi
Lindane	612±545	26.5 ± 0.92	57.3±51.7	281±332
Aldrin	41.8±23.6	91.7±1.35	3.29±2.20	102±99.7
Endosulfan	40.2±14.4	22.9±0.276	12.0±5.44	10.4 ± 0.18
p,p'-DDE	41.1±40.0	1.94± 0.08	9.77±7.83	15.7±10.5
Dieldrin	48.5±43.1	8.69 ± 0.15	11.2±3.25	43.1±38.1
p,p'-DDD	70.8±40.8	51.9±4.70	23.8±2.22	21.8±13.6
p,p'-DDT	17.9±4.31	21.8±7.46	10.4±1.26	17.9±7.94

sd:- Standard deviation BDL:- Below detection limit 6 samples per site

Other high values of lindane were reported in Suruga Bay, Japan and could suggest that fish are resistant to lindane. Aldrin, dieldrin and endosulfan residues were at comparable concentration levels of 41.8, 48.5 and 40.2 ppb lipid content, respectively. Among the metabolites of DDT, the concentrations of p,p'-DDD (70.8 ppb) were the highest and were approximately 4 times of p,p'-DDT and 2 times that of p,p'-DDE concentrations. The lowest mean concentrations in fish samples from the Sabaki site were those of p,p'-DDT (17.9 ppb lipid) with the least frequency of 40% of all the samples analysed.

At the Kilifi Creek, the major residue detected in fish was aldrin (91.7 ppb lipid content) but p,p'-DDE gave the lowest mean concentration of 1.94 ppb lipid. Other members of the DDT family were present in high amounts: p,p'-DDT (21.8 ppb lipid) and p,p'-DDD (51.9 ppb lipid).

content) had the highest mean residue concentration as well as the frequency of occurrences (80%) in the number of fish samples analysed.

Table 4.10 : Organochlorine pesticide residues detected in fish samples at different sites

Insecticide	Mean (±sd) residues in fish (μg/kg fat)			
	Sabaki	Kilifi	Mombasa	Ramisi
Lindane	612±545	26.5 ± 0.92	57.3±51.7	281±332
Aldrin	41.8±23.6	91.7±1.35	3.29±2.20	102±99.7
Endosulfan	40.2±14.4	22.9±0.276	12.0±5.44	10.4 ± 0.18
p,p'-DDE	41.1±40.0	1.94± 0.08	9.77±7.83	15.7±10.5
Dieldrin	48.5±43.1	8.69 ± 0.15	11.2±3.25	43.1±38.1
p,p'-DDD	70.8±40.8	51.9±4.70	23.8±2.22	21.8±13.6
p,p'-DDT	17.9±4.31	21.8±7.46	10.4±1.26	17.9±7.94

sd:- Standard deviation BDL:- Below detection limit 6 samples per site

Other high values of lindane were reported in Suruga Bay, Japan and could suggest that fish are resistant to lindane. Aldrin, dieldrin and endosulfan residues were at comparable concentration levels of 41.8, 48.5 and 40.2 ppb lipid content, respectively. Among the metabolites of DDT, the concentrations of p,p'-DDD (70.8 ppb) were the highest and were approximately 4 times of p,p'-DDT and 2 times that of p,p'-DDE concentrations. The lowest mean concentrations in fish samples from the Sabaki site were those of p,p'-DDT (17.9 ppb lipid) with the least frequency of 40% of all the samples analysed.

At the Kilifi Creek, the major residue detected in fish was aldrin (91.7 ppb lipid content) but p,p'-DDE gave the lowest mean concentration of 1.94 ppb lipid. Other members of the DDT family were present in high amounts: p,p'-DDT (21.8 ppb lipid) and p,p'-DDD (51.9 ppb lipid).

Of the pesticide residues analyzed in fish samples from the Mombasa site, lindane (57.3 ppb lipid) was present in the highest amounts, and frequency of occurrence at 80% in samples analysed. Levels of aldrin (3.29 ppb lipid) were slightly above their detection limits while its metabolite dieldrin was approximately 3 times more, suggesting decreased uptake of aldrin by fish. p,p'-DDD (23.8 ppb lipid) was the highest at about twice the concentrations of other DDT family compounds.

Lindane at concentration levels of 281 ppb (lipid) were detected in the highest mean concentration in fish samples from Ramisi site followed by aldrin (102 ppb lipid) which was 2 times more than its metabolite dieldrin. But the concentrations of endosulfan at 10.4 ppb lipid were the lowest while the members of DDT family had relatively a similar concentrations although p,p'-DDD (23.8 ppb lipid) was slightly higher.

Persistent organochlorines have high lipophilicity (Hassal, 1990). Therefore relatively high amounts of chlorinated compounds present in fish samples were not astonishing since fishes have high extractable lipid content From all sampling stations except at Kilifi Creek, lindane was present in highest concentrations suggesting high rates of continued usage of technical BHC formulations for soil treatment, foliage application on fruit and nut trees, vegetables, ornamentals, timber, and wood protection. Transportion of pollutants to the ocean waters and subsequent bioaccumulation in marine fish samples could have occurred.

In this study, concentrations of p,p-'DDT were less than its metabolite p,p-'DDD. Moreover, higher concentrations of p,p-'DDD than those of p,p-'DDE found in this study suggest anaerobic transformation of p,p-'DDT in fish lipids. Since p,p-'DDE is less toxic than p,p-'DDT, the breakdown of the parent compound probably represents a protective mechanism in fish.

The contamination of organochlorines in Suruga Bay (Japan) coastal fish were comparable to reported levels (especially of lindane at Kilifi and Ramisi) in this study: DDTs and HCHs

concentrations ranged from 80-1700 and 1.0-250 ppb lipid, respectively (Lee *et al.*, 1997).

Fish from Meghna-Dhonagoda River estuary in Bangladesh contained relatively much higher mean levels of residues than in the current study: p,p'-DDT and p,p'-DDD were at concentrations of 1280 and 1370 ppb lipid, respectively. Lindane levels were 26 ppb lipid while quantities of aldrin and dieldrin were not detectable (Matin *et al.*, 1997).

4.3.2 Seasonal Variations of Residue Concentrations

4.3.2.1 Water Samples

Organochlorine (OC) residues in water samples collected and analyzed from different sampling stations along the Kenyan coast during dry and rainy seasons are presented in Table 4.11.

Table 4.11: Concentration of residues in water sampled during dry and rainy seasons

Station	Mean (± sd) residue concentration in water (ppb)						
	Lindane	Aldrin	Endosulfan	p,p'-DDE	Dieldrin	p,p'-DDD	p,p'-DDT
No. 1							
Dry	BDL	BDL	0.182±0.04	0.191±0.12	0.245±0.12	0.132±0.01	BDL
Wet	0.241±0.07	0.038±0.01	0.152±0.06	0.232±0.15	0.257±0.05	0.377±0.09	0.168±0.01
No. 2							
Dry	BDL	0.020±0.01	0.140±0.02	0.354±0.03	0.162±0.09	0.071±0.01	BDL
Wet	0.503±0.25	0.002±0.001	0.440±0.01	0.189±0.04	BDL	0.229±0.01	BDL
No. 3							
Dry	BDL	0.044±0.01	0.241±0.04	0.106±0.01	0.257±0.05	BDL	BDL
Wet	BDL	58.9±0.85	0.712±0.15	0.225±0.02	0.744±019	0.072±0.01	BDL
No. 4							
Dry	BDL	18.8±5.26	0.134±0.05	0.064±0.01	0.123±0.05	0.056±0.01	0.121±0.07
Wet	BDL	31.1±9.85	0.197±0.05	64.6±5.57	0.164±0.09	0.063±0.01	0.267±0.05

No.1 - Sabaki No.2- Kilifi No.3- Mombasa No.4- Ramisi

BDL - Below detection limit sd:- Standard deviation 6 samples per site

Water samples from the mouth of Sabaki River gave p,p'-DDD (0.377 ppb) with the highest mean residue concentrations during the rainy season followed closely by dieldrin and p,p'-DDE. Lindane, aldrin and p,p'-DDT were below levels of detection in dry season but the three residues were detected in high amounts during the rainy season. Four residues were present in water samples in both seasons.

At the Kilifi Creek, lindane (0.503 ppb) was present in the highest residue concentration during the rainy season but could not be detected in the dry season. In the two seasons, p,p'-DDT was absent but its metabolites p,p'-DDE and p,p'-DDD were present in significant amounts suggesting that DDT pesticide may have been out of use during the sampling periods. Dieldrin (0.160 ppb) was approximately 8 times the concentration of its parent compound aldrin in the dry season while endosulfan was present in different seasons.

The metabolite p,p'-DDE had the highest mean residue concentration within the DDT family in both seasons in water samples from the shores of Mombasa Old Town. These results highlight the known stability and persistence of DDE in the environment. DDT is used for disinfection of the Kilindini Harbour and for the control of stalkborer in growing maize. Dieldrin and endosulfan were present in highest amount owing to their use in controlling banana weevils, beans and mango pests along the coast. Lindane and p,p'-DDT (probably due to its rapid transformation to DDE) were absent in dry and rainy seasons. It is probable that lindane is not extensively used around Mombasa.

No residues of lindane were found in water samples from the confluence of Ramisi River in either season (as found in Mombasa). The residue p,p'-DDE had the highest mean concentration of 64.6 ppb during the wet weather while the metabolites p,p'-DDT and p,p'-DDD were also present indicating extensive use of DDT in this region and its surrounding areas especially in Ramisi River valley. Six pesticide residues were detected in both seasons but their concentrations were higher during the rainy season.

In summary, a general trend was observed for water samples analyzed from the four sampling stations. In a few cases some pesticide residues were below their limits of detection during the dry season only to be detected during the rainy season. This observation can be explained from the basic fact that there is intense use of pesticides in the upcountry which are subsequently transported into the ocean as runoffs during the rain season. Some pesticide residues were below their detection limit in both seasons indicating that they were hardly in use in both seasons. Finally, pesticide residues were generally present in higher concentrations during the rainy season than in dry season. A similar correlation was observed in the estuary of the Hope River in Jamaica between 1989-1991 (Mansingh *et al.*, in press) whereby the concentration of organochlorine pesticide residue endosulfan ranged between 0.012-2.90 ppb and 0.002-36.6 ppb during the dry and wet seasons, respectively.

4.3.2.2 Seaweed Samples

Table 4.12 provides data for organochlorine residues in seaweed samples collected in different sampling stations along the Kenyan coast during the dry season (January, 1997) and the rainy

season (May 1997).

Table 4.12: Concentration of organochlorine pesticide residues in seawater sampled during dry and rainy seasons

Station		Mean (± s.d) residue concentration in seaweed (ppb)						
		Lindane	Aldrin	Endosulfan	p,p'-DDE	Dieldrin	p,p'-DDD	p,p'-DDT
No. 1								
	Dry	BDL	3.83±0.59	4.01±0.95	3.05±0.15	BDL	5.06±1.28	
	Wet	BDL	6.72±1.32	9.22±2.33	9.71±2.81	820±1.58	11.8±3.35	7.55±1.21
No. 2								
	Dry	BDL	BDL	6.37±0.52	3.67±0.21	4.82±1.22	1.61±0.01	BDL
	Wet	BDL	5.37±1.29	26.9±5.55	5.59±1.25	10.2±2.27	39.48±7.78	34.3±6.51
No. 3								
	Dry	BDL	0.91±0.15	9.59±0.22	2.77±0.91	4.43±1.21	1.55±0.09	BDL
	Wet	10.1±1.92	18.1±1.55	11.0±2.58	9.59±2.14	12.3±1.21	12.2±1.91	5.27±2.05
No. 4								
	Dry	BDL	BDL	13.0	2.38	BDL	BDL	BDL
	Wet	34.59±1.25	2.35±0.21	21.7±4.75	8.67±0.59	9.53±0.51	2.38±0.51	BDL

No.1 - Sabaki No.2 - Kilifi No.3 - Mombasa No.4 - Ramisi

BDL - Below detection limit sd:- Standard deviation 6 samples per site

Only lindane residues in seaweeds from the mouth of Sabaki River were absent in both seasons. The DDT metabolite p,p'-DDE and was present at 4 times its concentration in rainy season than in dry season, while p,p'-DDD was only detected in samples during the rainy season. DDT is used extensively for aerial spraying of cotton fields around Margarini in Malindi, while formulations containing DDT and dieldrin are used for spraying tsetse-infested areas north of Malindi. High concentrations of p,p-'DDD and p,p-'DDE in seaweeds indicate their high persistence in the biotic environment and possible biomagnifications. Dieldrin and p,p'-DDT residues were not detected in dry season but were present during the rainy season at Sabaki. Aldrin and endosulfan were detectable irrespective of the season of analysis.

The mean concentrations of p,p'-DDD (39.48 ppb) were the highest in seaweeds analyzed from Kilifi Creek during the rainy season while concentration levels of p,p'-DDT were relatively high, compared to that of p,p'-DDE. Quantities of aldrin and p,p'-DDT were below the level of detection only in the dry season whereas lindane was absent altogether at Kilifi. Only four

pesticide residues were detectable in seaweeds during both seasons, the levels being higher in the rainy season.

All the seven organochlorine pesticides were detected in seaweed samples from Mombasa Old Town during the rainy season but two residues were below the level of detection in the dry season. Aldrin (18.11 ppb) gave the highest concentrations in the rainy season in Mombasa Old Town probably due to its extensive use in controlling of banana weevils around Mombasa. During the wet weather, the concentrations of six residues were above 9.59 ppb in seaweeds except for p,p'-DDT at the levels of 5 27 ppb.

Samples from the confluence of Ramisi River had lindane (34.59 ppb) with the highest mean concentrations in rainy season but absent during the dry season. p,p'-DDE was the only member of the DDT family detected only in the dry season but p,p'-DDT was absent in both seasons. p,p'-DDE residue had also higher amounts implying its accumulation in seaweeds. The endosulfan residues were detected in significant amounts in both seasons suggesting its use to control maize stalkborer and army worms in Kwale district.

Generally, lindane was absent at Sabaki and Kilifi sites but detectable at Mombasa and Ramisi sites during the wet weather suggestive of its rampant use in the latter stations in the wet periods of the year. The rainy season had the higher concentration of residues in seaweeds in the four stations. In comparison to other coastal environments, a similar seasonal pattern of residue occurrence for DDTs and PCBs was established in biotic organisms along the Sado River estuary in Portugal (Castrol *et al.*, 1990).

4.3.2.3 Sediment Samples

Analytical data for the seven organochlorine pesticide residues in sediment samples from four sampling sites are summarized in table 4.13.

During the rainy season, sediments collected from the confluence of Sabaki showed dieldrin residues (44.5 ppb) having the highest concentrations while its parent compound aldrin was

approximately 7 times less. p,p'-DDT and p,p'-DDD were at least twice the concentrations of the persistent metabolite p,p'-DDE in the rainy season. Lindane was absent while endosulfan was only detected in rainy season. This trend indicates strong washout of DDT compounds, dieldrin and endosulfan from cotton and maize fields around Margarini in Malindi into the ocean.

Sediment samples from Kilifi Creek did not show any lindane residues in both seasons whereas aldrin was present only in the rainy season. During the dry and rainy seasons, concentrations of endosulfan and p,p'-DDD in surface sediments did not show identifiable geographic trend since they were similar. However, concentrations of dieldrin, p,p'-DDD and p,p'-DDT in sediment samples collected in the rainy season were higher than those in the dry season by a factor of two.

Table 4.13: Concentration of organochlorine pesticide residues in sediments sampled during dry and rainy seasons

Station		Mean residue concentration in water (ppb)						
		Lindane	Aldrin	Endosulfan	p,p'-DDE	Dieldrin	p,p'-DDD	p,p'-DDT
No. 1								
	Dry	BDL	0.71±0.21	BDL	2.36±0.27	11.9±0.92	2.15±0.03	4.66±0.32
	Wet	BDL	6.22±1.25	2.94±0.21	4.87±0.51	44.5±7.99	13.3±2.51	11.8±1.56
No. 2								
	Dry	BDL	BDL	6.33±0.91	6.86±0.82	6.21±0.09	3.95±0.05	6.91±1.21
	Wet	BDL	6.78±0.21	7.21±0.41	7.24±1.29	17.5±1.99	13.8±1.75	14.7±2.57
No. 3								
	Dry	2.26±0.21	BDL	2.69±0.11	0.954±0.01	3.67±0.21	1.38±0.02	BDL
	Wet	12.8±2.22	7.39±1.21	12.0±1.27	BDL	6.58±1.97	3.99±0.09	3.55±0.07
No. 4								
	Dry	8.32±0.21	BDL	4.69±0.22	4.83±0.11	7.37±0.91	3.17±0.99	3.29±0.01
	Wet	16.0±1.21	21.4	10.7±2.11	1.89±0.09	10.3±1.33	7.12±0.51	15.2±3.33

No.1 - Sabaki No.2 - Kilifi No.3 - Mombasa No.4 - Ramisi

BDL - Below detection limit sd:- Standard deviation 6 samples per site

The highest mean concentrations in sediments collected from Mombasa Old Town (contrary to that found in Kilifi and Sabaki) during the rainy season was that of lindane, followed closely by endosulfan. It is possible that there was increased usage of lindane (for seed dressing) and endosulfan (for tsetse control and cotton pest control) around Mombasa during the rainy season. Aldrin, dieldrin and p,p'-DDT residues were detectable in higher concentrations during the rainy season owing to their increased usage for mosquito control in public health.

From the confluence of Ramisi River (unlike in other sites), aldrin was quantified in sediments in significant concentrations of 21.4 ppb during the wet weather but it was the only residue not detected in dry season. Termites are very destructive in a dry period and it was likely that aldrin was used for termite elimination which was later washed away from inland areas into the marine environment. Apart from aldrin the rest of the pesticide residues were present in sediments in both seasons.

In conclusion, sediment samples collected in the four sampling stations showed higher organochlorine pesticide residue concentrations in rainy season than during the dry season. This trend could be explained by the fact that there was a strong washout of pesticide residues from inland agricultural and industrial regions to the marine ecosystems during the rainy seasons.

A similar seasonal pattern was established in sediments from estuarine zones of the Hope River in Jamaica: residues were detectable more frequently and at higher concentrations in rainy weather than in the dry period at ranges of 0.03-66.1 and 0.05-1.18 ppb for endosulfan; and 0.128-3.70 and 0.95-2.33 ppb for dieldrin, respectively (Mansingh *et al.*, in press). By contrast, sediment samples in coastal regions North of Vietnam had higher concentrations of organochlorine residues in dry season than in rainy conditions with ranges of 0.17-3.48 and 0.012-2.36 ppb, respectively (Nhan *et al.*, 1997).

4.3.2.4 Fish Samples

Concentrations of seven chlorinated pesticides measured in marine fish collected in the dry seasons (January, 1997) and in the rainy season (May, 1997) at four different stations are shown in Table 4.14.

Table 4.14: Concentration of organochlorine pesticide residues in fish sampled during dry and rainy seasons

Station	Mean (± s.d)residue concentration in fish (ppb lipid)						
	Lindane	Aldrin	Endosulfan	p,p'-DDE	Dieldrin	p,p'-DDD	p,p'-DDT
No. 1							
Dry	48.6±5.92	BDL	BDL	BDL	58.8±9.21	85.8±11.2	BDL
Wet	833±23.1	29.1±4.51	40.2±6.55	1.28±1.25	27.9±6.77	63.4±15.2	71.9±2.31
No. 2							
Dry	26.5±1.22	14.5±1.82	BDL	BDL	BDL	BDL	BDL
Wet	BDL	323±25.5	22.9±3.31	BDL	BDL	99.0±13.5	21.8±2.71
No. 3							
Dry	93.8±6.77	2.44±0.01	9.99±2.11	7.34±1.21	7.11±0.91	54.2±9.21	BDL
Wet	20.8±4.22	4.14±0.51	13.8±1.22	12.2±3.22	13.3±1.99	8.59±1.09	10.4±1.59
No. 4							
Dry	BDL	2.02±0.08	BDL	BDL	4.81±0.05	3.32±0.88	BDL
Wet	281±11.1	201±13.2	10.4±0.35	15.7±1.22	62.0±4.55	31.1±6.11	17.9±2.57

No.1- Sabaki No.2- Kilifi No.3- Mombasa No.4- Ramisi

BDL - Below detection limit sd:- Standard deviation 6 samples per site

Lindane residues showed the highest mean concentrations of 833 ppb lipid content in fish samples from the confluence of Sabaki River detectable during the rainy season. These concentrations suggested a point source of contamination for lindane since other residues had relatively low amounts ranging from 12.8 ppb for p,p'-DDE to 63.4 ppb lipid for p,p'-DDD. Four residues were absent in fish samples during the dry season but present in the rainy season. However, three residues were present in both seasons indicating their high frequency of use around Sabaki River and its environment, and also high persistence of those residues in lipophilic tissues of fish from that region.

Fish samples from Kilifi Creek showed no detectable quantities of p,p'-DDE and dieldrin in both seasons. Only lindane and aldrin were present during the dry season suggesting low levels of pollution of fish in that region in the dry spell. The highest levels of contaminantion were that of aldrin at concentrations of 323 ppb lipid in the rainy season. Aldrin was also

present at 14.5 ppb in the fish samples in the dry season, indicating the possibility of its frequent application in Kilifi region. Members of DDT family did not show significant contamination in fish since p,p'-DDD and p,p'-DDT were present only during the rainy season.

All the organochlorine residues under investigation in fish samples from Mombasa Old Town were detected in both seasons giving a strong indication of contamination of fish from that region except. However, p,p'-DDT was only present in the rainy season. Lindane was present in the highest concentration during the dry season followed by p,p'-DDD. It is probable that the use of DDT for public health in the harbour contaminated fish in this region in form of the anaerobic metabolite DDD especially in dry seasons. Most residues were present in fish samples from Mombasa probably due to the industrial and agricultural activities around the town.

As found in Mombasa, lindane had the highest mean residue concentration in fish samples from the mouth of Ramisi River followed closely by aldrin during the rainy season. Lindane, endosulfan, p,p'-DDE and p,p'-DDT were absent in fish samples during the dry season. However, aldrin, dieldrin and p,p'-DDD were detectable in both seasons. Aldrin had higher concentrations than its metabolite die drin in both seasons.

In conclusion, dieldrin and p,p-'DDD were present in fish samples from all the four sampling except at Kilifi site in both seasons. Of the DDT compounds, p,p'-DDD gave a general trend as dieldrin and could reliably be considered as indicators of fish pollution due to organochlorines along the coast of Kenya. Finally, residue levels of pesticides in fish samples were highest during the rainy seasons indicating severe transportation of contaminated materials by water from upland areas into the marine environment.

Other coastal areas of the world showed similar seasonal patterns in organochlorine pesticide residue concentrations. For instance, carp fish from the coastal region North of Vietnam had relatively higher occurrences of organochlorines in rainy weather than in dry season ranging between 0.23-120 and 0.15-109.7 ppb lipid content, respectively (Nhan *et al.*, 1997). However, chlorinated hydrocarbons in shellfish from the Northern Adriatic Sea did not show a clear seasonal pattern although higher PCB contents were found for stations influenced by discharges from River Po; values for DDTs and PCBs were between 2.1-18.3 and 3.2-12.1 ppb lipid, respectively in either season (Najdek and Bazulic, 1988).

4.4 Conclusion and Recommendations

4.4.1 Conclusion

Many tropical developing nations have used organochlorine pesticides in public health and agriculture in view of their availability at low costs, low mammalian toxicity and broad spectrum activity of long duration. Organophosphates which are widely used in temperate climates are expensive and due to their high toxicity are unsafe unless adequate precautions are implemented. Due to the population explosion and high demand for food, large amounts of pesticides are applied to achieve high crop yield. Unfortunately, pesticides enter drainage canals, rivers, lakes and oceans and hence become a serious source of marine environmental pollution. In this study, the distribution of organochlorine pesticides and their seasonal variations along the Kenyan Coast was investigated. Assessment of pesticide contamination used seawater and sediment as abiotic indicators while seaweed and fish as biotic indicators.

The analytical results obtained in this research allow us to draw several conclusions on the current levels and source of cyclic chlorinated pesticides along the Kenyan Coast. The degree of contamination of marine samples from the estuarine and shallow coastal regions of Kenya was assessed in terms of the concentration of seven pesticide residues (lindane, aldrin, dieldrin, endosulfan, p,p'-DDE, p,p'-DDD and p,p'-DDT) studied.

It was apparent from the mean residue concentrations of the seven organochlorines that seawater samples from all the four sampling stations were contaminated since most residues

studied were above their respective levels of detection. However, the frequency of detection varied with sites. It may be pointed out that the selection of sampling sites was part of the general ecological study of the coastal areas. In seawater samples, the highest mean residue concentration was that of lindane (0.503 ppb) at the Kilifi Creek followed by dieldrin (0.501 ppb) from Mombasa seawater. Of the pesticide residues detected from the study sites, levels of aldrin (0.019 ppb) were the lowest in Kilifi seawaters. In all cases, dieldrin was present in seawater in higher amounts than its parent compound aldrin. Seawater from Kilifi was heavily polluted by lindane (0.503 ppb) while that from Ramisi had p,p-'DDT as its highest pollutant. Pesticide residues in a large volume of seawater were likely to be considerably diluted. Insecticides in drinking water are generally present at levels that require preconcentration. The EC Drinking Water Directive (EEC 80/778) recommends that individual insecticides should not exceed 0.1 ppb. But the levels of a few residues in water from the coast of Kenya exceed this limit. This could pose a health risk to persons who depend on seawater for recreational and other needs.

Concentrations of DDTs in the seaweed were the highest among all the chlorinated hydrocarbons detected. Seaweeds analyzed from the Kilifi Creek were the most contaminated having 34.3 ppb of p,p-DDT. Seaweeds from all the sampling stations contained other pesticide residues analysed but at relatively lower concentrations. Aldrin was present in lower amounts than dieldrin indicating that biotransformation had occurred. Sea plants can play a key role in the process of micropolluntant dissemination along the coast of Kenya due to the high amounts of residues detected. They can store micropollutants by a mechanical and physical-chemical process and render them to the surface sediment and/or to the water body through dispersion of fine soft material in which they are transformed upon decomposition.

Sediments act as sinks to most organochlorine residues in aquatic environment as observed by Mbuvi (1997). Thus the presence of pesticide residues in sediments was not unexpected. Of the cyclodienes, aldrin was significantly higher at 21.4 ppb from Ramisi sediments. Aldrin is rarely found in the environment as a result of its rapid transformation into dieldrin. Therefore detection of aldrin in sediment suggested the direct input of this compound in the aquatic ecosystems from nearby point sources, followed by rapid burial and preservation under anaerobic sediments. Enhanced levels of p,p'-DDT (12.20 ppb) and dieldrin (22.74 ppb) were

detected at the confluences of Ramisi and Sabaki rivers, respectively. The concentration of p,p'-DDD in sediments along the coastline was always greater than that of p,p'-DDE implying that at least some degradation of p,p'-DDT had occurred anaerobically (as for aldrin). The sediment pesticide residue amounts found in this investigation are comparable to those shown by Everaarts *et al.* (1996) along the coast of Kenya but relatively higher than those detected by Prats *et al.* (1992) along the coast of Alicante in Spain which ranged between 0.002 ppb to 0.23 ppb.

In fish samples, lindane was established at highest levels in all stations which ranged from 26.5 ppb lipid (Kilifi Creek) to 612 ppb lipid (confluence of Sabaki River). The presence of a high proportion of p,p'-DDD and p,p'-DDE in relation to total DDT burden in coastal fishes indicated that either the migratory fish species, could have, perhaps, converted DDT rapidly to its metabolites because of high body metabolic rates or those areas along the coast were not threatened by new inputs of pesticides.

Small fishes of different species develop common fucultative mechanisms. They also have little fat reserves unlike big fishes, hence are less prone to adverse effects of some lipophilic pesticides (Munga, 1985).

In all the different compartments investigated, the results revealed that different sampling sites experienced different sources and levels of pesticide residue contamination. Changes in DDT and other organochlorine residues in the environment have been invoked as an important factor defining seasonal profiles in lipophilic organisms (Najdek and Bazulic, 1988). A general trend was observed for the seasonal variation of residues in marine samples. In a few cases, some pesticides were below their respective levels of detection during the dry season only to be quantified in the rainy season. Moreover, pesticide residues were generally present in higher amounts in environmental compartments during the rainy season than in dry season.

In marine compartments discussed in the present study, the absence or occurrences of individual pesticide residues and their metabolites could be explained in various ways. It was generally assumed that an increasing proportion of a metabolite in relation to the parent

compound reflected a decreasing exposure to new sources of pesticide pollution and vice versa.

Variability in the concentration of the residues of different organochlorine pesticides in the coastal compartments may be attributed to the presence of numerous rivers along the coast of Kenya such as Tana, Sabaki, Goshi, Mwachi and Ramisi rivers. Most of the samples were collected from the mouth of these rivers, and show an almost uniform distribution of residues between sites in the current study. Enhanced levels in estuarine and nearby coastal regions were due to river inputs, since pesticides such as aldrin, endosulfan, lindane and DDT are legally under restricted use in Kenya.

Increased organochlorines in marine compartments in rainy season appeared to be as a consequence of the sharp increase in pesticide residues in the environment. For example, a study carried out in the Red river Valley, North of Vietnam (Nhan *et al.*, 1997) indicated that concentrations of lindane in surface sediments collected in the rainy season, ranging from 0.025 to 0.16 ng/g, were lower than in the dry season, ranging from 0.14 to 0.62 ng/g. The results implied that there was strong washout of lindane from sediments in the wet period from the river valley to the ocean and hence may explain the increase in concentration of pesticide residues in marine samples as shown in the current study.

Apart from the hydrographic conditions, the chemical transition of compounds and eventual biotransformation in organisms determined their environmental fate.

Organochlorine residue concentrations in marine samples varied geographically and seasonally. Spatial variability is normally interpreted as different contamination in the environment, whereas seasonal fluctuations may result from temporal changes in organochlorines in the environment.

It could not be established how far the presence of these organochlorines and their concentration levels in marine biota have any ecological implications. One consequence might be an increased risk of bioaccumulation in birds since biomagnification was likely to occur from marine biota to birds. In instances where the levels were below the lethal concentrations, we must be concerned about the probable chronic effects on the marine fauna and flora.

With respect to human health it can be concluded that the concentrations of some of the residues measured, did not yet approximate to the maximum admissible concentration (MAC). In fish samples for instance, the MAC-value for dieldrin and total DDT is 500 and 2000-3500 ng/g on lipid, respectively based on recommended World Health Organization as reported by Everaarts *et al.* (1991).

Comparison of the organochlorine pesticide residue concentrations (ppb) in the current study with those for global coastal waters shows, for example, that in 1995 dieldrin (1.88), endosulfan (2.98) and p,p'-DDT (7.02) recorded in waters from Kingston Harbour (Jamaica) were about four, ten and twenty times higher than maximum mean values obtained in this study. This suggests that the coastal marine environment in Kenya is relatively unpolluted.

Finally, these data provide a baseline for future work in determining the concentrations of chlorinated cyclic pesticides in marine samples along the coast of Kenya.

4.4.2 Recommendations

There exists a general lack of awareness among the Kenyan populace on chemical handling. There also lacks effective enforcement of laws and inadequate technical information and know-how on environmental and health protection against dangers inherent in the use and disposal of pesticidal substances. It is recommended that development of relevant sensitization curricula for awareness campaigns on safe use of pesticides tailored to accommodate various echelons of society is a necessary step.

It is likely that other pesticides not studied in this investigation are used in both inland and coastal regions because the method of analysis is limited to organochlorines only. Since rivers link hinterland areas with those of the sea, it is recommended that careful assessment of marine pollution problems should be handled through an integrated watershed management.

It is recommended that further work on different pesticides be investigated in various edible marine macrobenthic invertebrates and vertebrates to assess the risks involved in feeding on seafoods.

Finally, it is recommended that the monthly pesticide residue concentrations along the coast of Kenya be monitored bi-annually to generate more data on seasonal patterns of pesticide contamination in marine ecosystems and necessary precautionary measures.

REFERENCES

BOYD, C.E. (1972). Insecticides cause mosquito fist to abort. **Progr. Fish Cult. 26.** 138.

BUTTLER, P.A. (1963). Commercial fisheries investigations. In: **Pesticide-Wildlife Studies. U.S. Fish Wildl. Serv. Circ. 167.** p. 11-25.

CASTRO, O., A.M. FERREIRA and C. VALE (1990). Organochlorine Compounds in the Portuguese Oyster: Importance of Seasonal Variations. **Mar. Poll. Bull. 21(11).** 545-547

ECONOMIC SURVEY (1997). Economic survey, Central Bureau of Statistics, Office of the Vive-President and Ministry of Planning and National Development, Republic of Kenya. Government press, Nairobi.

EDWARDS, C.A. (1966). Insecticide residues in soils. **Residue Review 13.** 83-132.

EDWARDS, C.A. (1973). Pesticide residues in soil and water. **Environmental pollution of pesticides.** Plenum press, London. p. 401-451

ELLGARD, E.G., J.C. OCHSNER and J.K. COX (1977). Locomotor hyperactivity induced in the bluegill sunfish (*Lepomis macrochirus*) by sub-lethal concentrations of DDT. **Can. J. Zool. 55.** 1077.

EVERAARTS, J.M., C. WASREEN and M.J. HILLEBRAND (1991). Cyclic chlorinated hydrocarbons in benthic invertebrates from three coastal areas in Thailand and Malaysia. **J. Sci. Soc. Thailand. 17.** 31-49.

EVERAARTS, J.M., E.M. VAN WEERLEE, C.V. FISHER and M. Th. J. HILLEGRAND (1996). Polychlorinated Biphenyls and cyclic pesticides in sediments and macroinvertebrates from the coastal regions of different climatological zones. Vienna, 1-5 July. **IAEA-SM-343/45.**

FAO/WHO (1996). Pesticide residues in food - 1995 report. FAO Plant Production and Protection Paper 133. Rome.

FOXALL, C.D. (1983). Pesticides in Kenya. **Swara 6.** 25.

GILBERT, F.F. (1969). Physiological effects of natural DDT residues and metabolites on ranch mink. **J. Wildl. Manag. 33.** 933-943.

GOLD-BOUCHOT, G., T. SILVIA-HERRERA and O. ZAPATA-PEREZ (1993). Chlorinated Pesticides in the Rio Palizada, Campeche, Mexico. **Mar. Poll. Bull. 26(11)**. 648-650

GRAHAM-BRYCE, I.J. (1977). Chemical control of pests and diseases. Ecological effects of pesticides. Eds. Perring, F.H. and K. Mellanby. Academic Press, London. P.47-60. 193pp.

GREICHUS, V.A., A. GREICHUS, B.D. AMMAN and J. HOPCRAFT (1978). Insecticides polychlorinated biphenyls and metals in Africa Lake ecosystem, III. Lake Nakuru, Kenya. **Bull. Environ. Toxicol. 19.** 455-461.

HANSEN, D.J. (1972). DDT and malathion: Effects on salinity selection by mosquito fish. **Trans. Am. fish. Soc. 101.** 346-360.

HASSAL, K.A. (1982). The chemistry of pesticides: their metabolism, mode of action and uses in crop protection. Macmillan press, London. p. 1-21. 372pp.

HASSAL, K.A. (1990). The biochemistry and uses of pesticides: structure, metabolism, mode of action and uses in crop protection. VCH Publishers Inc., New York. P.155-182. 536pp.

HICKEY, J.J., J.A. KEITH and F.B. COON (1966). An exploration of pesticides in a Lake Michigan Ecosystem. **J. Appl. Ecol. 3.** 141-154.

HILL, D.S. (1978). Agricultural insect pests of temperate regions and their control. Cambridge University Press, N.Y., USA. p. 137-138.

HINGCO, T.G. (1990). Pollution of Manila Bay. Tombuyog Development Centre. **Phil. Soc. Sci. Centre.** Quezon City, Philippines. P.5. 10pp.

HODGSON, E., R.M. ROE and N. MOTOYAMA (1991). Pesticides and the future: Toxicological studies on risks and benefits. **Rev. Pestic Toxicol. 1.** 3-12.

HOLDEN, A.V. and K.J. MARDSEN (1969). Single stage clean-up of animal tissue extracts for organochlorine residue analysis. **J. Chromat. 72.** 283.

IATRAPOULOS, M.J., W. HOBSON, V. KNOUF and H.P. ADAMS (1976). Morphological effects of HCB toxicity in femal rhesus monkeys. **Toxic. Appl. Pharmacol. 37.** 433-445.

KAINE, K.W.S. (1976). The control of tickborne diseases in cattle in Kenya. **Bulletin De L'office International. Epiz 86.** 71-75.

KITUYI, E.N., S.O. WANDIGA and I.O. JUMBA (1997). Occurrence of Chlorfenvinphos Residues in Cow's Milk Sampled at a Range of Sites in Western Kenya. **Bull. Environ. Contamin. Toxicol. 58.** 969-975.

KOEMAN, J.A., J.H. PENNINGS, J.J.M. DEGOLA, P.S. TJOE, T.M. OLINDA and J. HOPCRAFT (1972). A preliminary survey of possible contamination of Lake Nakuru in Kenya with some metal and chlorinated hydrocargon pesticides. **J. Appl. Ecol. 9.** 411-416.

LALAH, J.O. (1993). Studies on the dissipation and metabolism of a variety of insecticides under Kenyan environmental conditons. **Ph.D. Thesis,** University of Nairobi.

LEE, J.S., S. TANABE, N. TAKEMOTO and T. KUBOBERA (1997). Organochlorine Residues in Deep-Sea Organisms from Suruga Bay, Japan. **Mar. Poll. Bull. 34(4).** 250-258

LINCER, J.L., D. ZALKIND, L.H. BROWN and J. HOPCRAFT (1981). Organochlorine residues in Kenya's Rift Valley lakes. **J. Appl. Ecol. 18.** 157

MACPHEE, A.W.D., D. CHISHOLM and C.R. MACEACHERN (1960). The persistence of certain pesticides in the soil and their effects on crop yields. **J. Soil. Sci. 40.** 59-62.

MAITHO, T. (1978). Organochlorine and organophosphorous insecticides in milk and body fat. M.Sc. Thesis. University of Nairobi.

MANSINGH, A. (1993). Baseline studies on pesticide contamination and formulation of control measures. Jamaica, 1991-1992. **The IOC/SAREC/CAC/UNEP/UWI Project.**

MANSINGH, A and A. WILSON (1995). Insecticide contamination of the Jamaican environment III. Baseline studies on the status of insecticidal pollution of Kingston Harbour. **Mar. Poll. Bull. 30(10). 640-645**

MANSINGH, A., D.E. ROBINSON and A. WILSON (in press). Insecticide contamination of Jamaican environment ii. Patterns of fluctuations in residue levels in rivers of Hope Watershed during 1989-1991. **Jamaica J. Sci. Technol.**

MAROLI, L., B. PAVONI, A. SFRISO and S. RACCANELLI (1993). Concentrations of polychlorinated biphenyls and pesticides in different species of macroalgae from the Venice Lagoon. **Mar. Poll. Bull. 26(10).** 553-558.

MATHEWS, G.A. (1979). Pesticide Application Methods. The English Language Book Society, London.

MATHIESSEN, P., P.J. FOX, R.J. DOUTHWAITE and A.B. WOOD (1982). Accumulation of endosulfan residues in fish and their predators after aerial spraying for the control of tsetse flies in Bostwana. **Pestic. Sci. 13**. 39.

MATHIESSEN, P. and J.N. LOGAN (1984). Low concentration effects of endosulfan insecticide on reproductive behaviour in the tropical cichlid fish. *Saratherodom Mossambicus.* **Bull. environ. contamin. Toxicol. 33.** 375.

MATHIESSEN, P. and R.J. ROBERTS (1982). Histological changes in the liver and brain of fish exposed to endosulfan insecticide during tsetse fly control operations in Botswana. **J. Fish Diseases 5.** 153.

MATIN, M.A., E. HOQUE, J. KHATOON, M.S. RAHMAN, M. AMINUDDIN (1997). Pesticide residues in Bangladesh marine environment. **Progress Report R.C No. 7930/IAEA-MEL.** 4th Research Co-odination Meeting of the CRP, Nairobi, 16-20 June.

MATSUMURA, F. (1975). Toxicity of insecticides. Plenum Press, New York and London.

MBUVI, L.N. (1997). Distribution and fate of 14-DDT in a model ecosystem simulating conditions of the tropical marine enviroment. **M.Sc. Thesis,** University of Nairobi.

MEE, L.D., T.W. READMAN, F.J. CARRANZA and F. GONZALEZ (1991). Fate of agrochemicals in tropical coastal lagoon ecosystems. International scientific cooperation consolidated reports of activities. p 113-117.

MENASVETA, P. and V. CHEEVAPARANAPIWAT (1981). Heavy metals, organochlorine pesticides and PCBs in mussels and sediments of river mouth of Thailand. **Mar. Poll. Bull. 12.** 19-25.

MENZIE, C.M. (1972). Fate of pesticides in the environment. **Ann. Rev. Entomol. 17.** 119-222.

MILES, J.R.W. (1976). Insecticide residues in stream sediments in Ontario, Canada. **Pestic. Monit. J. 10.** 87.

MILLER, Ed (1978). Pesticide Background Statements Vol. III: Nursery Pesticides. **US Department of Agriculture**. Forest Source agriculture handbook No. 670.

MILLER, J.W. (1944). Pathological changes in animals exposed to a commercial chlorinated biphenyl. **U.S. Publ. Health Rec. 59.** 1085-1093.

MOUNT, O.B. (1962). Chronic effects of endrinon blunt-nosed minnows and guppies. **Res. Rep. 58, U.S. Fish Wildl. Serv.** 38 p.

MOYE, W.C. and W.H. LUCKMANN (1964). Fluctuations of populations of certain aquatic insects following application of aldrin granules to sugar creek, Iroquious County, Illinois. **J. ECON. ENTOMOL. 53.** 785-788.

MUNGA, D. (1985). DDT and endosulfan residues in the fish from Hola Irrigation Scheme, Tana River, Kenya. **M.Sc. Thesis,** University of Nairobi.

NDERITU, P.V.K. (1990). Investigation into the effect of pH on the availability of trace elements in soil. **M.Sc. Thesis,** University of Nairobi.

NAJDEK, D and D. BAZULIC (1988). Chlorinated hydrocarbons in mussels and some benthic organisms from the Northern Adriatic Sea. **Mar. Poll. Bull. 19(1)**. 37-38.

NHAN, D.D., N.M. AM, N.C. HOI, L.V. DIEU, P.F. CARVALHO, J.-P. VILENEUVE and C. CATTINI (1997). Organochlorine pesticides and PCBs in the Red River delta, North of Vietnam. **Progress Report of IAEA CRP**, Nairobi, Kenya. June 16-20.

O'BRIEN, R.D. and B.D. HILTON (1978). The effects of DDT and its analogs on the fragility of human erythrocytes. **Pestic. Biochem. Physiol. 9.** 231-236.

OGALLO, L.A. and R.W. MWANGI (1996). Implications of the Expected Climate Changes on the Low-Lying Parts of Kenya. **Environment and Development, A Public Lecture Series.** KNAS press, Nairobi.

PCPB (1987). The Pest Control Products Board of Kenya. A summary report of activities 1986.

PCPB (1996). The Pest Control Products Board of Kenya. A summary report of activities 1995.

PEAKALL, D.B. (1967). Pesticide-induced enzyme breakdown of steroids in birds. **Nature.** 216-505.

PRATS, D., F. RUIZ and D. ZARZO (1992). Polychlorinated biphenyls and organochlorine pesticides in marine sediments and seawater along the coast of Alicante, Spain. **Mar. Poll. Bull. 24(9)**. 441-446.

RUDD, R.L. and S.G. HERMAN (1972). Ecosystem transferral of pesticide residues in an aquatic environment. **Environmental toxicology of pesticides.** Eds. Matsumura, F., G.M. Boush and T. Misato. Academic Press, London. p. 471-485.

SARKAR, A. and R.S. GUPTA (1988). Chlorinated pesticide residues in marine sediments. **Mar. Poll. Bull. 19(1)**. 35-37.

SAXENA, M.C., M.K.J. SIDDIQUE, T.D. SETH, C.R.K. MURTI, A.K. BHARGAVA and D. KUTTY (1981). Organochlorine pesticides in specimens from women undergoing

spontaneous abortion, premature or full-term delivery. **J. Anal. Toxicol. 5.** 6-9.

SMITH, A.G. and J.K. GABRAL (980). Liver tumuor in rats fed with HCB. **Cancer Letters. II.** 169-172.

SOMERVILLE, L. and C.H. WALKER (Eds.) (1990). Pesticide Effects on Terrestial Wildlife. Taylor and Francis, London.

STICKEL, H.W (1974). Ecology Toxicology Research. Pollutants in Terrestial Ecosystem. Plenum Press, New York.

TAVARES, T.M. (1994). Distribution of organochlorine and organophosphorous pesticides in different environmental compartments of the Todos os Santos Bay, Salvador, Bahia, Brazil.

TAVARES, T.M. (1997). Distribution of organochloride and organophosphorous pesticides in different environmental compartments of the Todos os Santos Bay. **3rd Progress Report of IAEA CRP.** Nairobi, Kenya. June 16-20.

TONKELAAR, E.M. and H.G. VERSCHUUREN (1978). HCB toxicity in pigs. **Toxic. Appl. Pharmacol. 43.** 137-145.

UNEP (1982). Determination of DDTs, PCBs and other hydrocarbons in marine sediments by gas-liquid chromatography. **Reference Methods for Marine Pollution Studies No. 17.**

UNEP (1984). Marine and coastal conservation in the East African region. **UNEP Regional Seas Reports and Studies No. 39.**

UNEP (1990). The state of marine environment. **UNEP Regional Seas Reports and Studies No. 115.**

UNEP (1991). Sampling of selected marine organisms and preparation for the analysis of chlorinated hydrocarbons. Reference methods for marine pollution studies No. 12, Rev. 12.

VAN GELDER, G.A., W.B BUCK, R SANDLER, J. MALAND, G. KARAS and D. ELBERRY (1969). Physiological effects of dieldirn and Melene exposure on experimental behaviour and electroencephalogram. In: **The biological impact of pesticides in the environment.** Environmental Health Ser. 1, Oregon State Univ. p. 125-133, 220pp.

WANDIGA, S.O and MUTERE (1988) Determination of gamma-BHC in breast milk of Kenyan women. **Bull. Chem. Soc. Ethiopia, 2.** 39-44.

WARE, G.W. (1980). Effects of pesticides on non-target organisms. **Residue Review 76.** 173.

WASSERMAN, M., M.G. ROGOFF, L. TOMATIS, N.E. DAY, D. WASSERMAN, M. DJAVAHIERIAN and G. CUTTEL (1972). Storage of organochlorine insecticides in the adipose tissue of people in Kenya. **Soc. Belge. Med. Trop. 52.** 509-514.

ZITKO, V. and M. HANLON (1991). Pesticide residues in sediments from the West Coast of India. **Mar. Poll. Bull. 22(1).** 42-45

APPENDICES

APPENDIX I

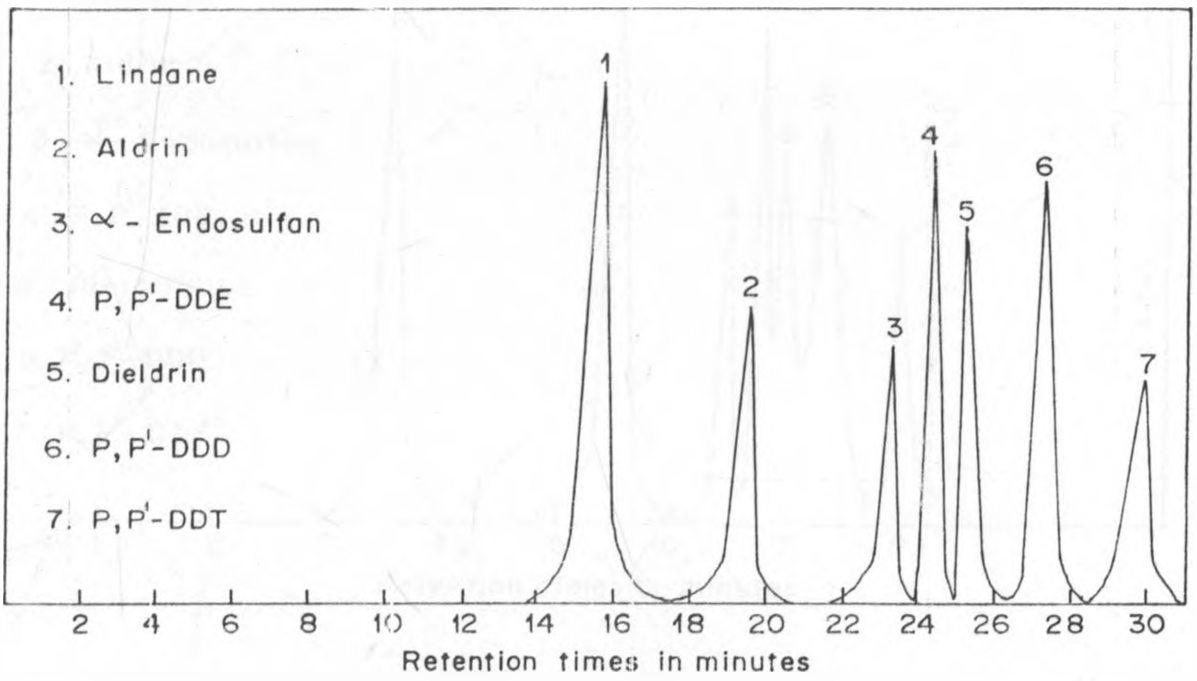


Fig. A1: Chromatogram of the standard chlorinated pesticide mixture for column SE-54

Col. type : SE – 54
Dim.: 30m x 0.25mm ID x 0.25μm film.
Temp prog.: Col. Temp.: 200°C to 260°C, ramp rate 4°C/min, flow rate 2ml/min, N_2, ^{63}Ni-ECD

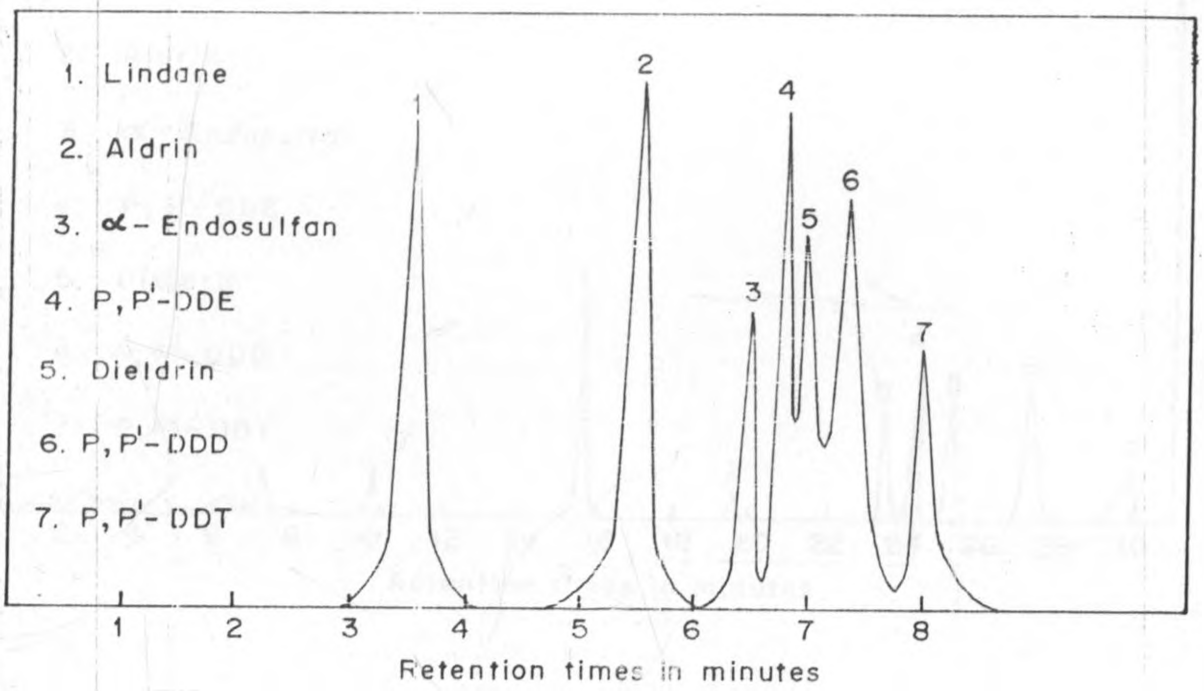


Fig. A2: Chromatogram of the standard chlorinated pesticide mixture for column DB-5

Col. type: DB – 5
Dim.: 15 m x 0.25 mm ID x 0.25 μm film.
Temp prog.: Col. Temp.: 100°C to 250°C, ramp rate 5°C/min, flow rate 5ml/min., N_2, ^{63}Ni-ECD

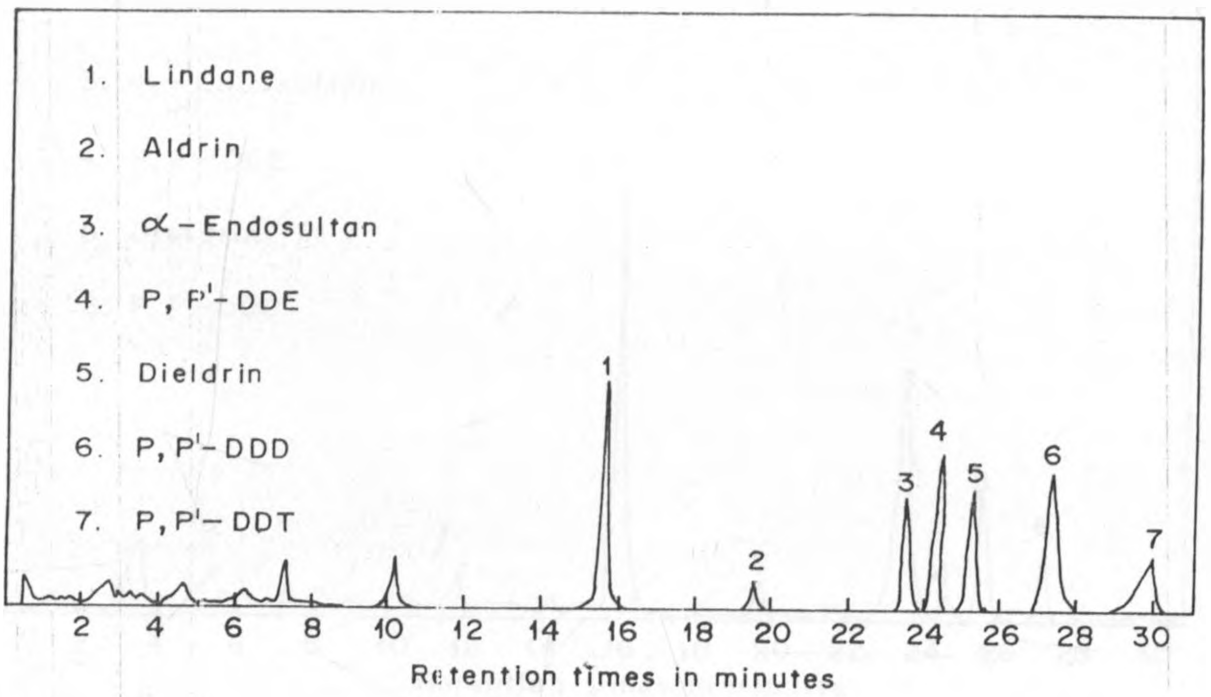


Fig. A3: Chromatogram from a water sample (Kilifi).

Col. type : SE – 54
Dim.: 30m x 0.25mm ID x 0.25μm film.
Temp prog. Col. Temp.: 200°C to 260°C, ramp rate 4°C/min, flow rate 2ml/min, N_2, ^{63}Ni-ECD

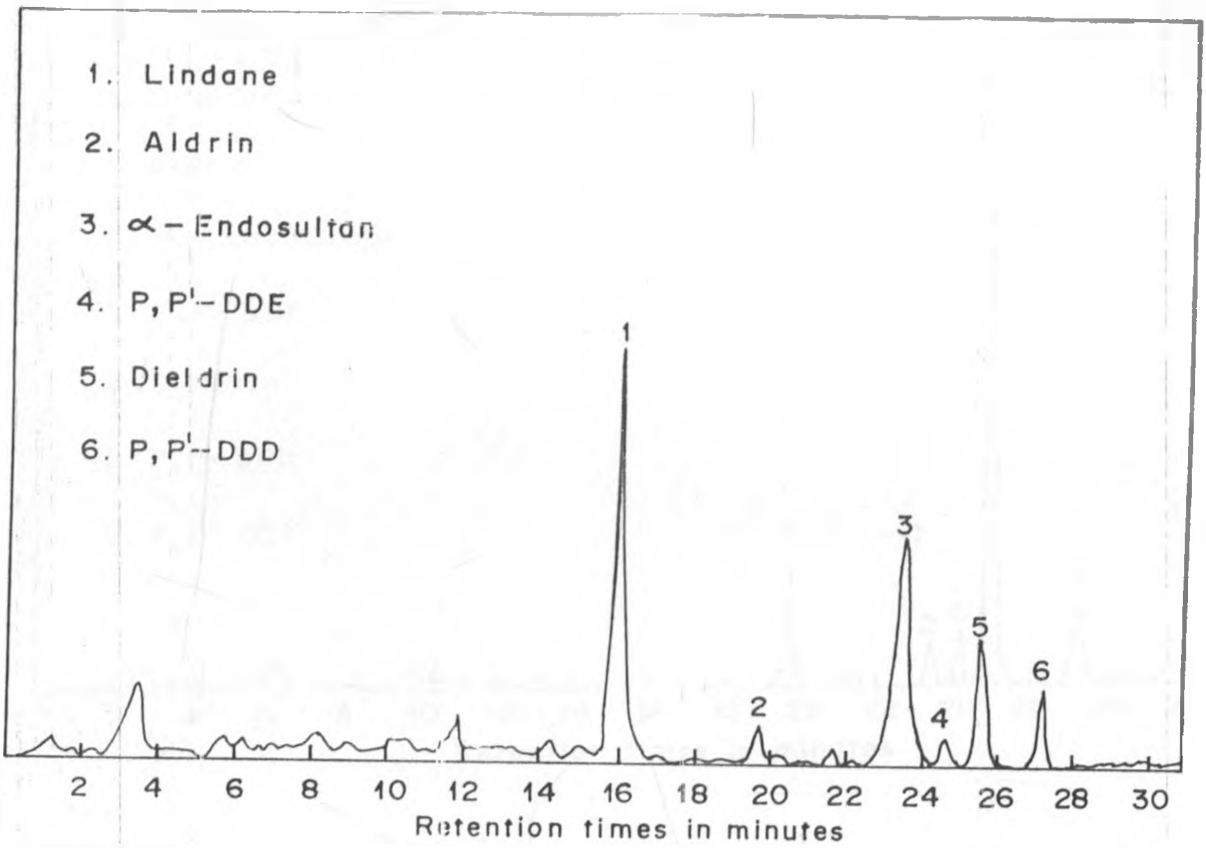


Fig. A4: Chromatogram from a seaweed (Ramisi).

Col. type : SE – 54
Dim.: 30m x 0.25mm ID x 0.25μm film.
Temp prog.: Col. Temp.: 200°C to 260°C, ramp rate 4°C/min, flow rate 2ml/min, N_2, ^{63}Ni-ECD

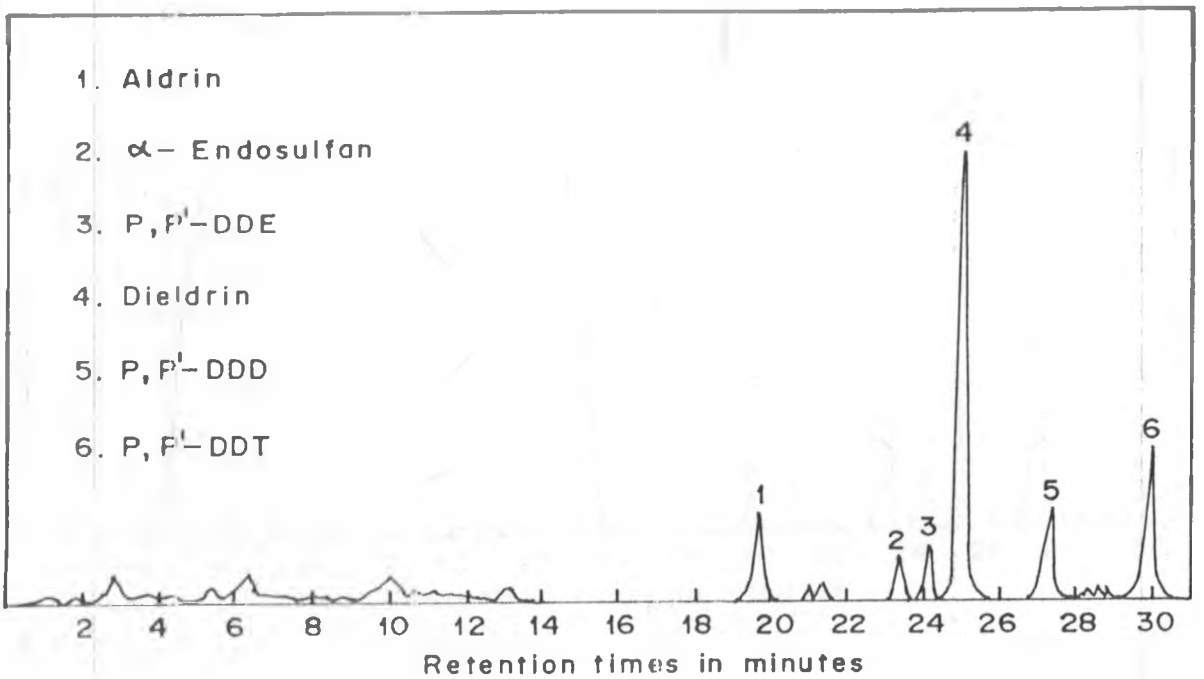


Fig. A5: Chromatogram from a sediment sample (Sabaki).

Col. type : SE – 54
Dim.: 30m x 0.25mm ID x 0.25μm film.
Temp prog.: Col. Temp.: 200°C to 260°C, ramp rate 4°C/min, flow rate 2ml/min, N_2, ^{63}Ni-ECD

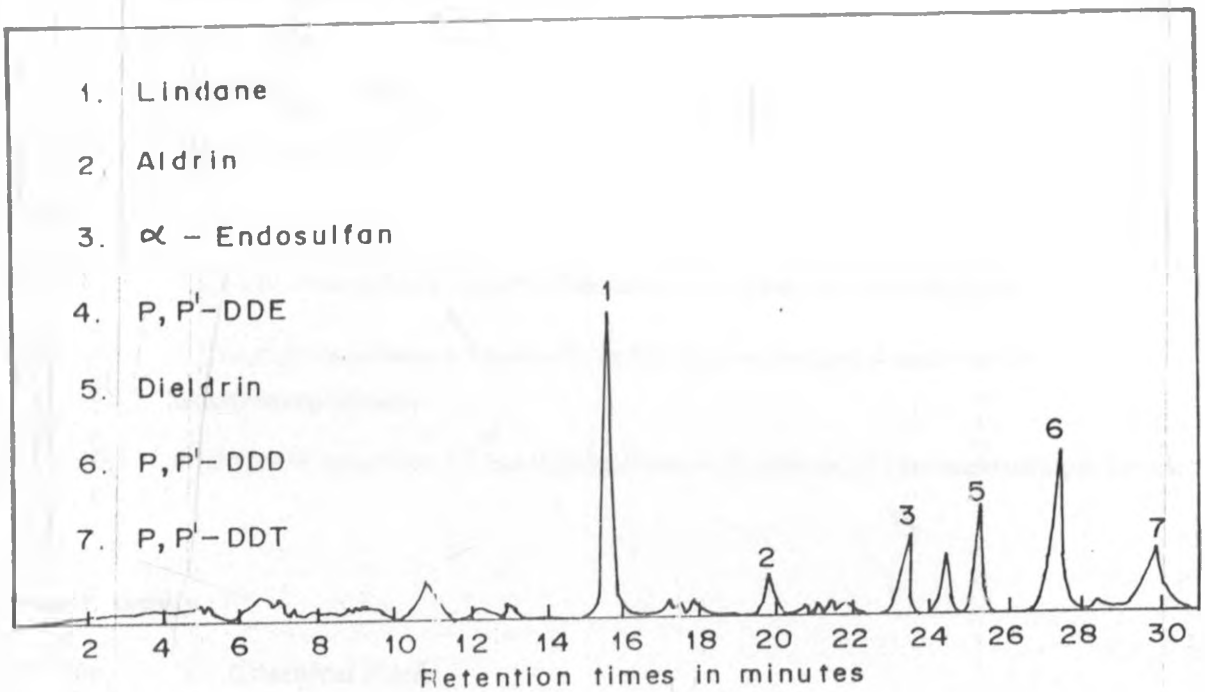


Fig. A6: Chromatogram from a fish sample (Mombasa).

Col. type : SE – 54
Dim.: 30m x 0.25mm ID x 0.25μm film.
Temp prog.: Col. Temp.: 200°C to 260°C, ramp rate 4°C/min, flow rate 2ml/min, N_2, ^{63}Ni-ECD

APPENDIX II

Table A1: Chemical names of some organochlorine pesticides

(a) Chlorinated cyclodiene family

Common Name	Chemical Name
Aldrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8ahexahydro-1,4:5,8-dimethanonaphthalene.
Dieldrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene.
Endosulfan	6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide

(b) DDT family

Common name	Chemical Name
DDD (TDE)	1,1-dichloro-2,2-bis(p-chlorophenyl)ethane.
DDE	1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene.
DDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane.

(c) HCH family (formerly BHC)

Common Name	Chemical Name
Lindane (gamma-HCH)	1,2,3,4,5,6-heptachlorocyclohexane.

Table A2: Pesticide residue ranges detected in waters collected from different stations

Pesticide	Residues in water (ppb)			
	Sabaki	Kilifi	Mombasa	Ramisi
Lindane	0.241	0.342-0.665	BDL	BDL
Aldrin	0.035 - 0.040	0.019-0.019	0.037-0.080	0.019-0.031
Endosulfan	0.152- 0.182)	0.118-0.440	0.222-0.712	0.075-0.197
p,p'-DDE	0.183-0.232)	0.163-0.545	0.064-0.385	0.025-0.103
Dieldrin	0.245-0.257)	0.160	0.152-1.28	0.122-0.202
p,p'-DDD	0.132-0.622	0.071-0.384	0.071-0.072	0.036-0.076
p,p'-DDT	0.100-0.235	0.370	BDL	0.121-0.267

BDL:-Below detection limit 6 samples per site

Table A3: Pesticide residue ranges detected in seaweeds collected from different stations

Pesticide	Residues in seaweeds ppb			
	Sabaki	Kilifi	Mombasa	Ramisi
Lindane	BDL	BDL	10.1	32.7-36.5
Aldrin	3.83-6.72	0.74-10.0	0.91-18.1	1.70-3.01
Endosulfan	4.01-13.8	5.31-48.0	9.38-12.6	12.9-27.8
p,p'-DDE	0.80-18.4	2.68-10.0	2.09-17.0	0.95-2.38
Dieldrin	0.32-16.1	3.06-17.3	4.43-16.1	9.53
p,p'-DDD	1.49-22.2	0.84-56.8	1.37-12.2	1.38-15.9
p,p'-DDT	5.78-9.31	8.53-60.0	5.26-5.28	BDL

BDL - Below detection limit 6 samples per site

Table A4: Pesticide residue ranges in sediments collected from different stations

Pesticide	Residues in sediment (ppb)			
	Sabaki	Kilifi	Mombasa	Ramisi
Lindane	BDL	BDL	1.66-20.3	8.32-17.1
Aldrin	0.71-6.76	6.76	2.45-12.3	0.79-48.6
Endosulfan	2.55-3.32	6.33-7.21	1.41-17.3	4.69-14.8
p,p'-DDE	2.19-4.87	1.74-11.9	0.95	1.90-7.13
Dieldrin	11.0-44.5	6.21-17.5	3.23-8.86	4.99-15.6
p,p'-DDD	1.56-13.3	3.95-20.9	1.38-3.99	3.17-10.2
p,p'-DDT	4.21-11.8	6.81-15.6	2.91-4.19	3.29-22.3

BDL- Below detection limit 6 samples per site

Table A5: Pesticide residue ranges in fish collected from different stations

Pesticide	Residues in fish ng/g lipid			
	Sabaki	Kilifi	Mombasa	Ramisi
Lindane	48.6-1445	26.5	16.1-145	42.6-750
Aldrin	11.3-67.1	1.55-323	1.20-7.00	2.02-201
Endosulfan	25.9-54.6	22.6-23.1	5.92-19.8	10.4
p,p'-DDE	9.44-97.5	1.94	2.65-21.7	5.26-26.2
Dieldrin	9.10-109	8.69	7.11-14.9	4.81-95.1
p,p'-DDD	15.1-112	4.95-98.9	1.68-54.2	3.32-35.8
p,p'-DDT	13.6-22.2	14.3-29.3	9.11-11.6	10.0-25.9

6 samples per site