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THE DISTRIBUTION OF ORGANOCHLORINE PESTICIDES IN MARINE SAMPLES ALONG THE INDIAN OCEAN COAST OF KENYA

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ABSTRACT

The concentrations of organochlorine residues of lindane, aldrin, ∝- endosulfan, dieldrin, endrin, p,p'-DDE, p,p'-DDD and p,p'-DDT in samples of seawater, sediment, fish and seaweed from different locations along the coast of Kenya are discussed in relation to the geographical location of the sampling sites and potential sources of residue over a period of two years. All sediment samples were found to contain very low levels of organic carbon except those sampled from Sabaki River that had high (4.7%) organic carbon due to greater primary activity. Most of the pesticides residues (112 samples analysed in 1997 and 258 analysed in 1998/99) were detected in fish, water, sediments and seaweed. The concentration of some residues was higher during the wet season than the dry season in 1997, but no marked seasonal variation was observed in 1998/99. Lindane, aldrin, p,p'-DDT and p,p'-DDE were the most frequently observed residues in all samples while ∝-endosulfan, dieldrin, p,p'-DDD and endrin were either present in low concentrations or absent in most samples. Water samples had the lowest concentrations of residues (range 0.503 - 9.025 ng g^{-1}). Sediments had the second highest levels of pesticides residues with a range of 0.584 – 59.00 ng g^{-1} while fish lipid content had the highest levels of residues in 1989/99 with p,p'-DDT concentration of 1011 ng g^{-1} and 418 ng g^{-1} p,p'-DDD in *Siganus rivulatus*.

Keywords: Organochlorines, marine samples, season variability

INTRODUCTION

The use of pesticides in agriculture and public health vector control in Kenya has been increasing steadily due to the rapidly rising population (currently at 2.8% p.a.) and as a result of the consequent increase in demand for agro-industrial activities. In 1995, some 5108 tonnes of different types of pesticides formulations and active ingredients were imported into the country which consisted of 39.8% insecticides and acaricides, 17.6% herbicides and 38.4% fungicides [1]. Some of the imported pesticides like p,p'-DDT, lindane, aldrin and dieldrin, which have now been banned in most industrialised countries due to their persistence in soil and aquatic environments are still popular in this country and are used mainly for public health vector control such as in control of mosquitoes [2, 4].

Kenya is located in East Africa between latitudes $5^0 4'$ N and $4^0 4'$ S and between longitudes $33^0 50'$ W and $41^0 45$ E, with a coastline of 640 km characterised by fringing reefs and a shallow narrow lagoon system linking it to the mainland. It has altitudes varying between 0 and 2610 m above sea level from the Indian Ocean coast to the inland Rift Valley regions [5]. The mean annual rainfall at the coast is about 1090 mm, 40% of which is received in the long rains period (March-June), 20% during the short rains season (October-December) and the remaining 40% constituting the out-of-season rainfall received during the monsoon periods (July-September) [6]. The relative humidity averages 75% while evaporation is about 170 mm, due to the influence of sunshine (8.65 hours), radiation (449 Langleys) and surface winds (4.5 m s^{-1}).

There are several rivers and canals that pass through towns and other human settlement areas and through agricultural farmland discharging into the Indian Ocean. Intensive large-scale agricultural activities are practised in the upper middle sections along these river watersheds and canals resulting in transport of a number of contaminants such as pesticide residues to the ocean. The Athi and Tana Rivers, for example, have been reported to carry a number of pesticides residues from the extensive agricultural activities of the central highlands [7]. The coastal region of the country

also has abundant agricultural activities that include sugar cane, citrus fruit and cotton farming. Pesticides are used in these plantations. p,p'-DDT, for example, has been used extensively up to very recently in aerial spraying of cotton fields around Margarini in Malindi and for disinfecting Kilindini Harbour. Formulations containing p,p'-DDT and dieldrin have also been used for spraying tsetse-infested areas north of Malindi, while 2,4 - D and 2,4,5-T have been used in sugar cane plantations in coastal areas around Ramisi for control of weeds [2, 3, 6].

Marine pollution research has been one of the priority concerns of our laboratory and the Kenya Marine Fisheries Research Institute (KMFRI) in Mombasa. The objective of this present study was to determine the concentrations of organochlorine pesticide residues in marine sediments, fish, water and seaweed from the coastal sites in January and May 1997, July and September 1998 and 1999 during the dry, wet and short rainy seasons. This paper discusses some of the results that have been obtained so far.

MATERIALS AND METHODS

In 1997, sampling was done in four sites along the coast, namely: Funzi Lazy Lagoon next to the confluence of Ramisi River, Mombasa Old Town, Kilifi Creek near the confluence of Goshi River and the confluence of Sabaki River near Malindi as shown on the map (Figure 1). In 1998 and 1999 sampling was done during the months of January, May, July

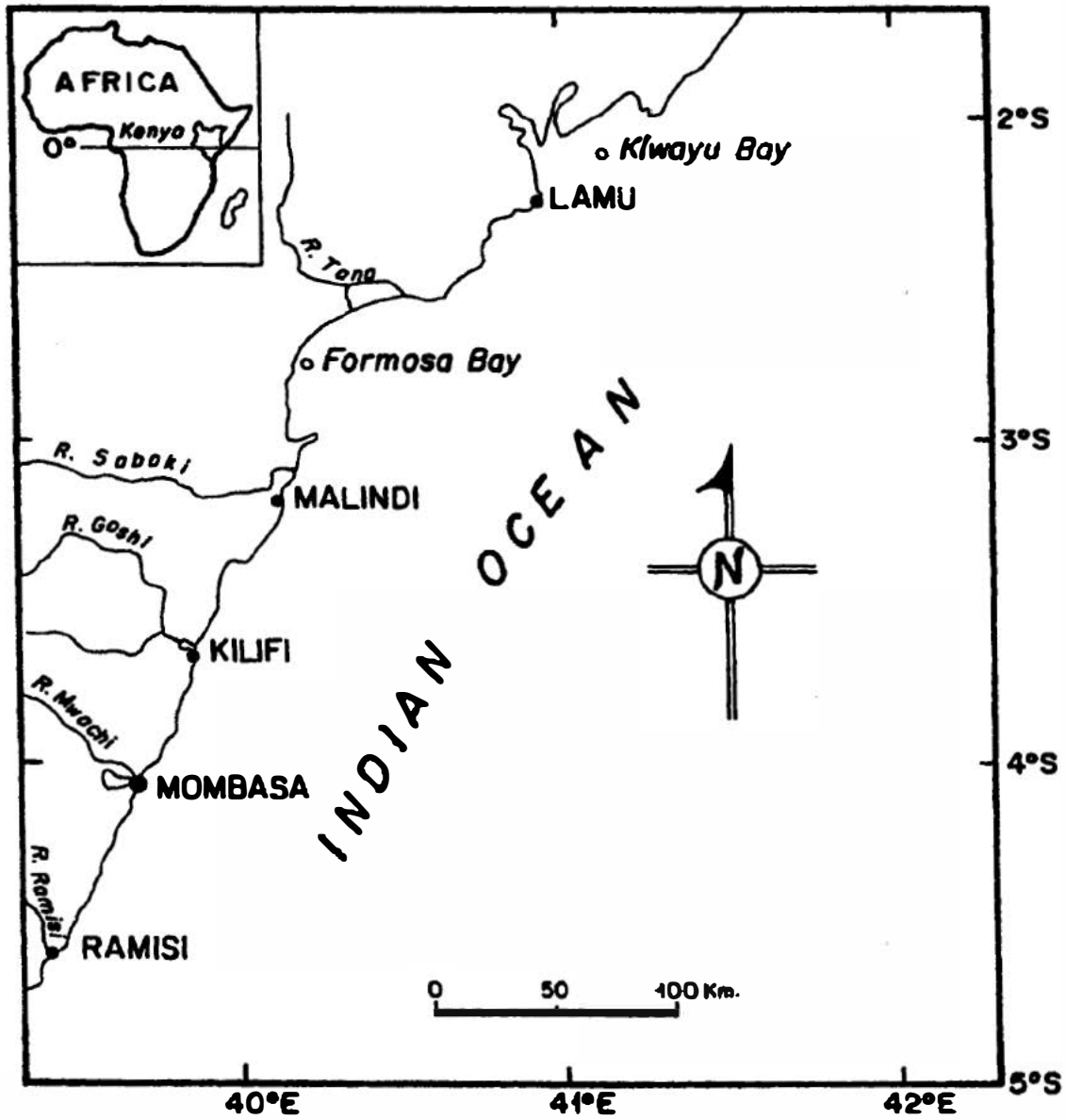

Figure 1. The study region of Kenya.

and September from Kilifi around the Goshi confluence, Malindi beaches around the Sabaki confluence, Mokowe beaches, and along Rivers Sabaki and Tana (Fig 1). Samples of seaweed, sediment, fish and seawater were taken twice during the above named months corresponding to the hot and dry north-east monsoon season (dry season) and the warm and wet long rains (wet season), and short rainy seasons, respectively. All samples were collected in triplicate and within a distance of 100 metres from the coastal shores and labelled appropriately. They were taken at a depth of between 0-10 meters above and below sea surface and immediately stored in an icebox. The preserved samples were then transported to Nairobi where they were transferred to a deep-freezer while awaiting analysis.

Water samples were collected in *n*-hexane-rinsed 1-l brown bottles with screw caps lined with *n*-hexane-rinsed aluminium foil. The sample bottles were lowered to fill against the sea tide at knee-height. Sediment samples were collected by lowering an augur and scooping up the top 2 cm undisturbed layer. They were then wrapped in aluminium foil, fastened by masking tape and placed in self-sealing polythene bags and then kept in the icebox. Seaweed was harvested using a knife. The samples were washed with seawater, wrapped in aluminium foil, placed in a labelled polythene bag and then transferred to the icebox. Five to ten (10) specimen samples of small fresh fishes were bought from lots caught by fishermen along the shores of the ocean. Sardines, *Sardinella fimbrita*, of length 19.23 cm and 27.04 g weight, were sampled from Sabaki, while prawns, *Penaeus sp.*, of average length and weight (18.5 cm and 62.66 g) and silver pomfret, *Pampus argenteus*, of average length and weight (15.34 cm and 54.72 g) were taken from Kilifi, Mombasa Old Town and Ramisi, respectively. The wrapped samples were placed in a polythene bag and carried in an icebox to the laboratory. Table 1 gives a full list of sampled fish and locations of collection.

For seaweed, sediment and fish, 30 g samples were taken in triplicates and mixed with 20 g portions of anhydrous sodium sulphate in a mortar and crushed well with a pestle to give a homogenous dry mixture. The mixture was then Soxhlet extracted for three hours with 100 cm^3 of solvent (85% *n*-hexane, 10% acetone and 5% deionized water). The Soxhlet extracts were evaporated to dryness in a rotary evaporator at reduced pressure and the residue taken up in 15 cm^3 *n*-hexane. For seawater, one litre samples were shaken with 100 ml *n*-hexane for 30 minutes, left to settle for 10 minutes and then the *n*-hexane layer taken up in a round bottom flask. This extraction was done three times and the *n*-hexane extracts pooled and evaporated to 15 cm^3 in a rotary evaporator and dried with anhydrous sodium sulphate.

The extracts were cleaned up in a Florisil column (height: 10 cm) with a 2 cm layer of anhydrous sodium sulphate at the top. The extracts were eluted with 30 cm^3 *n*-hexane, then with 30 cm^3 5% acetone in *n*-hexane, and finally with 30 cm^3 of 10% acetone in *n*-hexane. The three fractions were pooled together and reduced until only fatty residues were left. The residues were then redissolved in 1 cm^3 of *n*-hexane, placed in the Florisil column and eluted with 30 cm^3 *n*-hexane, then with 30 cm^3 1% acetone in *n*-hexane and then 30 cm^3 2% acetone in *n*-hexane. The eluates were combined and reduced under nitrogen to 0.5 cm^3 for GC analysis.

Table 1. Characteristics of the fishes bought from fishermen along the cost.

Species	Station	Date	Mean weight (g)	Mean length (cm)	Moisture %	Lipid % (Lateral muscle)
Lethrinus harak	Kilifi	May '98	255.80	16.7	63.03	0.26
Lethrinus nebulose	Kilifi	May '98	30.48	16.5	79.09	0.38
Siganus rivulatus	Malindi	May '98	139.51	19.6	71.07	0.27
Siganus rivulatus	Malindi	July '98	134.90	21.0	78.95	0.27
Lithanus russeli	Malindi	July '98	226.12	20.0	75.39	1.71
Tilapia zilli	Tana river	Sept '98	83.14	19.5	75.41	0.32
Mondactilus argentus	Malindi	Sept '98	44.30	15.4	73.02	0.43
Epinephalus caerulaeopunctatus	Malindi	Jan '99	233.69	20.41	69.93	0.62
Carcharhinus macloti	Kilifi	Jan '99	204.498	31.1	81.18	0.84
Valamugil buchsrhinus	Kilifi	Jan '99	182.32	18.1	77.18	0.46
Siganus rivulatus	Kilifi	Jan '99	132.81	16.0	80.01	0.28
Lethrinus nebulose	Kilifi	Jan '98	83.14	18.5	75.06	0.39
Siganus rivulatus	Malindi	Sept '98	142.55	22	79.62	0.28
Sardinella fimbrita	Sabaki	Jan '97	27.04	19.23	73.36	3.92
Penaeus Sp	Kilifi	May '97	77.05	18.54	79.52	4.36
Apolectus niger	Mombasa	May '97	62.66	18.50	74.27	3.25
Pampus Argenteus	Ramisi	Jan '97	54.72	15.34	75.66	3.74

Characteristics of Sampled Materials

The marine sediments had a pH range of 7.4 to 8.4 and organic content of 0.12 to 0.15 % except for Sabaki River, which was 4.70%. All marine sediments were characterised as sandy (mean sand 97.3%; clay 2%) while the Sabaki River sediment was silty clay (silt, 42.5%; clay, 30.2%). The high clay content was due to heavy upstream soil erosion.

The characteristics of fish bought along the coast are given in Table 1. The fish species had comparable lipid contents (mean 0.54%; range 0.26% to 1.71%) in their lateral muscles except for *Lutianus russeli* whose mean lipid content was 1.71%. The obtained lipid content are comparable to those detected by Munga [9] for Tana River fish *Clarias mossambicus*, *Oreochromis mossambicus* and *Tilapia zilli* (range 0.075% to 1.0%) and Subramanian *et al.* [10] for Tamil Nadu 14 fish species (range 0.02% to 1.99%).

Samples Analysis

Gas chromatographic analysis of 258 samples were done on a Hewlett Packard 5890 equipped with a ^{63} Ni-electron capture detector having a SE30 packed quartz capillary column (60 m x 0.319 mm x 0.25 µm). Carrier gas was nitrogen at a flow rate of 0.84 ml min^{-1}, injection volume, 1 µl, attenuation of the integrator was 0, chart speed 0.5 cm min^{-1}, injector and detector temperatures 250°C and 310°C respectively. The initial column temperature was 160°C programmed at a rate of 5°C/min to 255°C and held for 10 minutes before increasing at 20°C min^{-1} to, and holding at 280°C for 20 min.

Organochlorine samples were identified by comparison with standard retention times and quantified by extrapolation of corresponding sample peak areas of known standards for each pesticide. Calibrations were repeated after every nine runs of samples, Figures 2 and 3 give example chromatograms for sediment and fish. Recoveries of the different pesticides analysed in various matrices ranged from 74.7% to 92.1%.

112 samples collected in 1997 were analysed chromatographically using Perkin – Elmer model 8500 gas chromatograph and Varian 3400 gas chromatograph both equipped with ^{63}Ni-ECD detectors. White spot nitrogen with a flow rate of 2 ml min^{-1} was used as carrier gas. The perkin-Elmer chromatograph had an SE-54 fused silica capillary column of dimensions 30 m x 0.25 mm i.d. x 0.25 film thickness while the Varian instrument was fitted with a DB – 5 capillary column of dimensions 15 m x 0.25 mm i.d. x 0.25 µm film thickness. The carrier gas flow rate was the same in both. The column and oven temperature for the second instrument were set at 200 °C and 260°C respectively, while the temperature change was programmed to ramp at 4° C min^{-1} with a 17 min hold at 260° C. The injector and column temperatures of the second instrument were set at 230°C and 250°C respectively. The ramp rate between 100°C and 250°C was 5°C min^{-1}.

The instruments were calibrated using standard solutions of 0.01 – 0.10 mg kg^{-1} for Perkin-Elmer and 0.02 – 0.6 mg kg^{-1} for Varian. 1 µl solutions of standards and samples were injected for analysis. The limit of detection for the SE-54 column ranged between 0.00015 – 0.0098 ng g^{-1} and for DB-5 ranged 0.00025 – 0.0050 ng g^{-1}.

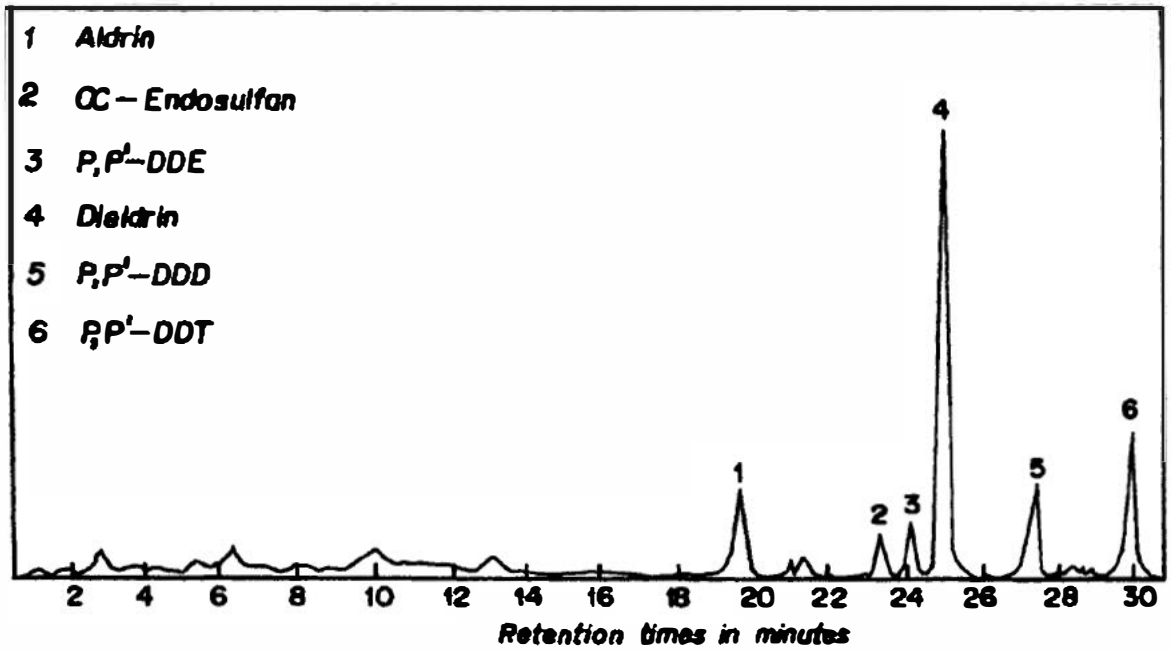

Figure 2. Chromatogram for sediment sample. (Sabaki).

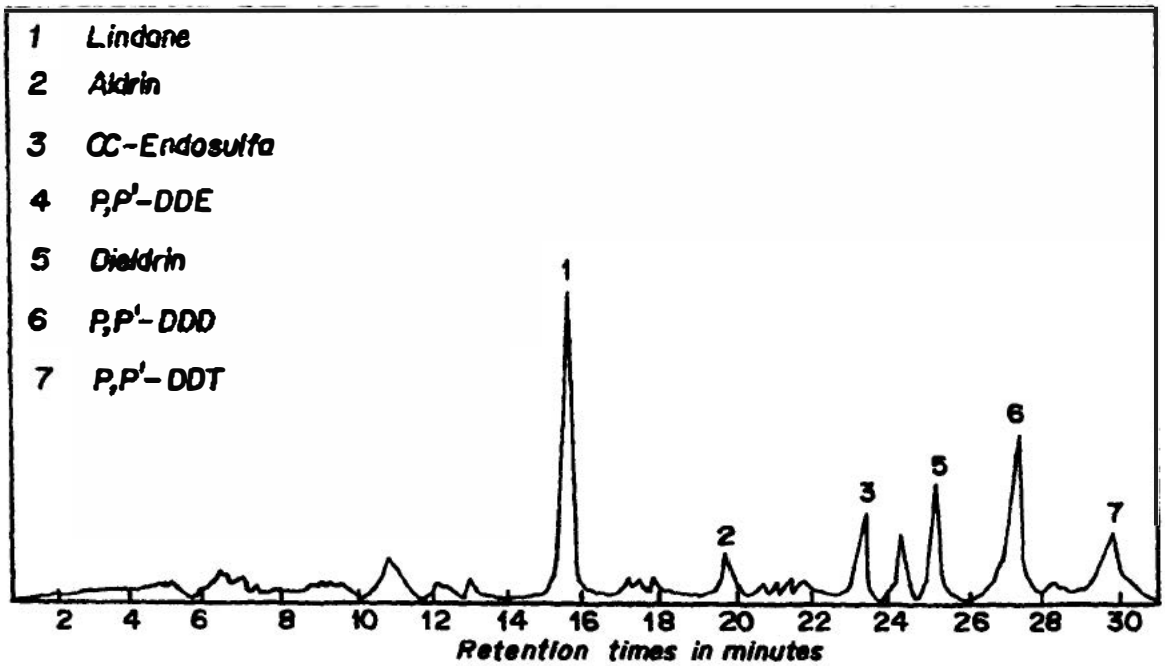

Figure 3. Chromatogram for a fish samples (Mombasa).

RESULTS

Eight (8) triplicate samples of seawater and ten (10) triplicate samples each of seaweed, sediment and fish were analysed from the eight sites. The moisture content in the seaweed was about 69% by weight compared with their organic matter content (9%). The sediment samples along the coast appeared to be very heterogeneous except their pH and moisture content, which were found to be similar in samples taken from the eight sampling locations. The organic carbon content was generally below 1% except for Sabaki station, which showed a high value probably due to the greater primary activity at the river mouth. Similarly, Sabaki and Tana station sediment had higher values of silt and clay compared with sediments from the other six stations, which contained a lot of sand. These investigations were important since the chemical and physical properties of an ecosystem such as pH, mineral composition, organic matter content and moisture content determine the behaviour of pesticides in the aquatic environment. Residues persist longer in sediments with high organic matter content which binds the residues more tightly compared with sandy soils which allows easy solubility in water, cycling in the water and loss through volatilisation.

The moisture content in fish samples was found to account for three-quarters of their mass on wet weight basis, with organic matter and lipid content constituting the remaining weight. The values obtained were comparable to those obtained by Nhan for samples taken from the Red river estuary in Vietnam [8]. Munga found 3.62% lipid in fish samples from Tana River and Everaarts obtained 2.09% lipid in fish from Formosa Bay adjacent to the confluence of Sabaki River [9,10]. Generally, the marine fish samples from different sampling locations showed similar trends in composition of moisture, organic matter and lipid in this study. All types of fish analysed are the migratory type and are well distributed along the coast at an ocean depth between 30 and 210 m.

DISCUSSION

Surface Water Samples

The mean residue concentrations of the organochlorine compounds in seawater samples show that water from all the sampling locations were contaminated with lindane, aldrin, α- endosulfan, p,p'-DDE, dieldrin, p,p'-DDD and p,p'-DDT in 1997 (Table 2) and 1998/99, except for endrin that was observed only in 1998/99 (Table 3). In water samples from the confluence of Sabaki River which flows from the central highlands, a region with intensive agricultural and human load activities, all the pesticides except endrine were detected, the highest mean concentration being that of p,p'-DDD (0.295 ng g^{-1}) and aldrin (0.378 ng g^{-1}) obtained in samples taken during the rainy season in 1997. Lindane, aldrin and p,p'-DDT were not detected in water samples taken from Sabaki during the dry season, but were detected in relatively high concentrations during the rainy season in 1997. In 1999 all were detected during the two seasons. The concentrations of p,p'-DDD, p,p'-DDE and dieldrin were slightly higher in water samples taken during the rainy season from Sabaki in 1997 and 1998/99. In Kilifi Creek, all the residues were detected in surface seawater with lindane,

Table 2. Residues detected in 1997 water samples at the different sites.

Insecticide	Mean (residues in water (ng g^{-1} ± sd)			
	Sabaki	Kilifi	Mombasa	Ramisi
Lindane	0.241*	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	0.196 ± 0.057
p,p'-DDE	0.213 ± 0.032	0.299 ± 0.175	0.175 ± 0.458	0.064 ± 0.035
Dieldrin	0.251 ± 0.006	0.160*	0.501 ± 0.458	0.144 ± 0.034
p,p'-DDD	0.295 ± 0.231	0.177 ± 0.146	0.072*	0.058 ± 0.017
p,p'-DDT	0.168 ± 0.067	0.370*	BDL	0.194 ± 0.073

* detected in one sample only; sd: Standard deviation; BDL: Below detection limit

Table 3. Insecticide residues in seawater (6 replicates).

Date site	Insecticide Residues (Mean ± sd) (ng g^{-1})							
	Aldrin	∝-Endosulfan	Dieldrin	Endrin	DDT	DDE	DDD	Lindane
May '98								
Kilifi	0.099± 0.005	<0.042	<0.006	<0.004	0.462± 0.023	0.140± 0.012	0.124± 0.020	0.037± 0.020
Malindi	0.032± 0.005	0.012± 0.002	<0.006	<0.004	0.491± 0.044	0.261± 0.011	0.326± 0.024	0.096± 0.017
July '98								
Kilifi	0.260± 0.007	0.066± 0.001	<0.006	0.734± 0.028	0.282± 0.033	0.148± 0.009	<0.009	0.054± 0.075
Malindi	0.030± 0.007	0.172± 0.003	<0.006	1.834± 0.077	0.402± 0.040	0.386± 0.21	0.282± 0.28	0.098± 0.041
River Tana	0.037± 0.006	<0.042	<0.006	0.484± 0.022	0.260± 0.027	0.090± 0.001	0.025± 0.022	0.058± 0.19
September '98								
Kilifi	0.071± 0.006	<0.042	0.023± 0.016	0.039± 0.006	0.155± 0.24	0.286± 0.003	0.286± 0.023	0.066± 0.019
Malindi	0.574± 0.007	<0.042	<0.006	0.146± 0.006	0.092± 0.030	0.104± 0.003	<0.009	0.030± 025
Lamu	<0.007	<0.042	<0.006	0.121± 0.27	0.055± 0.27	0.063± 0.002	<0.009	0.075± 0.019
January '99								
Kilifi	0.02± 0.007	<0.042	<0.006	0.012± 0.007	<0.003	0.132± 0.012	<0.009	0.038± 0.025
Malindi	0.026± 0.007±	0.050± 0.001	<0.006	<0.004	<0.003	0.082± 0.002	<0.009	0.026± 0.026
River Sabaki*	0.018± 0.007	0.050± 0.001	<0.006	<0.004	<0.003	0.026± 0.035	<0.009	0.0058± 0.025

*refers to concentration in river water (fresh water)

∝-endosulfan and p,p'-DDE at relatively higher levels than those found in water samples from Sabaki in 1997. During the first year of study lindane was detected with highest mean concentration of 0.503 ng g^{-1} while p,p'-DDT was below detection limit in all samples from Kilifi. Goshi River, which flows through Taita Hills and enters the Indian Ocean at Kilifi Creek, is a possible carrier of pollutants including pesticide residues. Seawater samples from Mombasa Old Town contained high levels of dieldrin with a mean concentration of 0.501 ng g^{-1} compared with all the other residues in 1997 and was only detected in 6% of 66 samples in 1998/99 (Table 3). However, lindane and p,p'-DDT were below the detection limits. Of the p,p'-DDT metabolites, p,p'-DDE and p,p'-DDD were detected with mean concentrations of 0.175 and 0.072 ng g^{-1} in 1997 in water samples from the same sites. ∝-endosulfan was also detected with a high mean concentration of

0.744 ng g^{-1} obtained in samples taken during the rainy season in 1997 but were below detection limit in most of the samples in the 1998/99 study. It has been reported that p,p'-DDT is used for disinfecting Kilindini Harbour while dieldrin and ∝-endosulfan are used in controlling banana weevils, beans and mango pests around this area [2, 3].

In general, the mean concentrations of residues found in water samples taken from Ramisi were slightly lower than those obtained from samples taken from the other three stations in 1997. p,p'-DDT and its metabolites were detected with mean p,p'-DDT concentrations of 0.194 ng g^{-1} during the 1997 rainy season while lindane was below the detection limits in 1997 and averaged 0.058 ng g^{-1} at other sites in 1998/99. The Ramisi area is fairly remote with few human activities since the closure of the Ramisi Sugar factory. However the presence of dieldrin (an epoxide metabolite of aldrin), ∝-endosulfan and p,p'-DDT indicates recent use of pesticides in the area. The occurrence of residues in coastal shallow waters at the eight sampling locations is not surprising since endosulfan, lindane, dieldrin and p,p'-DDT are still used restrictively in this area. Besides these anthropogenic sources, tides also have the potential to transport pollutants from one area to another as this has been found to contribute to contamination of coastal surface waters globally [9].

For comparison, water samples taken from the sea coast of Portland in Jamaica have been reported to contain ∝-endosulfan and p,p'-DDE with mean concentrations of 0.042 and 0.83 ng g^{-1}, respectively [12]. In later studies, Marsingh *et al.* also reported the presence of dieldrin, ∝-endosulfan and p, p'-DDT with mean concentrations of 1.88, 2.98 and 7.02 ng g^{-1}, respectively in Kingston Bay Harbour in Jamaica [13]. These Jamaican coastal areas are therefore relatively more polluted with respect to p, p'-DDT than the area along the Kenyan coast. In contrast, recent findings in studies of coastal waters from the Bay of Bengal in India have reported mean lindane concentration of 0.002 ng g^{-1} in seawater [142] which is lower than the mean value 0.186 ng g^{-1} in 1997 and 0.095 ng g^{-1} obtained in 1998/99. However, these small variations may reflect the common status of pesticide regulation and use trends in these developing countries. There was slight variation in quantities of residues obtained from all the eight different sampling locations in our analysis.

Seaweed Samples

Residues of the eight pesticides analysed were detected in measurable quantities in most seaweed samples taken from the six sampling points (Tables 4) except for endrin that was not detected in 1997 samples. Mean residue concentrations in seaweed samples from Mombasa Old Town were highest for aldrin (18.1 ng g^{-1}) during the 1997 rainy season and lowest (0.91 ng g^{-1}) during the dry period, while mean concentrations

Table 4. Insecticides residues in seaweed (6 replicates).

Date site	Insecticide Residues (Mean + sd) l^{-1} (ng g^{-1})							
	Aldrin	∝-Endosulfan	Dieldrin	Endrin	DDT	DDE	DDD	Lindane
May '98								
Kilifi	2.511± 0.005	1.994± 0.100	0.444± 0.005	0.561± 0.005	1.372± 0.0260	0.794± 0.0340	0.767± 0.190	0.800± 0.020
Malindi	3.100	<0.042	0.300± 0.014	<0.004	<0.003	<0.036	<0.009	0.744± 0.015
July '98								
Kilifi	<0.007	1.300± 0.025	0.539± 0.015	<0.004	0.2800± 0.024	2.300± 0.033	<0.009	0.417± 0.019
Malindi	0.975± 0.060	0.054± 0.002	1.417± 0.014	<0.004	0.402± 0.260	2.442± 0.047	<0.009	0.833± 0.019
September '98								
Kilifi	<0.007	<0.042	<0.006	<0.004	5.533± 0.027	4.867± 0.172	<0.009	8.133± 0.026
Malindi	2.756± 0.005	0.311± 0.002	<0.006	7.800± 0.016	6.711± 0.030	4.933± 0.091	1.167± 0.019	8.222± 0.035
January '99								
Kilifi	1.400± 0.007	<0.042	<0.006	<0.004	<0.003	2.200± 0.029	<0.009	4.833± 0.023
Malindi	7.033± 0.007	<0.042	<0.006	<0.004	<0.003	2.467± 0.076	<0.009	4.833± 0.023
River Sabaki*	11.900± 0.007	0.867± 0.012	<0.006	0.933± 0.006	<0.003	5.200± 0.092	<0.009	5.367± 0.024

* Weed samples from each site

of dieldrin (9.68 ng g^{-1}), lindane (10.1 ng g^{-1}) and ∝-endosulfan (10.68 ng g^{-1}) were comparable in samples taken during the rainy period. The concentration levels found in 1998/99 seasons were considerably lower than those observed in 1997 except for 11.90 ng g^{-1} aldrin in fresh water weeds of Sabaki River. Aldrin, ∝-endosulfan, endrin, p, p'-DDE and lindane were detected in reasonable levels in the 1998/99 studies.

Aldrin was detected in 40% of the samples with a mean concentration of 6.72 ng g^{-1}, slightly lower than its metabolite dieldrin (8.20 ng g^{-1}) in 1997 while lindane was detected in 94% of the 54 seaweed samples analysed in 1998/99. High concentrations of p, p'-DDT (mean of 34.26 ng g^{-1}) and p, p'-DDD (mean 15.27 ng g^{-1}) were found in seaweed samples collected in Kilifi during the 1997 rainy season. Table 4 shows that all 8 pesticides were present at lower concentration at this site in 1998. The concentrations of the residues in seaweed samples from Kilifi were generally higher compared with samples taken from the other three sampling locations in 1997 than in 1998/99 samples. Concentrations of lindane (mean of 34.6 ng g^{-1}) was the highest of all samples from the confluence of Ramisi River in all years of study though medium concentrations of p, p'-DDE (mean of 1.66 ng g^{-1}) and p, p'-DDD (mean of 6.41 ng g^{-1}) were detected in samples collected during the 1997 wet season . The seasonal variation of the levels of residues was very significant in seaweed samples with higher levels recorded in all samples during the 1997 rainy period. However, in the 1998/99 studies p, p'-DDT and its metabolites and lindane did not show a consistent seasonal variation trend. The concentrations were either high in the dry season, low in the rainy season or short rainy season or vice verse. From other studies, different species of macroalgae from the Venice Lagoon were reported to have mean concentrations of lindane and p, p'-DDT of 1.33 ng g^{-1} and 2.05 ng g^{-1}, respectively [15]. In these studies, it was also found that the variation in residue concentration levels depended on the structure of fronds, the life time and constituents of the fronds and the period of sampling [15]. These concentrations are approximately 4 times less than the highest found in our 1997 study.

Sediment Samples

There were, on average, higher concentrations of total residues found in sediment samples taken during the 1997 wet season and the 1998 short rainy season (Table 5). This trend was similar to that found in surveys done in Jamaica

Table 5. Insecticide residues in marine sediments (6 replicate analyses).

Date site	Insecticide Residues (Mean + sd) l^{-1} (ng g^{-1})							
	Aldrin	∝-Endosulfan	Dieldrin	Endrin	p,p'-DDT	p,p'-DDE	p,p'-DDD	Lindane
May '98								
Kilifi	<0.007	<0.042	<0.006	<0.004	<0.003	0.650± 0.021	<0.009	0.284± 0.020
Malindi	<0.007	<0.042	<0.006	<0.004	1.267± 0.032	1.800± 0.022	<0.009	1.533± 0.024
July '98								
Kilifi	0.950± 0.006	1.633± 0.001	<0.006	<0.004	3.150± 0.023	1.67± 0.026	<0.009	0.750± 0.019
Malindi	0.867± 0.007	<0.042	4.070± 0.017	<0.004	4.000± 0.031	4.800± 0.043	<0.009	1.200± 0.025
September '98								
Kilifi	2.067± 0.007	<0.042	<0.006	25.000± 0.027	59.000± 0.19	25.000± 0.184	15.333± 0.0027	16.733± 0.040
Malindi	<0.007	<0.042	0.889± 0.014	<0.004	2.111± 0.026	2.289± 0.032	<0.009	2.550± 0.017
Lamu	0.584± 0.005	<0.042	<0.006	<0.004	0.933± 0.027	1.734± 0.103	<0.009	1.507± 0.017
January '99								
Kilifi	1.033± 0.007	<0.042	<0.006	<0.004	<0.003	1.600± 0.024	<0.009	0.800± 0.025
Malindi	0.467± 0.007	<0.042	<0.006	<0.004	<0.003	1.300± 0.030	<0.009	0.733± 0.025
River Sabaki*	5.100± 0.001	<0.042	<0.006	<0.004	<0.003	<0.036	<0.009	6.933± 0.025

* refers to river sediments.

[13] but differed from surveys recently done in Vietnam where the concentrations of residues detected during the dry season were reported to be slightly higher than those obtained during the rainy season, ranging from 0.17-3.48 and 0.012-2.36 ng g^{-1}, for dry and rainy seasons respectively [8]. In our analysis, p, p'-DDT and its metabolites, p, p'-DDE and p, p'-DDD were present in sediment samples from all the four sampling stations in 1997 while in1998/99 their presence in all stations was not detected. Ramisi sediment samples had slightly higher concentrations of all the pesticide residues in all sites in 1997 except for dieldrin which gave a highest mean concentration of 44.5 ng g^{-1} at Sabaki. In the subsequent two years only lindane was observed at all sites (Table 5). The 1997 concentration levels of residues in Kilifi sediment samples were relatively much higher than those detected by Prats *et al* [16] along the coast of Alicante, Spain where organochlorine residue concentrations ranging from 0.002-0.23 ng g^{-1} were obtained while the 1998 levels at this site were much closer to the Alicante levels. In old Mombasa town sediment samples had dieldrin and lindane at mean concentrations of 8.85 and 7.55 ng g^{-1}, respectively and showed highest frequency of occurrence (80%) of all residues analysed in 1997. The 1998/99 study showed no such high concentrations. In a recent study by Everaarts *et al.* [9], sediment samples taken from the shallowest point next to the Sabaki River were found to have dieldrin at concentrations averaging 98.5 ng g^{-1} organic carbon (OC). These concentrations indicate the higher applications of dieldrin in nearby areas before 1986, the year the government banned its use. He also reported p,p'-DDE residue concentrations ranging from 65.5-1038 ng g^{-1} OC, wet weight, while those of lindane and p,p'-DDD were reported at 31.5-137 ng g^{-1} OC and 185 ng g^{-1} OC, wet weight, respectively. In sediment samples taken from Gazi next to Ramisi, he reported the presence of lindane at a concentration of 215 ng g^{-1} OC. In Everaarts *et al.*'s survey, the samples were taken in the early 1990s following a period of very successful agricultural farming in the upper Tana River delta region which included irrigation farming of cotton and rice with aerial spraying of farms with p,p'-DDT and also aerial spraying of cotton fields near Margarini in Malindi before the p,p'-DDT ban in agriculture in 1986. This can account for the high p,p'-DDE and p,p'-DDD residue levels in sediment samples taken near the Sabaki River mouth. Aldrin, dieldrin and p,p'-DDT are now only allowed in public health control such as in control of mosquitoes while lindane is allowed for seed dressing and termite control only.

Residue concentration trend in sediments along the west coast of India was reported to decrease as follows-dieldrin <aldrin<HCH<p,p'-DDT with the highest values of total p,p'-DDT ranging from 32 to 43 ng g^{-1} wet weight [17] while the east coast was reported to have aldrin in the range 20-530, lindane 10-210, dieldrin 50-510 and total p,p'-DDT at 0.02-078 ng g^{-1} wet weight [18]. In Kingston Harbour in Jamaica, sediment samples were found to contain aldrin in highest concentration of all the organochlorines with a mean value of 36.7 ng g^{-1} [13] and from the estuary of Palizada River in Mexico, sediments were found to contain lindane, p,p'-DDE and aldrin at concentrations of 0.57,17.67 and 9.02 ng g^{-1}, respectively [19] which are quite comparable to our values.

The occurrence of high concentrations of dieldrin in sediment in 1997 samples from the Sabaki confluence and at Kilifi Creek suggested a prevailing pollution source. The concentrations of aldrin were much higher than those of dieldrin in the Mombasa and Ramisi samples. Aldrin is rarely found in the environment as a result of its rapid transformation into dieldrin. Therefore the presence of aldrin in sediment suggested direct input into the aquatic environment from nearby sources. It is most likely that aldrin was released directly into coastal waters from the industrial run-off in Mombasa and from domestic waste from Ramisi. Termites are very destructive during dry periods in this area and lindane is used to control them. This could contribute to the high levels of lindane residues detected in the samples taken in the dry season.

Fish Samples

1997 data obtained from analysis of fish samples taken from Sabaki showed that lindane (mean concentration of 612 ng g^{-1}) gave the highest mean residue concentration as well as frequency of occurrence (80%). The same high concentration persisted in 1998 at Malindi (next to Sabaki River) and Kilifi (Table 6). From other studies, high values of lindane have also been reported in fish samples from Suruga Bay, Japan which suggests that this residue is capable of high bioaccumulation in fish [20]. The high concentrations of lindane in fish samples from Mombasa, Sabaki and Ramisi, (Malindi and Kilifi in all years of study) is due to the use of technical BHC formulations for soil treatment, foliage application on fruit and nut trees, vegetables, ornamentals and for timber preservation along the coast in these regions. Aldrin, dieldrin and α-endosulfan residues were comparable with high mean concentrations of 41.8, 48.5 and 40.2 ng g^{-1}, respectively. Only aldrin concentration remained high in 1998 (Table 6). The concentrations of p,p'-DDT (mean of 30.28 ng g^{-1}) were very low in fish samples taken from all four stations in 1997 compared with other residues except for p,p'-DDD and p,p'-DDE and was detected in 40% of the samples analysed from this station. However, p,p'-DDT and p,p'-DDE were present in high concentrations in all fish analysed for Kilifi, except for Malindi *Lethrinus harak* in 1998. Besides p,p'-DDT and p,p'-DDE, the 1997 samples showed average high levels of aldrin and lindane at all the four sites. Other residue concentrations were low in both years of study. At Ramisi, lindane concentration was highest (mean of 281 ng g^{-1}) of all the organochlorines followed by aldrin (mean of 1.02 ng g^{-1}) while other residues were in much lower concentrations. A significant seasonal variation in the concentration levels was found for all residues with higher concentrations being recorded during the wet season except in 1997, lindane and p,p'-DDD gave higher concentrations in fish samples taken

Table 6. Insecticide residues in fish (6 replicates).

Date site	Insecticide Residues (Mean + sd) l^{-1} (ng g^{-1})							
	Aldrin	∝-Endosulfan	Dieldrin	Endrin	p,p'-DDT	p,p'-DDE	p,p'-DDD	Lindane
May '98								
KFI	250.038± 0.808	<0.042	<0.006	<0.004	<0.003	<0.036	<0.009	42.346± 3.000
KFII	411.842± 0.368	<0.042	<0.006	<0.004	76.316± 1.632	82.316± 1.211	<0.009	47.368± 1.316
MFIII	<0.007	<0.042	<0.006	<0.004	1011.11± 5.89	159.22± 4889	418.556± 2.869	47.368±
July '98								
MF VI	37.05± 0.124	<0.042	135.882± 0.300	<0.004	28.588± 0.600	91.765± 3.194	<0.009	38.824± 0.441
TFV	<0.007	<0.042	109.375± 1.125	<0.004	<0.003	140.625± 1.688	<0.009	131.250± 1.500
September '99								
MFVII	0.071± 0.006	<0.042	0.023± 0.016	0.039± 0.006	0.155± 0.24	0.286± 0.003	0.286± 0.023	0.066± 0.019
KFIII	0.574± 0.007	<0.042	<0.006	0.146± 0.006	0.092± 0.030	0.104± 0.003	<0.009	0.030± 0.25
MFII	<0.007	<0.042	<0.006	0.121± 0.27	0.055± 0.27	0.063± 0.002	<0.009	0.075± 0.019
January '98								
MFVII	20.952± 0.389	<0.042	<0.006	<0.004	27.435± 1.694	70.948± 1.065	<0.009	0.038± 0.025
MFVIII	17.857± 0.250	35.714± 0.393	<0.006	<0.004	<0.003	99.036± 1.464	<0.009	0.026± 0.026
KFIX	23.934± 0.457	<0.042	<0.006	<0.004	78.261± 2.152	89.152± 1.360	80.413± 1.761	0.0058
KFIII	<0.007	139.286± 1.286	<0.006	<0.004	42.857± 3.750	142.82± 4.607	<0.009	24.964± 2.786

* - Fresh water fish Notes: M - Malindi, K-Kilifi, T-river Tana station. KEY FI *Lethrinus harak*, FII *Lethrinus nebulose*, FIII *Siganus rivulatus*, FIV *Ludanus reseli*, TFV *Tilapia Zilli*, FVI *Monadactilus argenis*, FVII *Epinephelus cerulopunctatus*, FVIII *Carchahinus macloti*, FIX *Valamugil buchanani*

from Mombasa during the dry period (Table 6)

The organochlorine contamination of Suruga Bay in Japan coastal fish seems to be comparable to that found in the 1997 data, especially for lindane at Kilifi and Ramisi. The concentrations of p,p'-DDTs and hexachlorohexane (HCHs) isomers were reported in the range between 80-1700 and 1-250 ng g^{-1} of lipid, respectively, in fish samples from Suruga Bay [20]. However, fish samples from Meghna-Dhonagoda River estuary in Bangladesh contained much higher concentrations of organochlorines including, p,p'-DDT and p,p'-DDD at concentrations of 1280 and 1370 ng g^{-1} lipid, respectively [14]. No such levels were observed in Kenya. Lindane concentration values were lower (26 ng g^{-1}) while both aldrin and dieldrin were not detected in the same fish samples in Matin's survey. Our survey show higher levels in the Kenyan coast. Lower concentrations of PCBs and p,p'-DDTs have also been reported in shellfish samples taken at the mouth of the River Po in the Northern Adriatic Sea, ranging from 2.1-18.3 and 3.2-12.2 ng g^{-1}, respectively [21]. The Kenyan coast shows lower p,p'-DDT levels in fish than found in the Adriatic sea.

CONCLUSIONS

Many tropical developing nations have continued to use organochlorine pesticides in view of their availability at low costs, low mammalian toxicity and broad spectrum activity for long duration. Organophosphates which are now widely used in temperate regions are expensive and due to high toxicity are unsafe unless adequate precautions are taken. Due to the high increase in population and the subsequent high demand for food, large amounts of pesticide residues enter drainage canals and rivers and discharge into lakes and oceans and hence become a serious source of marine environmental pollution. The high concentrations of residues found in the Kenyan coast as well as in other tropical coastal areas indicate recent usage of organochlorine pesticides in these areas. The variations in concentrations of organochlorine residues found in this study reflect trends in

usage and state of legislation enforcement regarding pesticide use in Kenya.

From our 1997 studies it was found that seawater from Kilifi was most polluted while that taken in Ramisi was least polluted. The EC Drinking Water Directive [22] recommends that individual insecticides should not exceed 0.1 ng g^{-1} levels in drinking water. However, the levels of some of the organochlorine residues in marine water from the sampling locations, especially in Kilifi, exceeded the limit. This could pose a health risk to aquatic organisms.

Sea plants can play a key role in the process of micropollutant dissemination and cycling along the coast as shown by the high residue concentrations detected in seaweed in this region. They can store and distribute micropollutants by both physical and biochemical processes and transfer them to surface waters through dispersion of fine soft material in which they are transformed during decomposition and also through food chain transfer processes in aquatic ecosystems.

The p,p'-DDT concentrations determined in the sediment and fish samples were much lower than the Food and Agriculture (FAO)/World Health Organisation (WHO) tolerable levels of 50-700 ng g^{-1} day^{-1}. The acute toxicity levels, LC_{50}, for various fish species range between 16 and 1900 ng ml^{-1} [23,24] and at the concentration levels of these pesticides present at the Kenyan coast, they may not pose ill health to fish. However, several pesticides were detected in some fish species and the combined synergetic effects of these pesticides on species is not certain. Furthermore, the effect of chronic poisoning combined with bioaccumulation of these pesticides can only be speculated.

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