ORGANOCHLORINE PESTICIDE RESIDUES IN WATERS FROM THE COASTAL AREA OF DAR ES SALAAM AND THEIR EFFECT ON AQUATIC BIOTA

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ABSTRACT

Water samples from Msimbazi and Kizinga rivers in Dar es Salaam and from the coastal marine environment receiving waters from these rivers were analyzed for various organochlorine pesticide residues using GC-ECD and GC-MS. p,p'-DDE, p,p'-DDT, dieldrin and γ-HCH were the only organochlorine pesticide residues detected at significantly greater concentrations above the detection limits. There was a marked difference in the frequency of pesticide residue detection during the dry and wet seasons. All the wet season samples and 37.5 % of the dry season samples revealed presence of p,p'-DDE at concentrations ranging from 0.05 to 0.45 mgl^{-1} and 0.08 to 0.20 mgl^{-1} respectively. p,p'-DDT was detected in 25% of the dry season samples at a concentration range of 0.1 - 0.4 mgl^{-1} and in 81 % of the wet season samples at concentrations ranging from 0.1 - 0.3 mgl^{-1}. Dieldrin and γ-HCH were only detected during the wet season. Dieldrin amounts ranging between 0.2 and 2.5 mgl^{-1} were detected in all wet season samples whereas γ-HCH (0.2 mgl^{-1}) was found in only one wet season sample. Recoveries of pesticides ranged from 65 to 108%. The present study suggests that the current levels of pesticides detected in these waters have no acute effects to aquatic biota.

However, the levels of total DDT and dieldrin present during the wet season suggest a possibility for chronic effects on aquatic biota.

INTRODUCTION

Pesticides have become essential components of modern agricultural systems and in public health programmes. Their use has been considered to be absolutely vital in reducing dramatic loss of crops and control of vectors that transmit disease to man and livestock. However, organochlorine pesticides such as DDT and aldrin, which have been extensively used in agriculture and public health programmes, are very persistent in nature. Their persistence and lipid solubility make them major environmental pollutants. Accumulation of low concentration of these pesticides in the body fat of mammals might pose potential hazards in the long run (Jensen 1983).

Pesticides may exist in target organisms and soil systems for a considerable period of time. They also enter into natural waters by percolation and runoff from agricultural land and channels, and from urban city sewage sites, thus affecting the quality of various water sources. Persistence of these organochlorines in water has a special significance as they are taken up by organisms like planktons and thus enter into the food chain.

Tanzania, like any other tropical country, has extensively used organochlorine pesticides in both agriculture and public health programmes. The exact amount of organochlorine pesticides that has been used is not known; official data was not available for the present study. The general use of some of pesticides such as DDT and dieldrin, was banned while a significant amounts were still in stock. Companies were asked to stop importing but were allowed to continue selling the stock. Customers also shied out from buying the stock and as there were no disposal alternatives given; this resulted into accumulation of the obsolete pesticides. Tanzania is estimated to have around 1000 tons of obsolete pesticides and veterinary drugs; most of them being persistent organochlorines including DDT and dieldrin (Mmochi & Mberek 1998). Due to effectiveness of DDT as an insecticide, some of the pesticide dealers have been illegally importing, formulating and selling banned pesticides under different names (Anon 1994).

The present study investigated patterns of occurrence and distribution of organochlorine pesticide residues in waters of Msimbazi and Kizinga rivers in Dar es Salaam and at the coastal marine environment between these rivers during dry and wet seasons. The study also assessed the potential risk such pesticide levels might have on aquatic organisms. Among the major reported chronic effect to the aquatic biota associated with organochlorine exposure (DDT in particular) in sediments is reproductive depression (Murdoch *et al.*1997).

METHODS

The study was conducted within the Msimbazi and Kizinga rivers as well as the Dar es Salaam marine coastal environment (Fig. 1) between December 1996 and January 1998. River Msimbazi is about 35 km long, passes through the city industrial area and its catchment is 300 square kilometres (Kondoro 1997). Its basin is a significant agricultural zone supplying the city with part of the vegetable demands (Stevenson *et al.* 1994). The river receives municipal and untreated waste from industries, forming the common outlet to the Indian Ocean for different types of factories (Anon 1982).

River Kizinga originates in the Kazimzumbwi forest reserve and discharges into the Indian Ocean at Mtoni mangrove stand. On its way to the Dar es Salaam coastal marine environment, River Kizinga drains through agricultural and residential areas. Water from Msimbazi and Kizinga rivers is normally used for watering adjacent vegetables, washing and occasionally drinking.

Dar es Salaam coastal waters receive municipal discharges via Msimbazi and Kizinga rivers as well as chemicals generated from ship fumigation activities at the harbour.

Eight sampling stations were selected basing on proximity to industrial, agricultural and harbour activities. Samples were collected twice each season, at the commencement and the end of dry seasons as well as during early and late rains.

Water samples were collected into pre-cleaned 1-litre glass bottles with Teflon lids or glass stoppers. Samples were preserved with 3% dichloromethane to stop biological activities and transported to the laboratory for extraction procedures.

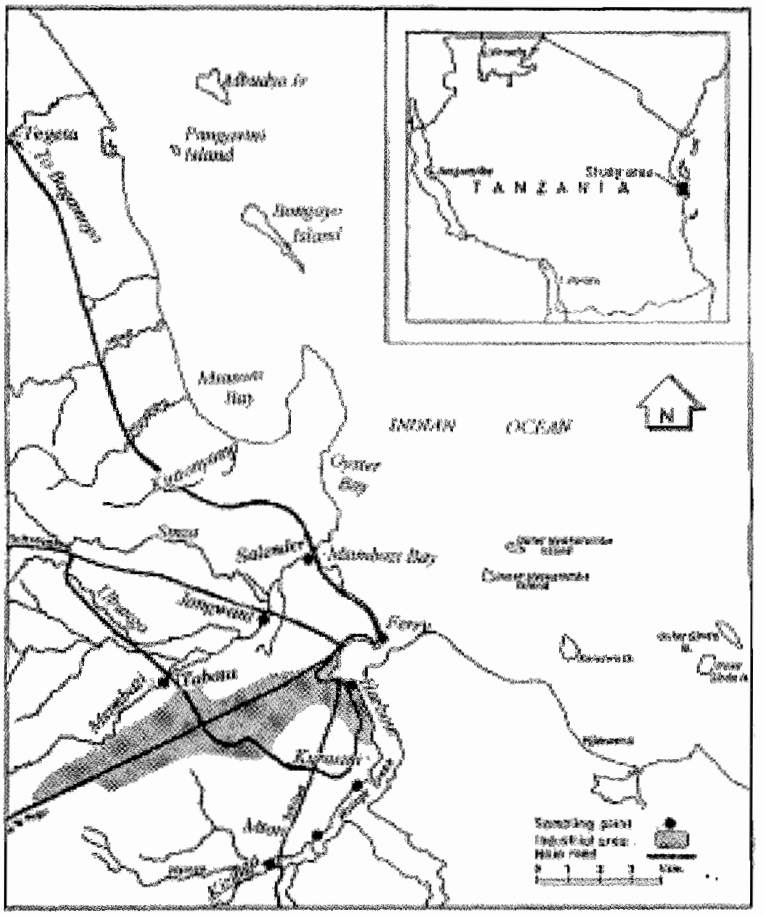

Fig. 1: Map of the study area in Dar es Salaam showing the sampling sites

Unfiltered water samples were extracted by liquid-liquid extraction using a series of 60, 30 and 30 cm^3 dichloromethane. The combined extracts were dried over anhydrous sodium sulphate prior to concentration and cleanup.

The extracts were then cleaned-up by Gel Permeation Chromatography (GPC) using ethyl acetate/cyclohexane 1:1 mixtures as eluents. Cleaned extracts were concentrated using a rotary evaporator to a final volume of 2 cm^3 cyclohexane/acetone 1:1 mixture. In some cases destructive clean-up using sulphuric acid and potassium hydroxide was employed (kerblom 1995).

Gas Chromatographic (GC) analysis

Analysis of the samples was carried out on a Varian 3400 gas chromatograph fitted with a ^{63}Ni electron capture detector with both SE-30 and OV 1701 mega bore columns (30 m x 0.32 mm x 0.5 m). The GC parameters and operational conditions were as follows: Gases: Carrier gas (H_2); flow rate 5 ml/min and makeup gas (N_2); flow rate of 25 ml/min. Temperature programme: 90°C (1 min) at 30°C/min to 180°C at 4°C/min to 260°C (10 min).

The external reference standard and relative retention times technique was used for the identification and quantification of the peaks in the samples. External reference standards were run in parallel with samples and identification of unknown peaks accomplished by comparison of their retention times in both columns. The identity of the peaks was confirmed by use of GC-MS at the Department of Environmental Assessment of the Swedish University of Agricultural Sciences, Sweden. Concentrations of the pesticide residues were calculated by comparison of sample peak height to that of its corresponding peak from the reference standard.

RESULTS

The average recoveries and method detection limits for identified residues are given in Table 1. (values were not corrected for recoveries). Among the wide range of analysed organochlorine pesticides in 32 water samples of both dry and wet seasons, only p,p'-DDT, p,p'-DDE, dieldrin and γ-HCH (lindane) were detected. During the dry season only p,p'-DDT and p,p'-DDE were identified whereas in wet season samples, dieldrin and γ-HCH were also detected at levels above the method detection limits.

Table 1: Average percentage recoveries and method detection limits for identified organochlorine pesticides

Pesticide	Average percentage recovery and range, (n=4)	average method detection limit (mgl^{-1})
p,p'-DDT	108 (98 – 114)	0.10
p,p'-DDE	92 (86 – 97)	0.05
dieldrin	106 (95 – 112)	0.04
γ–HCH	65 (61 – 72)	0.05

There was a marked difference in the detection frequencies of pesticides between the two seasons. A much higher frequency of pesticide detection was observed in wet season samples (Figs. 2-5, Appendix 1).

The p,p'-DDT was detected in 25% of the dry season samples and 81% of the wet samples at a concentration ranging from Below Detection Limit (BDL) to 0.4 μgl^{-1} and from BDL to 0.3 μgl^{-1} respectively. The mean concentration values of the detected p,p'-DDT for both dry and wet season was 0.2 ± 0.06 μgl^{-1}. This suggests no significant difference ($p = 0.45$) on the levels of identified p,p'-DDT residues between wet and the dry season, regardless of the notable difference in frequency of detection. The highest concentrations for both seasons were obtained at Jangwani. All dry season samples which contained p,p'-DDT residues were from Msimbazi river while in the wet season samples p,p -DDT was found in almost all the sites.

All the wet season samples and only 37.5% of the dry season samples revealed presence of p,p'-DDE at concentrations ranging from 0.05 to 0.45 μgl^{-1} and BDL to 0.2 μgl^{-1} respectively. The highest concentration in the dry season samples was also found at Jangwani area whereas during wet season, the highest concentration was detected at both Jangwani and Tabata areas. The mean p,p'-DDE concentration was 0.23 ± 0.05 μgl^{-1} in the wet season and 0.12 ± 0.04 μgl^{-1} in the dry season . Total p,p'-DDT (p,p'-DDT + p,p'-DDE) that was detected in 37.5% of the dry season samples and 100% of the wet season samples ranged from BDL to 0.5 μgl^{-1} and 0.05 to 0.8 μgl^{-1} respectively. The mean concentrations were 0.27 ± 0.1 μgl^{-1} in dry season and 0.4 ± 0.1 μgl^{-1} in wet season samples. Dieldrin and γ-HCH were only detected at significantly greater concentration above detection limits during wet season. γ-HCH was found at a concentration of 0.2 μgl^{-1} in one sample collected at Kurasini estuarine mangrove areas during early rains. Dieldrin amounts ranging between 0.2 and 2.5 μgl^{-1} were detected in all wet season samples. Maximum concentrations were detected near Salender Bridge during early rains and at Kurasini during late rains. The seasonal mean value of dieldrin was 0.7 ± 0.04 μgl^{-1}. Dieldrin concentration values between early rain season and late rain were not significantly different ($p = 0.47$).

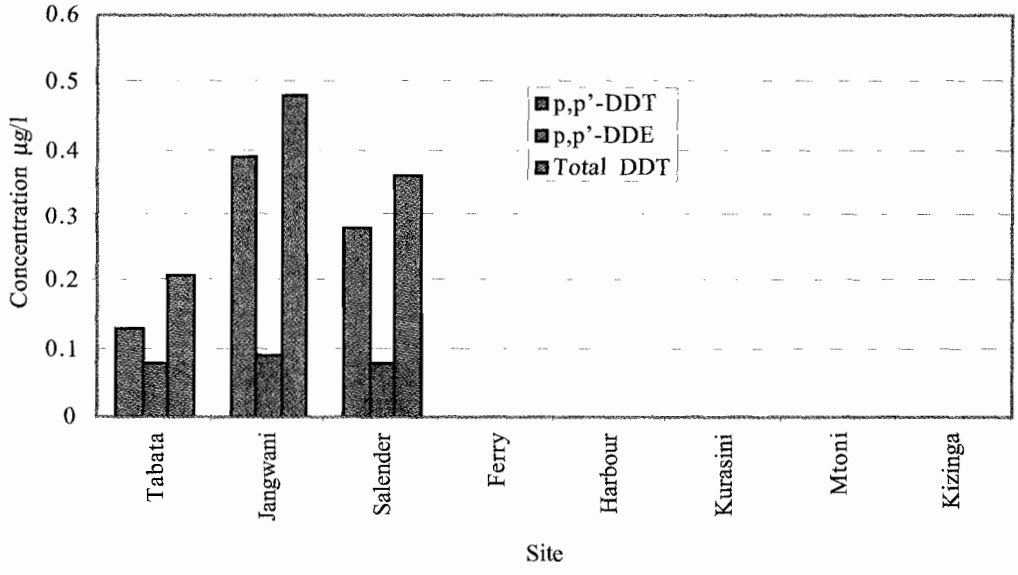

Fig. 2: Levels of pesticide residues detected in early dry season water from Dar es Salaam, Tanzania, 1996-1998

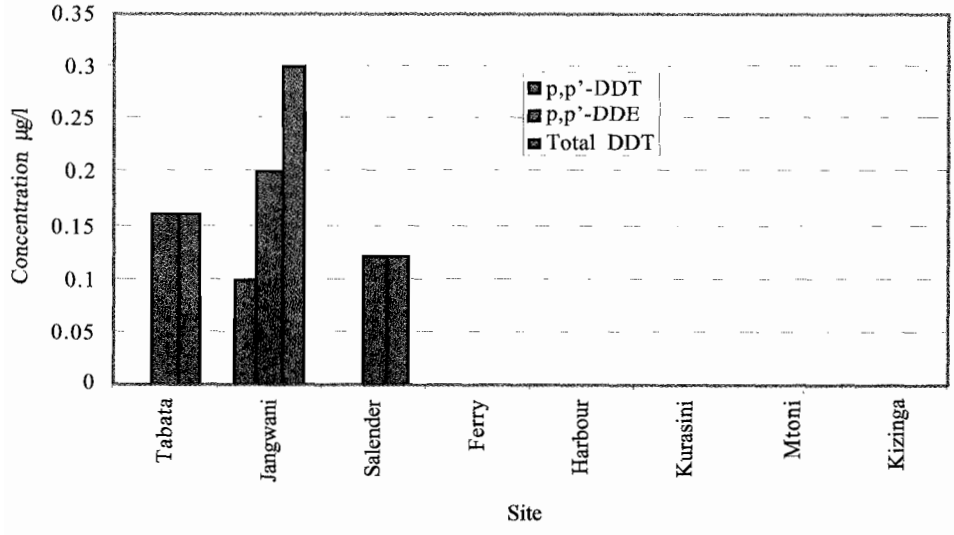

Fig. 3: Levels of pesticide residues detected in late dry season water samples from Dar es Salaam, Tanzania, 1996-1998

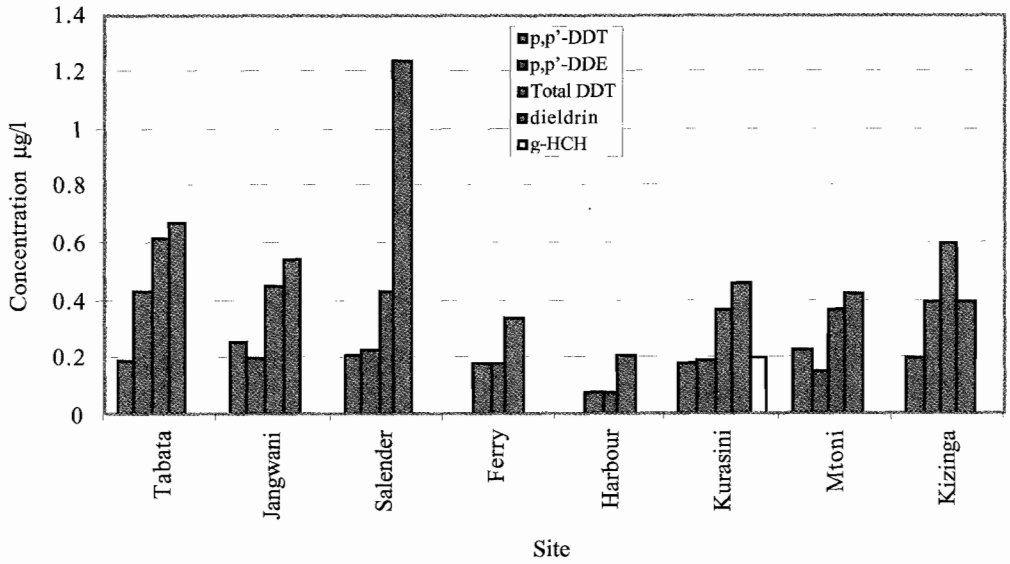

Fig. 4: Levels of pesticides residues detected in early wet season water samples from Dar es Salaam, Tanzania, 1996-1998

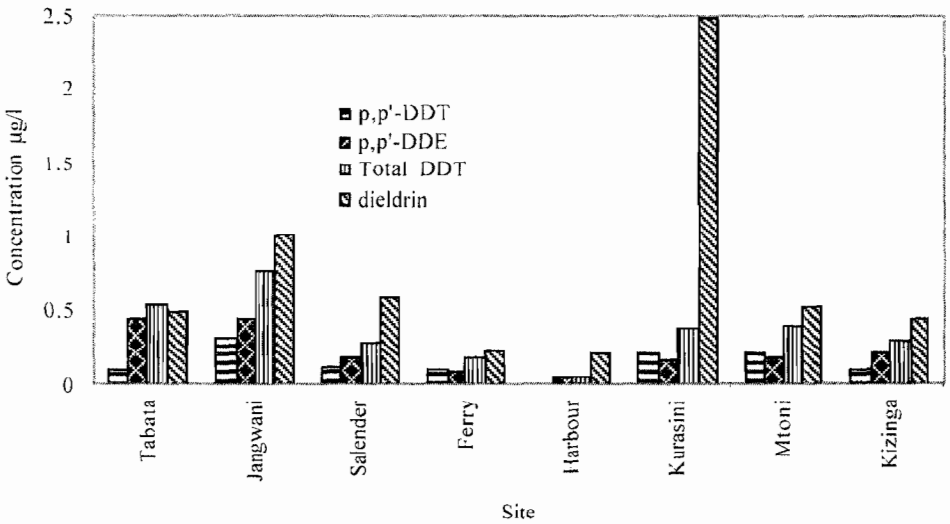

Fig. 5: Levels of pesticides residues detected in late wet season water samples, from Dar es Salaam, Tanzania, 1996-1998

Table 2: Average pesticide residue levels in the water samples collected during wet and dry seasons in Dar es Salaam, Tanzania, 1996-1998

Season	Type of Pesticide	Percentage of sample with pesticide	Mean concentration (μgl^{-1})	Concentration range (μgl^{-1})
Dry Season	p,p'-DDT	25.0%	0.20 – 0.06	BDL - 0.40
	p,p'-DDE	37.5%	0.12 – 0.04	BDL - 0.20
	Total DDT	37.5%	0.27 – 0.1	BDL - 0.50
Wet Season	p,p'-DDT	81.0%	0.20 – 0.05	BDL - 0.30
	p,p'-DDE	100.0%	0.23 – 0.06	0.05 - 0.45
	Total DDT	100.0%	0.40 – 0.1	0.05 - 0.80
	Dieldrin	100.0%	0.65 – 0.04	0.2 - 2.50
	γ–HCH	6.0%	0.20	BDL - 0.20

DISCUSSION

The frequency of detection of pesticide residues showed a marked seasonal variation. The frequency of all detected pesticides were observed to increase from dry to wet season. p,p'-DDT had an increase from 25% to 81%, p,p'-DDE detection frequency increased from 25% to 100%, dieldrin changed from 0% to 100% and γ-HCH increased from 0% to 6%. Mwanthi (1998) reported similar seasonal variations in surface water used for community water supplies in Kiria, Kenya. This increase of detection frequency might be caused by agricultural and domestic runoff draining into the rivers, which seem to be a potential source of pollution for surface water during rainy season. Ability of pesticide residues to be bound to soil (sediment) particles depends on their lipophilicity, which is estimated by their octanol-water partition K_{ow}. Higher K_{ow} of DDT and its metabolites ($\log K_{ow} = 6$) as well as that of dieldrin ($\log K_{ow} = 4.8$) may account for their significant increase in detection frequency from dry to wet seasons. The lower detection frequency of γ-HCH during the wet season reflects its relatively lower K_{ow} ($\log K_{ow} = 3.7$) and relatively quicker breakdown than the other residues regardless of the presence of suspended solids in the water.

The changes from dry to wet seasons were such that the maximum concentrations of p,p'-DDE changed from 0.2 to 0.5 μgl^{-1}, that of total DDT changed from 0.5 to 0.8 μgl^{-1} while dieldrin and γ-HCH changed from non detectable levels to 2.5 μgl^{-1} and 0.2 μgl^{-1} respectively. Such changes in

concentration can be accounted for by runoff which washes and releases pesticides bound to soil particles and other matrix from treated areas directly into the rivers. The increase in concentration is also likely to be agrevated by suspended particles, as the water samples were not filtered. MacKenzie-Smith *et al.* (1994) also reported an increase in concentration in their study of organochlorine pesticide residues in water from different rivers. In their study they found that more than 70% of pesticide residues in unfiltered water was associated to suspended particles and in some samples 100% of dieldrin was associated with suspended particles. These results are comparable and may give some explanation for detection of dieldrin during the rainy season only.

However, the maximum concentration of p,p'-DDT was almost the same for the seasons. The detection of similar values for maximum concentration of p,p'-DDT at the Jangwani site in both seasons suggests the presence of point sources such as illegal use of DDT along the river bank. This may also explain the presence of DDT in Msimbazi river sites only during the dry season.

In most cases the lowest concentration of detected residues were measured at the Harbour sampling site followed by the Ferry sampling sites. This could be due to the influence of dilution with seawater as both are marine sites and due to lack of turbulent flow as this reduces the amount of suspended solids in water.

The only maximum residue level limits for surface fresh water and coastal and marine waters found in literature were those published for Philippines. According to the Philippines water quality criteria for toxic and deleterious substances for coastal and marine water, the maximum limits for total DDT, dieldrin and γ-HCH are 50 μgl^{-1}, 1 μgl^{-1} and 4 μgl^{-1} respectively (Anon 1990). The mean values of DDT, dieldin and γ-HCH found in the present study were thus below the Philippines standard limits. However, individual sites such as Salender Bridge, during early rains and Jangwani and Kurasini during late rains, showed higher levels of pesticide residue than the Phillipines limits.

Fresh water from the rivers was occasionally used for domestic purposes. Drinking water limit values of the WHO are 1 μgl^{-1} and 0.03 μgl^{-1} for DDT and dieldrin respectively (Dahi 1989). In the present study, the mean values

of DDT for both dry and wet seasons were below the WHO limit values but the mean value of dieldrin was about 20 times above the WHO limits. This suggests that water from Msimbazi and Kizinga rivers was not safe for human use, particularly during the wet season.

However, the residue levels found in the present study were generally lower than those previously reported for other Tanzania water bodies (Mmochi & Mberek 1998) and were much lower than those determined from surface waters in India (Nayak *et al.*1995).

The average residue concentrations in water in both seasons were below the USA acute criteria for protection of aquatic life (Table 3). The levels were also below the Quebec acute criterion of DDT and its metabolites (1.1 μgl^{-1}) for protection of aquatic life (MacDonald 1994). However, the wet season concentration of dieldrin at Kurasini was comparable to the USA dieldrin acute criterion for protection of aquatic life. All the wet season average concentrations of total DDT, dieldrin, and the dry season average concentration of total DDT in Msimbazi exceeded the USA chronic criteria as well as the recommended concentration of unfiltered sample of Ontario jurisdictions for protection of aquatic life.

The γ-HCH levels in Kizinga river, during the wet season, were lower than the USA set levels for chronic toxicity but higher than the Ontario recommended levels for unfiltered samples. The average levels of DDT, dieldrin and γ-HCH from the present study were above the criteria for protection of aquatic life (DDT; 0.004 μgl^{-1}, dieldrin and γ-HCH; 0.01 μgl^{-1}), based on the Canadian guidelines (MacDonald 1994). Therefore, the levels of pesticides found in the present study indicate no acute effects to aquatic organisms. However, the levels of total DDT and dieldrin during wet season show the possibility of causing long term effects to aquatic biota.

Table 3: Comparison of water from water in Msimbazi and Kizinga rivers (Dar es Salaam, Tanzania) residue levels with the water quality criteria and guidelines for the protection of aquatic life (Macdonald 1994)

	Average concentration of residues in μgl^{-1}					
	total- DDT		dieldrin		γ HCH	
Season	dry	wet	dry	wet	dry	wet
Present study						
Msimbazi river	0.3	0.5	BDL	0.8		
Marine waters					BDL	BDL
Kizinga river		0.1	BDL	0.3	BDL	BDL
	BDL					
	BDL	0.4	BDL	0.8	BDL	0.07
USA: acute	1.1		2.5		2	
chronic	0.001		0.001		0.08	
Ontario unfiltered sample	0.003		0.001		0.01	

BDL — Below Detection Limit

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APPENDIX 1: Organochlorine pesticide residues ($\mu g l^{-1}$) measured at the different sites

Dry Season results

	EARLY			LATE		
	DDT	DDE			DDT	DDE
TW1	0.13	0.08		TW2	BDL	0.16
JW1	0.39	0.09		JW2	0.1	0.2
SW1	0.28	0.08		SW2	BDL	0.12
FW1	BDL	BDL		FW2	BDL	BDL
HW1	BDL	BDL		HW2	BDL	BDL
KrW1	BDL	BDL		KrW2	BDL	BDL
MW1	BDL	BDL		MW2	BDL	BDL
KW1	BDL	BDL		KW2	BDL	BDL

Wet Season results

EARLY					LATE				
	DDT	DDE	dieldrin	γ–HCH		DDT	DDE	dieldrin	γ–HCH
TW3	0.19	0.43	0.67	BDL	TW4	0.1	0.45	0.49	BDL
JW3	0.25	0.20	0.54	BDL	JW4	0.33	0.45	1.02	BDL
SW3	0.21	0.22	1.24	BDL	SW4	0.11	0.18	0.59	BDL
FW3	BDL	0.18	0.34	BDL	FW4	0.1	0.08	0.24	BDL
HW3	BDL	0.08	0.21	BDL	HW4	BDL	0.05	0.22	BDL
KrW3	0.18	0.19	0.46	0.2	KrW4	0.22	0.17	2.49	BDL
MW3	0.22	0.15	0.42	BDL	MW4	0.22	0.18	0.52	BDL
KW3	0.20	0.4	0.4	BDL	KW4	0.1	0.2	0.45	BDL

BDL — Below detection limit

(**Sites**: TW — Tabata, JW — Jangwani, SW–Salender Bridge, FW —Ferry, HW — Harbour, KrW — Kurasini, MW — Mtoni, KW — Kizinga)