PESTICIDE RESIDUES IN WATER FROM TPC SUGARCANE PLANTATIONS AND ENVIRONS, KILIMANJARO REGION, TANZANIA

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ABSTRACT

We report herein, the analysis of water samples collected from TPC Sugarcane Plantation and its environs in Kilimanjaro region, which is the earliest intensive user of pesticides in Tanzania. A total of 50 water samples collected from 18 sampling sites between 2000 and 2001 were analyzed for pesticide residues. The organochlorines aldrin, dieldrin, heptachlor epoxide, HCHs, endosulfans and DDTs were detected with mean concentrations ranging from 1.1 to 636.7 ng/l. DDT and its metabolites were the most dominant in the detected residues whereas the endosulfans were the least dominant The residues' concentrations were higher in the sugarcane fields than in the environs, although the fresh use of banned pesticides was evident in samples collected from the plantation's environs. In most of the sites, samples had higher concentrations and frequencies during the dry season than the rainy season. It is worth noting that the water from the rivers in the immediate environs of the plantation, which are also used for domestic purposes, had residue levels below the WHO recommended maximum residue levels for drinking water with the exception of River Kikavu.

INTRODUCTION

The Tanganyika Planting Company (TPC) sugarcane estate in Kilimanjaro has an over 50 year-history of pesticide usage. TPC was established in 1930 initially as a sisal estate, which was converted into sugar estate in 1932. A devastating outbreak of insect pests at the estate since the early 1940s necessitated the use of chemical pesticides to reduce crop yields. Analysis of the yield data from TPC indicated losses of up to 25% during periods of intense pest infestations (TPC 2002). Pesticides such as the organochlorines, organophosphorous, carbamates, pyrethrins and others were intensively used over the years. Consequently, there rose a concern over the environmental quality of the estate and its immediate environs. The objectives of the present study were therefore to investigate on the occurrence, types and concentrations of pesticide residues, as well as their seasonal variations in the TPC estate and its immediate environs.

MATERIALS AND METHODS

Sampling Sites

The TPC sugarcane estate is located in the Northern part of Tanzania, about 50 km to the south of Mount Kilimanjaro, and 20 km from Moshi Municipality, at Arusha Chini wetlands and Kahe plains. TPC is not just an estate and a factory; it is a small town of its own, with a population of about 50000 people. The estate covers an area of about 14000 ha of cultivated land, surrounded by nice villages namely Chekereni, Kiyungi, Kikavu, Newland, Mtakuja, Mserekia, "Msitu wa Tembo", Samanga and Mikocheni. There are also five camps where workers and their families live. Figure 1 gives the layout of the plantation and its immediate environs.

Water samples were collected from 18 different sampling sites. With the exception of three sites, each site was sampled both during the dry and the wet seasons. Sampling sites were grouped into two, those within the estate itself, and those in its immediate environs. Estate samples were

collected from the three major drains collecting excess waters from the estate, namely Donga A, Donga B and Drains 6C. One stream, at A1 sugarcane plot and another at Samanga, which collects water from the three drains before discharging it into river Pangani, were also sampled. Samples from the environs were collected from the upper environs of the estate: the four rivers flowing around the plantations, namely rivers Weruweru, Karanga, Kikavu and Kikuletwa and from "Msitu wa Tembo" stream. Tap water for community supply was also sampled.

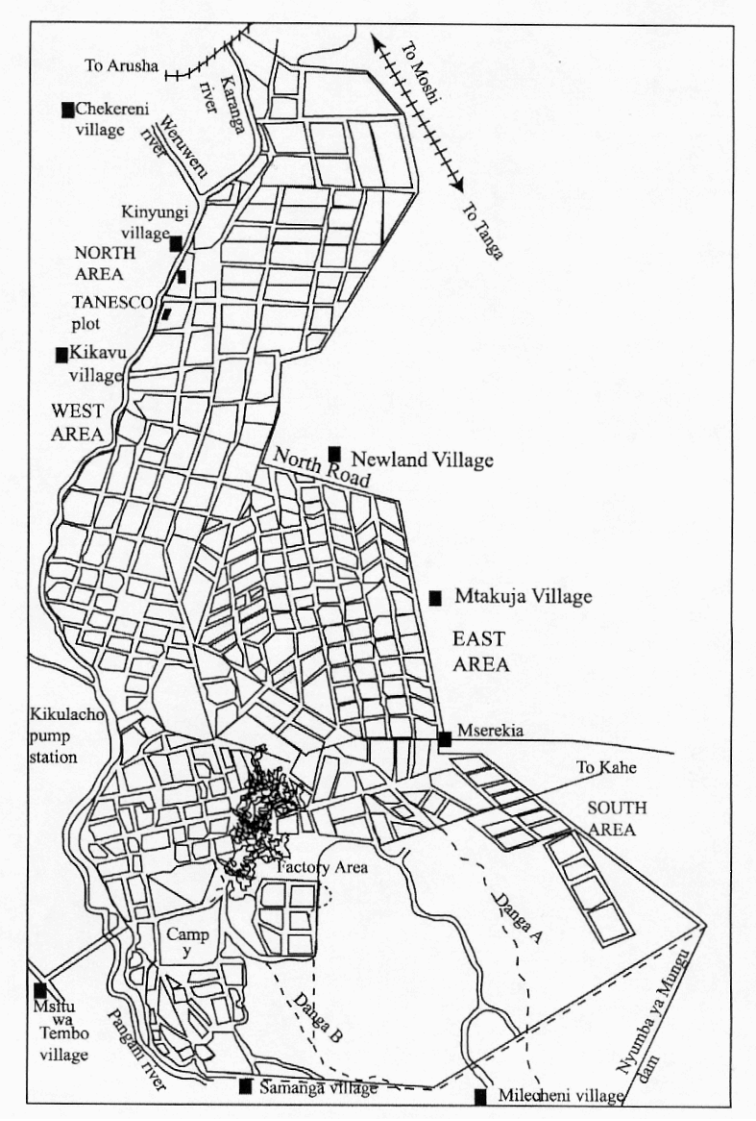

Figure 1: Map of TPC Estate and its immediate environs

Sample Collection
The sampling was done using standard methods as described by Åkerblom (1995). Samples were taken in duplicate. The first set was taken for on site determination of some physico-chemical parameters, namely temperature, conductivity, pH and TDS (Total Dissolved Solids). The second set was collected for pesticide residue analysis.

MATERIALS
All glassware used had teflon-stoppers. All the reagents used were of analytical grade whereas all solvents used were of chromatographic grade. Eighty (80) different pesticide standards ordered from Dr. Ehrenstorfer GmbH (Ausburg, Germany) were used. Working standard solutions were made by diluting the stock standards. Mixtures of standards of different concentrations were used in most cases for the screening of the pesticide residues.

Sample Preparation and analysis
Extraction and clean up of water samples
Unfiltered water samples, previously preserved with 10% NaCl, were extracted by Liquid-Liquid Extraction (LLE) method (Åkerblom 1995). Each sample (1 l) was quantitatively transferred to a one litre-separating funnel and the bottle rinsed with dichloromethane (30 ml), and combined with the sample in the separating funnel. The combined contents were then successively extracted with dichloromethane (3 x 50 ml). The organic layer was filtered through a plug of glass wool containing anhydrous sodium sulphate (*ca* 30g) for drying. The sodium sulphate was later rinsed with dichloromethane (2 x 3 ml), the combined extract concentrated *in vacuo* at 30 ^{o}C, and the solvent changed to cyclohexane. The volume was adjusted in a stream of air to 2 ml in 9:1 cyclohexane: acetone (v/v) ready for GC analysis. The water extracts appeared clean and were not subjected to further clean up. However, on injection into GC, the peaks for dieldrin and *p,p'*-DDE in the SE 30 column may overlap, and hence to remove any ambiguity, sulphuric acid treatment was employed to destroy dieldrin (Åkerblom 1995).

Analysis and quantification
Analysis of the residues was done as described by Åkerblom (1995). Varian Star 3400 and Hewlett Packard 5890A gas chromatographs equipped with ^{63}Ni Electron Capture, (EC) and Nitrogen-Phophorous, (NP) detectors were used for analysis. Non-polar (SE-30) and semi-polar (OV-1701) capillary columns of dimensions 30 m x 0.32 mm x 0.25 mm were used. Nitrogen was used as both a carrier and make up gas in the ECD at a flow rate of 30 ± 1ml/min. In the NPD, helium was used as a carrier gas at a flow rate of 0.5-1 ml/min and nitrogen at a flow rate of 29 ± 1 ml/min was used as a make up gas. The temperature programme was 90 ^{o}C held for 1 min, 30 ^{o}C/min to 180 ^{o}C, 4 ^{o}C/min to 260 ^{o}C held for 12 min. The injector and detector temperatures were 250 ^{o}C and 300 ^{o}C, respectively.) Identification of residues was effected by running samples and external reference standards in GC and then comparing the chromatograms. A peak was not considered relevant unless it appeared in both columns in a given detector. Representative samples were analysed on a GC-MS for confirmation of the results.

Blanks and recoveries
Blanks and recovery experiments were done using standard methods (Åkerblom 1995) and the recoveries of the detected pesticides ranged between 70-120 % and hence needing no correction to recoveries. Table 1 gives the method detection limits for the detected pesticide residues.

RESULTS AND DISCUSSION
The physico-chemical parameters measured in each sampling site for the two seasons are shown in Table 2. Three of the sites, namely Samanga A, Samanga B and Drain 6C were sampled during the dry season only because they were inaccessible during the rainy season. As expected temperature and pH were generally higher during the dry season

whereas, the reverse was observed for conductivity and TDS.

Table 1: Method detection limits of the detected pesticides/metabolites (ng/L)

Pesticide/metabolite	Detection limit	Pesticide/metabolite	Detection limit
α–HCH	0.1	*p,p'*-DDD	0.2
β–HCH	0.2	*p,p'*-DDE	0.3
γ–HCH	0.2	o,p'-DDT	0.3
δ–HCH	0.3	*p,p'*-DDT	0.3
Aldrin	0.1	Endosulfan-α	0.2
Diedrin	0.2	Endosulfan-β	0.2
Heptachlor epoxide	0.2	Endosulfan sulphate	0.3

Table 2: Physico-chemical parameters

Site	pH		Temperature (^{0}C)		Conductivity (ms/cm)		TDS (g/l)	
	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry
Stream G1	5.60	6.55	26.2	26.8	0.62	0.24	0.10	0.12
Donga A	6.42	7.81	24.5	26.1	0.41	0.72	0.50	0.37
Donga B	6.45	7.33	25.0	28.3	0.43	1.00	0.30	0.50
Drain 6C	-	7.74	-	33.6	-	1.00	-	0.50
River Weruweru	7.32	6.71	23.4	23.7	0.68	0.52	0.43	0.26
River Kikuletwa	7.49	8.01	22.6	23.4	0.59	0.52	0.24	0.26
River Karanga	7.18	7.22	20.5	21.0	0.31	0.22	0.51	0.10
River Kikavu	7.20	7.49	22.0	22.2	0.22	0.16	0.04	0.07
Samanga A	-	7.40	-	32.6	-	0.56	-	0.27
Samanga B	-	7.40	-	32.8	-	0.56	-	0.27
Tap water	7.10	6.95	24.0	27.7	0.20	0.07	0.09	0.07
Drinking water	7.12	6.90	23.9	25.6	0.18	0.06	0.01	0.05
Msitu wa Tembo	7.90	8.06	23.2	24.3	0.42	0.76	0.34	0.38

Levels of pesticide residues detected

A total of 14 different types of pesticide residues and metabolites were detected in varying concentrations during both the rainy and the dry seasons. They are the HCH-isomers (α, β, g, and δ), DDT together with its metabolites (*p,p'*-DDE and *p,p'*-DDD), aldrin, heptachlor epoxide, dieldrin, endosulfan-a, endosulfan-b and endosulfan sulphate. Figures 1 and 2 summarize the mean concentrations of the detected residues in each site for the two seasons. All of the detected residues and metabolites were of organochlorine insecticides. This is most probably due to the persistent nature of this class of insecticides compared to the other classes (Buchel 1983). No residues from the other classes of insecticides used at the estate such as organophosphorous and pyrethroid pesticides were detected in the samples. These classes of pesticides are degraded rather rapidly, and their residues are relatively short-lived (Cremlyn, 1979).

HCH residues

The HCH isomers, namely α-HCH, β-HCH, γ-HCH and δ-HCH were detected in samples from most of the sites in both seasons, with the b- isomer being by far the most abundant. Occurrence of higher levels of β-HCH as compared to other isomers is a clear indication of the use of technical HCH, which contains only 10 - 15% of the pesticidal isomer, g-HCH, commonly

known as lindane (Takeoka *et. al* 1991). The detection of δ-HCH, which is the least persistent of the HCH isomers and thus seldom found in environmental samples, strengthens the evidence that technical HCH must have been used just before sampling, at least in the environs. Technical HCH is banned in Tanzania (TPRI 2002).

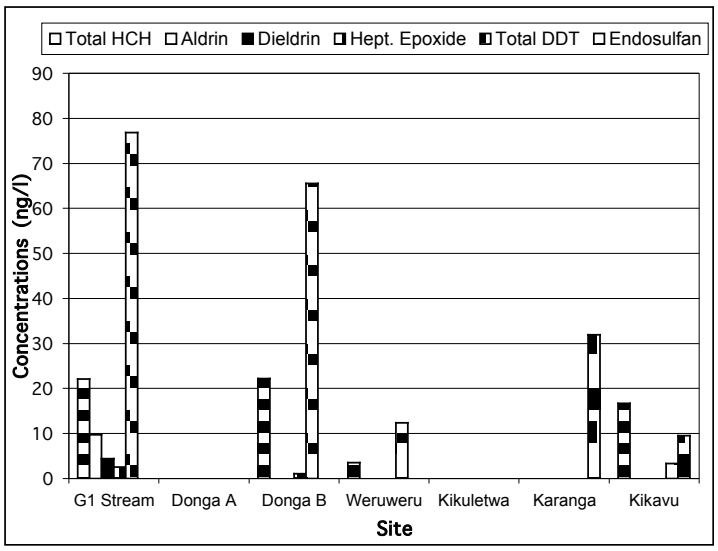

Figure 2: Pesticide residue concentrations in rainy season samples

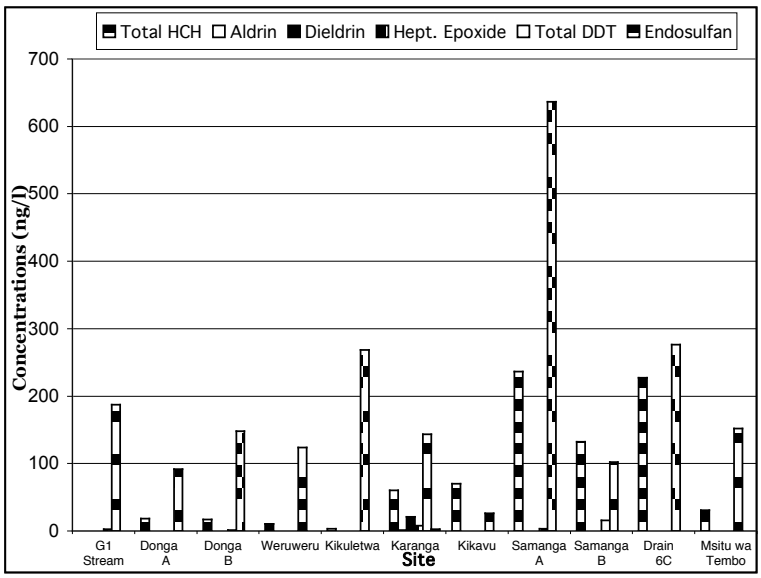

Figure 3: Pesticide residue concentrations in dry season samples

Total HCH concentrations were highest (236.4 ng/l) at Samanga stream. This stream collects water from the Donga A, Donga B and Drain 6C, the three collective drains

carrying excess water from the sugarcane plantation. Drain 6C had 227 ng/l of total HCH during the dry season, whereas Donga A had 18.3 ng/l detected during the dry season only, and Donga B had 22.2 and 17.1 ng/l during the rainy and the dry seasons, respectively. Tap-water from the estate community supply as well as borehole drinking water were also sampled and analyzed for pesticide residues. However, the samples had no detectable pesticide residues. HCH which concentrations detected in this study were all below the WHO (1984) recommended MRL (Maximum Residue Level) for HCH is 300 ng/l. These levels are also all well below those found at Vikuge, Coast Region (Mihale and Kishimba 2004, Elfvendahl et al. 2004, Marco 2004), in Southern Lake Victoria and its basis (Henry and Kishimba 2003) and those found in Cheju-Mapopwe and Mahonda-Makoba drainage basins, Zanzibar (Kishimba et al. 2004, Mmochi 2005). These levels are too low to be of any concern environmentally.

HCHs have been detected in surface and drinking waters, industrial effluents and sewage in many parts of the world (Kurtz 1990). HCHs are slightly soluble in water (0.007g/l), and volatilize into the atmosphere, thus persist in the environment. The US EPA (1989) declared HCHs as persistent, bio-accumulative and toxic chemicals. The relatively high volatility of HCH has led to global transport, even into formally pristine locations such as the Arctic Circle (Kurtz 1990).

DDT residues

DDT and its metabolites, *p,p'*-DDE and *p,p'*-DDD, were the most frequently detected residue. DDT and/or at least one of its metabolites were detected in 74% of the samples in significant concentrations, despite the claim that DDT has not been used in this area for the past two decades (TPC, 2000). Total DDT (∑DDT, which is, the sum of *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT) ranged between 6.5 ng/l and 636.7 ng/l. The highest concentration of total DDT was found in Samanga A. The lowest level of total DDT was found in river Kikavu. Generally, samples from within the plantations, such as G1 plot, Donga B, Samanga A and B and Drain 6C had higher levels of DDTs than those taken from the rivers in the environs. In all the water samples analyzed the DDTs concentrations were lower than the recommended WHO (1989) guidelines value for DDT and metabolites in drinking water of 1mg/l. Among the DDT's, *p,p'*-DDT was the most dominant, a clear indication that DDT has recently been used in the environs.

The DDT levels in river waters from the TPC environs obtained in the present study are higher than those reported in other studies conducted in other parts of Tanzania, such as Arusha (A'Khabuhaya and Lodenius 1988), Zanzibar (Mmochi 2005), Dar es Salaam (Mwevura et al. 2002), Southern Lake Victoria and its basin (Henry and Kishimba 2003) and Vikuge, Coast region (Mihale and Kishimba 2003). This might be due to the intensity of agricultural activities associated with the pesticide use as well as pesticides application history among these areas. After all TPC is the oldest intensive user of pesticides in the country.

Heptacholor residues

Heptacholor epoxide residues were detected in samples from Plot G1, Donga B, Samanga and River Karanga with concentrations ranging from 1.1 - 15.8ng/l. The highest levels of heptachlor epoxide, 15.8 and 15.6ng/l, were detected in river Karanga and drain Samanga B, respectively. According to WHO (1989) practically all heptachlor is transformed through both biotic and abiotic processes to heptachlor-epoxide. Consequently, heptachlor is rarely found in environmental samples. In agreement with this observation, only heptachlor epoxide was found in 10% of the water samples, whereas heptachlor was not detected. The US EPA Maximum Contaminant Level (MCL) for heptachlor epoxide in water is 200ng/l (US EPA 1986).

Heptacholor residues have never been found in environmental samples collected from Tanzania.

Endosulfan residues

Although endosulfan was for a long time used at TPC plantations, none of its residues were found in the plantation samples. Relatively low concentrations of endosulfan residues, consisting of endosulfan-a, endosulfan-b and endosulfan sulphate were detected in samples from the environs only. These were River Karanga, whose samples had 31.0 ng/l of total endosulfan during the rainy season, and 5.1ng/l during the dry season. The other site was River Kikavu, whose samples had 18.9 ng/l of total endosulfan detected during the rainy season only. This implies the possibility that the residues were from run-offs. Endosulfan was the least detected pesticide among all. It is also interesting to note that this compound has the shortest half-life compared to the other detected pesticides, and therefore is the least persistent among the list. This probably is the reason behind its non-detection in samples from the plantations where its use has been discontinued.

Aldrin and dieldrin residues

Aldrin and dieldrin were both detected in samples from two sites only. During the rainy season, both aldrin and dieldrin at the levels of 9.7 and 4.4 ng/l, respectively were detected in G1 plot samples. The presence of dieldrin at this site may be due to the degradation of aldrin. However both were not detected in this site again during the dry season. Instead, 1.1 and 20.9 ng/l of aldrin and dieldrin respectively were detected in river Karanga, which drains the upper environs of the sugar estate. This is a clear indication that these banned pesticides are no longer used in the plantations.

WHO (1989) recommended that the concentrations of aldrin and dieldrin in aquatic environments should be normally less than 10ng/l. Higher levels are attributed to contamination arising from industrial effluents and soil erosion from agricultural land. This is in agreement with the findings of the present study, because wherever detected, aldrin and dieldrin concentrations were below 10ng/l, except in samples from river Kikavu which had as high as 41.8ng/l of dieldrin. The WHO Guidelines for Drinking-water Quality recommends a health-based limit of 30 ng/l for aldrin and dieldrin residues, either separately or together. The WHO limits are based on toxicological data and they therefore consider pesticides individually as pesticides differ from one another on their toxicological properties (WHO 2000). This means that River Kikavu water is not safe for domestic use; and in case there are edible organisms in the river, the possibility of bio-concentration and bio-accumulation of DDTs in them to levels higher than WHO set MRLs cannot be ruled out.

Seasonal variations of levels of pesticide residues

Seasonal variation in the occurrence and concentration of pesticide residues in water were studied by comparing the detection frequencies and concentration levels of pesticides in samples collected from the same site for the two seasons. This was therefore done for only those sites that were sampled in both seasons. Table 3 compares the detection frequencies of all detected pesticides, whereas Figure 4 compares their mean concentrations between the two seasons.

The detection frequencies as well as the mean concentrations of most of the pesticides were higher during the dry season than the rainy season. This might be attributed to the fact that during the dry season the water content in the soil is low and therefore allows more pesticides to reach bare soil, whereas during rainfall, pesticides are washed out from the soil surface and taken away by the water flow.

Table 3: Seasonal variation in pesticide residues' detection frequencies

	Rainy Season (n=20)		Dry Season (n=20)	
Pesticide	**Detection frequency (%)**	**Mean conc. (ng/l)**	**Detection frequency (%)**	**Mean conc. (ng/l)**
HCH	40	9.6	70	23.1
Aldrin	20	1.0	20	0.2
Dieldrin	20	0.4	20	4.2
Heptachlor epoxide	20	0.5	10	1.6
DDTs	40	16.5	90	108.6
Endosulfans	20	5.0	10	0.5

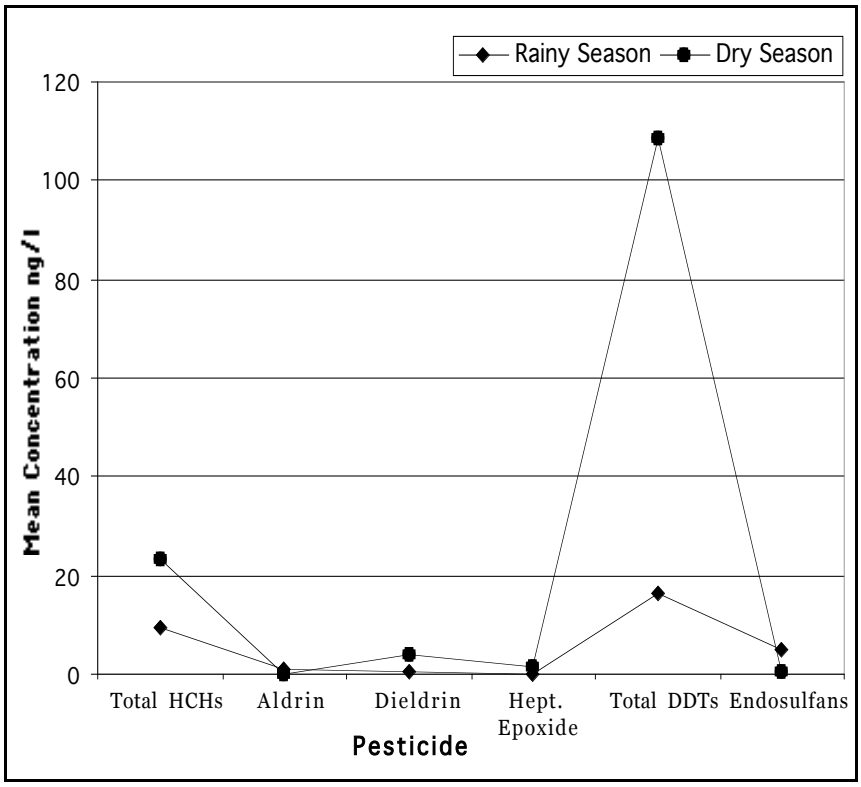

Figure 4: Seasonal variations in means concentrations of the detected residues

CONCLUSION

The levels of pesticide residues found in this study at TPC and its environs, although some are higher than those found in other parts of the country studied (Kishimba et al, 2004), are generally lower than those set by WHO and the US EPA, with the exception of river Kikavu. However, the fact that these chemicals still persist in the environment after a period of nearly two decades after cessation of use emphasizes the need to ensure that persistent organochlorines are no longer used in the country. The need to continually monitor the levels of these persistent eco-toxic environmental pollutants which bio-concentrate and bio-accumulate

can not be over emphasized . There is also a need to sensitize the farmers in the areas surrounding TPC estate against the illegal use of banned pesticides.

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