



Pesticide residues in four rivers running through an intensive agricultural area, Kilimanjaro, Tanzania

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ABSTRACT: Organochlorine pesticide (OCP) residues were determined in water and bottom-sediments from four rivers running through sugarcane plantations in Kilimanjaro Tanzania. The aim was to assess the levels of pesticide contamination as the rivers are important sources of domestic water in the area. Water samples were extracted by liquid–liquid extraction method, and ultrasonic-assisted liquid-solid extraction coupled with gel permeation chromatography was employed in sediment preparation, before analysis by GC-ECD and GC-MS. Blank and spiked recovery tests were used to validate the analytical procedure. Data were assessed by using descriptive statistics and multivariate analysis to study correlations between different parameters, evaluate the contamination patterns and describe their spatial and seasonal trends. The percentage recoveries ranged from 75.0 ± 2.4 to 89.8 ± 1.5 in water, and 70.5 ± 1.7 to 86.2 ± 2.3 in sediments, which are within the acceptable ranges. The OCP concentrations ranged from trace (endrin) to 120 ng/l (*p,p'*-DDD) in water, and from trace (aldrin) to 132 ng/g-dry weight (*p,p'*-DDD) in sediments, and were higher during the dry season. A notable water contamination that exceeded the European Union maximum acceptable concentration for the protection of human health was detected in river Kikavu. @ JASEM

Keywords: Pesticide residues, Surface water, Sediment, Environmental contamination

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Surface water contamination with pesticide residues, associated with decreased water quality and increased exposure of human and wildlife has been detected in lakes, rivers and streams in various locations, especially in areas with intense and prolonged pesticides applications (Zhou et al., 2006; Gao et al., 2008; Poolpak, 2008). Pesticides can reach surface waters through various pathways, including agricultural run-offs, spray drifts during applications, atmospheric fallout, direct spills and accidental discharge. Irrigation waters, which are frequently taken from surface water sources in agricultural areas, may also transfer contaminants from land to the water body (Zhang et al., 2002). The types and concentrations of pesticides found in surface waters can be affected by a number of factors including properties of the chemical, application history, season of the year, and physicochemical characteristics of the water and the underlying sediments (Carabias et. al., 2003).

Water and sediments play an important role in the distribution of contaminants in aquatic environments. While pesticide molecules can dissolve in water, a large proportion binds to suspended particles and settles at the bottom of the water body, producing contaminated sediments (Lalah et al., 2003). Some pesticides, particularly those with hydrophobic nature and low water solubility can be retained on the organic phase of sediments through sorption, and thus found in higher concentrations than those detected in the overlying waters (Zhou et al., 2006). The analysis of pesticide residues in sediments and water has therefore proved to be an important approach in assessing the fate of these contaminants in aquatic environments and contamination history of an area. While the analysis of water samples gives important information on the water quality and the detection of any potential risks, sediment analysis enables the detection of pollutants that could not be quantified by the water analysis.

The Kilimanjaro region, northern of Tanzania is one of the intensive agricultural areas in the country, owing to its rich volcanic soil from the slopes of Mount Kilimanjaro, with varieties of crops being produced in the region. The production of these crops has been enabled through heavy use of agrochemicals, particularly pesticides. This study therefore aims to assess the levels of pesticide contamination in four important rivers in the region. It seeks to determine the types of pesticide residues present, quantify their concentrations, establish their spatial and seasonal variation trends and evaluate the effects of different physicochemical parameters. The findings obtained can be used as baseline information on the water quality of the four rivers and establishment of its suitability for human consumption.

MATERIALS AND METHODS

Description of the study area: Sugarcane (*Saccharum officinarum*) is an important cash crop grown intensively in the plantations located in Arusha Chini wetlands and Kahe plains in the region. Operational since 1930s and covering about 14,000 ha of cultivated land with long growing season, the plantation is one of the oldest large scale users of pesticides in the country. Different types of pesticides, including organochlorines, organophosphorous and carbamates have been used in the plantations from the early 1940s. The organochlorines hexachlorocyclohexane (HCH), endosulfan, DDT and others were extensively employed for the control of devastating sugarcane infesting insect pests such as white sugarcane scale (*Aulacaspis tegalensis*), white grub (*Cochliotus melolothoides*), stem borer (*Eldane sacchari*) and termites (*Pseudocanthotermes militaris*) since then till their countrywide ban in early 1980s.

Weruweru, Karanga, Kikavu and Kikuletwa are important rivers in Kilimanjaro and the other neighbouring regions. Apart from being used in agricultural and industrial activities, they are sources of domestic water supply for the about 1.5 million population of the region. Running close to the sugarcane plantations at some points, the rivers receive agricultural runoffs, effluents and agrochemical inputs.

Sampling and sample characterization: Eight sampling stations were selected in this study, two for each river, as indicated in Table 1 and Figure 1. A total of 16 water and 16 sediment samples were simultaneously collected from the same locations in two sampling campaigns; dry season and rainy season. Sample collection was done using standard methods as described by Åkerblom (1995). Water samples (1 L) were taken in duplicate, the first set was used for on site determination of physicochemical parameters; pH, temperature, electrical conductivity and total dissolved solids, and the second set for pesticide residue analysis. Samples for pesticide analysis were preserved with ~ 100 g of 10 % NaCl in 1 L glass teflon-stoppered sampling bottles. About 50 g of sediment samples were collected from each site, carefully wrapped in aluminium foils and stored in cold boxes. Water and sediment samples were immediately transferred to the laboratory of the Department of Chemistry, University of Dar es Salaam for preparation and analysis.

Sample preparation and extraction: Immediately upon arrival at the laboratory, 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 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 obtained extract was concentrated *in vacuo* at 30 °C, and the solvent changed to cyclohexane. The water extracts appeared clean and were not subjected to further clean up. The volume was adjusted in a stream of air to 2 ml in 9:1 cyclohexane: acetone (v/v) ready for GC analysis. Sediments samples, previously stored at -18 °C were extracted by the Liquid-Solid Extraction (LSE) method using a mixture of cyclohexane and acetone 1:1 v/v. Homogenized 10 g sample portions were crushed, mixed with anhydrous sodium sulphate and ground with a mortar and pestle to a free flowing powder. The samples were then soaked in 100 ml of the extracting solvent in a conical flask for 30 min, passed through an ultrasonic bath (50–60 KHz) for 30 min and manually shaken for 30 min. Sodium sulphate (*ca.* 10 g) was then added to remove trace amount of water in the extracts. Sediment sample extracts were cleaned-up by gel permeation chromatography (Åkerblom 1995),

followed by concentrating to 2 ml in cyclohexane/acetone (9:1 v/v) using a vacuum rotary evaporator at 30 °C and stored in teflon-stoppered glass sample vials at 4 °C awaiting GC analysis. For determination of water content, the sediment samples were oven-dried (*ca.* 5 g of the sample) at 105 °C for 12 h to constant weight and measuring the change in weight after cooling to room temperature. Organic matter content was estimated by the calcination method, whereby the previously oven dried samples were dry-ashed at 550 °C for 12 h in a furnace, cooled to room temperature and re-weighed to determine the loss-on-ignition. The percentage weight loss was then equated to the percentage of organic matter content in the sample.

Table 1: Sampling sites

Site code	Site name
S1	Karanga 1
S2	Karanga 2
S3	Weruweru 1
S4	Weruweru 2
S5	Kikavu 1
S6	Kikavu 2
S7	Kikuletwa 1
S8	Kikuletwa 2

Table 2. Physicochemical parameters of water and sediment samples from the four rivers

Parameter	River Karanga	River Weruweru	River Kikavu	River Kikuletwa
<i>Water</i>				
pH	7.2 ± 0.1	6.9 ± 0.3	7.3 ± 0.2	8.1 ± 0.5
Temperature (°C)	20.5 ± 0.5	23.4 ± 0.4	22.0 ± 0.2	22.6 ± 0.8
Conductivity (µS/cm)	275 ± 59	600 ± 84	190 ± 35	555 ± 41
TDS (mg/L)	265 ± 92	350 ± 49	70 ± 35	252 ± 7
<i>Sediment</i>				
Water content (%)	21.1 ± 1.2	18.5 ± 0.5	23.5 ± 0.6	29.3 ± 1.5
Organic matter (%)	17.2 ± 1.4	12.3 ± 2.1	15.4 ± 1.7	8.3 ± 0.9
Temperature (°C)	20.0 ± 0.5	23.0 ± 0.2	21.5 ± 0.4	22.0 ± 0.6

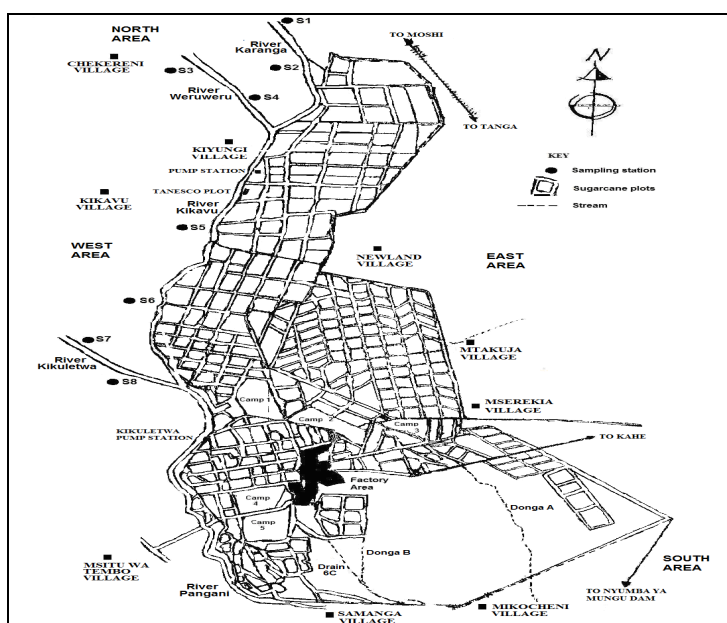


Figure 1: Map of TPC sugarcane plantations showing the sampling stations

Sample analysis: The sample extracts were analyzed by a Varian Star 3400 gas chromatography equipped with ⁶³Ni electron capture detector (ECD) at the Department of Chemistry, University of Dar es Salaam, Tanzania. Non-polar (SE-30) and semi-polar

(OV-1701) capillary columns of dimensions 30 m x 0.32 mm x 0.25 µm liquid thickness were used. Nitrogen was used as both a carrier and make up gas, flowing at the rate of 30 ± 1 ml/min. The injector and detector temperatures were set at 250 °C and 300 °C, respectively. The column temperature was initially set

at 90 °C, held for 1 min and then raised to 180 °C at the rate of 30 °C/ min. It was further raised to 260 °C at the rate of 4 °C/ min and maintained at this temperature for 12 min.

Pesticide residues were identified and quantified by using external reference standards. Retention times and peak heights of the detected residues were compared to those of the pesticide references standards. Parathion was used as an internal reference standard for the determination of compounds' relative retention times (RRT). Identified peaks were confirmed by analyzing the same sample extracts by a Hewlett Packard model 5890 GC-MS with CP-Sil 19 CB and CP-Sil 5 CB columns, 20 m x 0.32 mm i.d. x 0.25 µm liquid thickness (Chrompack Sverige AB, Nacka Sweden), at the Department of Environmental Assessment, SUAS, Sweden. Helium was used as a carrier gas at 1.9 ml/min. Hydrogen and air were flowing at 120 and 100 ml/min, respectively. The injector and detector temperatures were set at 270 °C and 300 °C, respectively. The column temperature was initially set at 70 °C, held for 1 min and then raised to 230 °C at the rate of 30 °C/ min. It was further raised to 280 °C at the rate of 4 °C/ min and maintained at this temperature for 10 min.

Quality control and quality assurance: All reagents used were of analytical grade, and the solvents were of chromatographic grade. Pesticide standards solutions (99% certified purity) were ordered from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Sodium chloride and anhydrous sodium sulphate were heated at about 400 °C for two hours and allowed to cool to

constant temperature in desiccators to remove interfering substances before use. Glassware used had Teflon caps, where needed, and were cleaned with detergents and distilled water, thoroughly rinsed with acetone and dried overnight in an oven before use.

The method detection limits (MDLs) of the organochlorines were determined as the concentrations of analytes in a sample that gives rise to a peak with a signal-to-noise ratio (S/N) of 3. Deionized water and laboratory-grade sediment spiked with target compounds were used for evaluation of the detection limits for the samples. Blank tests were conducted to check for interference and cross-contamination (Hill, 2000). For every batch of water and sediment samples analysed, 2 blank and 2 recovery test samples were simultaneously analysed. The method validation was done by spiking blank samples with mixtures of organochlorine pesticide standard solutions of known concentrations (50–300 ng/l), that were extracted, cleaned-up and analysed as the ordinary samples. The percentage recoveries were calculated as the ratio of the actual concentrations obtained after GC analysis to the added (spiked) concentrations.

Statistical analysis: Mean concentrations of pesticide residues in the samples were calculated using a statistical package INSTANT[®]. Multiple comparison with one way ANOVA were used to test the significance differences of pesticide concentrations among the sampling sites and across the two seasons ($\alpha=0.05$).

Table 3. Mean percentage recoveries and detection limits of the analyzed organochlorines

Pesticide	Water samples		Sediment samples	
	% Mean recovery \pm SD (n = 4; CL 95%)	MDL (ng/l)	% Mean recovery \pm SD (n = 4; CL 95%)	MDL (ng/g – d.w)
α -HCH	81.5 \pm 0.7	0.2	72.3 \pm 0.7	0.4
β -HCH	78.0 \pm 0.9	0.1	68.5 \pm 1.9	0.3
γ -HCH	80.5 \pm 1.8	0.2	77.5 \pm 0.6	0.2
δ -HCH	75.0 \pm 2.4	0.3	72.4 \pm 1.2	0.5
Aldrin	77.3 \pm 2.6	0.1	73.2 \pm 1.4	0.3
Heptachlor	74.9 \pm 2.2	0.3	70.8 \pm 0.9	0.2
Heptachlor epoxide	78.8 \pm 2.3	0.3	76.7 \pm 1.3	0.3
Dieldrin	79.2 \pm 1.5	0.4	70.5 \pm 1.7	0.6
Endosulfan- α	80.1 \pm 2.5	0.2	76.3 \pm 1.4	0.3
Endosulfan- β	82.5 \pm 1.4	0.2	80.7 \pm 0.5	0.3
Endosulfan sulphate	81.6 \pm 0.9	0.3	78.1 \pm 1.9	0.5
<i>p,p'</i> -DDE	88.3 \pm 1.0	0.3	85.4 \pm 1.2	0.4
<i>p,p'</i> -DDD	87.2 \pm 2.7	0.2	84.6 \pm 1.5	0.3
<i>p,p'</i> -DDT	89.8 \pm 1.5	0.2	86.2 \pm 2.3	0.2

RESULTS AND DISCUSSIONS

Physicochemical characteristics of the samples: The water quality parameters and the sediment characteristics are summarized in Table 2. The water samples were near neutral to slightly alkaline, with pH values ranging from 6.9 to 8.1. These values are within the acceptable range for natural river water (Chapman & Kimstach 1996), and were within the WHO maximum permissible limits of 6.5 – 9.2 for

portable water (WHO, 1988). The pH values were lower during the rain season than during the dry season. This slight decrease in pH during the rain season may be attributed to the rise in water table during rainfalls which in turn may increase the H⁺ concentration. Water temperatures ranged between 20.5 - 23.4 °C, and were generally higher during the dry season than the rainy season, reflecting the climatic condition of the area. Electrical conductivity

ranged between 190 – 600 $\mu\text{S}/\text{cm}$. Normally, the electrical conductivity of natural waters is found to vary between 50 – 1500 $\mu\text{S}/\text{cm}$ (Bartram & Balance, 1996) whereas the WHO maximum permissible value for portable water is 2500 $\mu\text{S}/\text{cm}$. The total dissolved solids (TDS) in river water ranged between 70 – 350 mg/L, which is within the normal range for natural river water of 0 – 1000 mg/L (WHO, 1988). The spatial distribution of TDS followed exactly the same trend as that of electrical conductivity. This is expected due to the fact that conductivity is directly related to dissolve solids.

Sediment temperatures (Table 2) reflected a similar trend as those of the water samples, but were slightly lower than the water temperature. Water contents in the sediment samples ranged between $18.5 \pm 0.5\%$ to $29.3 \pm 1.5\%$. The organic matter contents ranged from 8.3 ± 0.9 to 17.2 ± 1.4 , and were at the highest in river Karanga. The study of these parameters is important due to their implications in contaminants availability. Organic matter present in sediments constitutes a minor but important fraction of sediments (Page, 2003) since it influences sediment structure (particles layout) which in turn determines the amount and strength of

pollutants binding to the sediments. Organic contaminants, such as the organochlorine pesticide residues, preferentially partition to organic matter in sediment. In agreement with this, the total DDT concentrations in this study were positively correlated to the organic matter content of the sediments as illustrated in Figure 2.

Spiked recoveries and blank tests: The mean percentage recoveries of spiked water and sediment samples, as well as the detection limits of the quantified pesticide are summarized in Table 3. The obtained data indicate the recovery ranges of 74.9 ± 2.2 to $89.8 \pm 1.5\%$ and 70.8 ± 0.9 to $86.2 \pm 2.3\%$ in water and sediments, respectively. These values were within the normal acceptable ranges of 70 – 120 % (Åkerblom 1995). Recovery values were higher in water samples than the sediment samples for all compounds. This may be attributed to the interferences from organic matter and other compounds that are found more in the sediments than the water samples. The blank reference samples had no traces of the targeted analytes, and thus confirming the practicability of the analytical protocols employed in the determination of the pesticide residues

Table 4 Concentration ranges (ng/l) of pesticide residues in water samples during the two seasons

Pesticide	Sampling sites							
	River Karanga		River Kikavu		River Weruweru		River Kikuletwa	
	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
α -HCH	9.5 – 28.3	Bdl – 4.2	4.2 – 24.7	Bdl – 8.5	Bdl – 2.4	Bdl – 6.9	Bdl	Bdl
β -HCH	15.6 – 25.0	1.2 – 21.3	75.0 – 106.0	2.5 – 29.5	Bdl – 16.9	Bdl – 10.0	Bdl	Bdl
γ -HCH	Bdl – 1.9	Bdl	Bdl	Bdl – 3.8	Bdl – 4.3	Bdl	Bdl	Bdl
δ -HCH	Bdl	Bdl	Bdl – 2.3	Bdl	Bdl – 6.9	Bdl	Bdl	Bdl
\sum HCH	Bdl – 55.2	Bdl – 25.5	Bdl – 133	Bdl – 41.8	Bdl – 30.5	Bdl – 16.9	Bdl	Bdl
Aldrin	Bdl – 2.3	Bdl	Bdl – 10.2	Bdl	Bdl	Bdl	Bdl	Bdl
Dieldrin	Bdl	Bdl	Bdl – 41.8	Bdl	Bdl	Bdl	Bdl	Bdl
Endrin	Bdl	Bdl	Bdl – 3.0	Bdl	Bdl	Bdl	Bdl	Bdl
Endos- α	Bdl	Bdl – 10.0	Bdl	Bdl – 9.1	Bdl	Bdl	Bdl	Bdl
Endos- β	Bdl	Bdl – 9.5	Bdl	Bdl – 9.8	Bdl	Bdl	Bdl	Bdl
Endo. sulph	Bdl – 5.1	Bdl – 11.5	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
\sum Cyclod.	Bdl – 7.4	Bdl – 31.0	Bdl – 55.0	Bdl – 18.9	Bdl	Bdl	Bdl	Bdl
Hept.	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Hept. epox	Bdl	Bdl – 15.8	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
\sum Hept.	Bdl	Bdl – 15.8	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
p,p' -DDE	Bdl – 15.7	Bdl	Bdl – 75.7	Bdl – 22.4	Bdl – 1.9	Bdl	Bdl – 36.2	Bdl
p,p' -DDD	Bdl – 49.9	25 – 24.2	15.6 – 120.0	15.6 – 34.2	Bdl – 13.7	Bdl – 17.2	13.7 – 50.9	Bdl
p,p' -DDT	Bdl	Bdl – 35.7	14.0 – 22.4	Bdl – 11.3	Bdl – 24.9	Bdl – 7.7	Bdl – 36.1	Bdl
\sum DDTs	Bdl – 65.6	Bdl – 59.9	Bdl – 218	Bdl – 67.9	Bdl – 40.5	Bdl – 24.9	Bdl – 123.2	Bdl
\sum OCP	Bdl – 128.2	Bdl – 132.2	Bdl – 406.0	Bdl – 128.6	Bdl – 71.0	Bdl – 41.8	Bdl – 123.2	Bdl

Pesticide residues detected in water and sediments: A total of 14 organochlorine pesticide residues and metabolites were detected in the water and sediment samples in varying concentrations (Table 4 and 5). The detected residues were the hexachlorocyclohexanes (α -, β -, γ -, and δ - HCH isomers), the cyclodienes (aldrin, dieldrin, endrin, endosulphan- α , endosulphan- β and endosulphan-sulphate), heptachlor epoxide and DDTs (p,p' -DDE, p,p' -DDD, and p,p' -DDT). The presence of

organochlorine pesticides residues both dissolved in the surface water and sorbed onto sediments in this area can be envisaged to wide past applications in the nearby sugarcane plantations, their persistence nature and slow degradation. Analysis of agricultural effluents from the sugarcane plantations that are likely to be discharged into the rivers revealed the presence of the same organochlorine pesticide residues in concentrations ranging from 1.1 to 636.7 ng/l (Hellar and Kishimba, 2005).

Concentrations of hexachlorocyclohexane (Σ HCH) in the four rivers ranged from trace to 133 ng/l in the water samples, and from 9.7 to 57.1 ng/g-dw in the sediment samples.

Table 5. Concentration ranges (ng/g-dry weight) of pesticide residues in bottom-sediments from the four rivers during the two seasons

Compound	Sampling sites							
	River Karanga		River Kikavu		River Weruweru		River Kikuletwa	
	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
α -HCH	Bdl	Bdl	2.8 – 22.7	4.4 – 10.0	Bdl – 4.1	Bdl – 2.2	Bdl – 12.4	Bdl – 5.4
β -HCH	Bdl	Bdl	6.9 – 26.7	5.3 – 12.1	Bdl – 5.6	Bdl – 3.5	Bdl – 13.6	Bdl – 7.5
γ -HCH	Bdl	Bdl	1.2 – 4.6	Bdl	Bdl – 2.4	Bdl – 1.2	Bdl – 4.3	Bdl
δ -HCH	Bdl	Bdl	Bdl – 3.1	Bdl	Bdl	Bdl	Bdl	Bdl
$^a\Sigma$ HCH	Bdl	Bdl	10.9 – 57.1	9.7 – 22.1	Bdl – 12.1	Bdl – 6.9	Bdl – 30.3	Bdl – 12.9
Aldrin	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Dieldrin	Bdl	Bdl	Bdl – 46.8	Bdl	Bdl	Bdl	Bdl	Bdl
Endrin	Bdl	Bdl	Bdl – 12.5	Bdl	Bdl	Bdl	Bdl	Bdl
Endos- α	Bdl	Bdl	Bdl – 22.9	Bdl	Bdl	Bdl – 6.2	Bdl	Bdl
Endos- β	Bdl	Bdl	Bdl – 10.8	Bdl	Bdl	Bdl – 7.2	Bdl	Bdl
Endos sulph	Bdl	Bdl	Bdl – 16.7	Bdl	Bdl	Bdl	Bdl	Bdl
$^b\Sigma$ Cyclod.	Bdl	Bdl	Bdl – 110	Bdl	Bdl	Bdl – 13.4	Bdl	Bdl
Heptachlor	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Hept. epox	Bdl – 23.6	Bdl	Bdl – 32.7	Bdl	Bdl	Bdl	Bdl	Bdl
$^c\Sigma$ Hept.	Bdl – 23.6	Bdl	Bdl – 32.7	Bdl	Bdl	Bdl	Bdl	Bdl
p,p' -DDE	Bdl	Bdl	5.5 – 85.8	2.3 – 43.4	1.5 – 11.4	Bdl – 9.3	Bdl – 87.7	Bdl
p,p' -DDD	3.2 – 94.7	Bdl	12.3 – 132.0	7.6 – 53.6	2.4 – 73.2	Bdl	Bdl	Bdl – 5.2
p,p' -DDT	Bdl	Bdl	24.3 – 62.4	Bdl – 33.4	Bdl	Bdl	Bdl	Bdl
$^d\Sigma$ DDTs	3.2 – 94.7	Bdl	42.1 – 280.0	9.9 – 130.0	3.9 – 84.6	Bdl – 9.3	Bdl – 87.7	Bdl – 5.2
$^e\Sigma$ OCP	3.2 – 118.3	Bdl	10.9 – 480	19.6 – 152.5	7.8 – 96.7	Bdl – 29.6	Bdl – 118.0	Bdl – 18.1

Bdl = below the detection limit of this method;

^aFor summation all Bdl's were assigned values of zero

^a Σ HCH = α -HCH + β -HCH + γ -HCH + δ -HCH; ^b Σ Cyclodienes = Aldrin + Dieldrin + Endosulfan- α + Endosulfan- β + Endosulfan sulphate;

^c Σ Hept. = Heptachlor + Heptachlor epoxide; ^d Σ DDTs = p,p' -DDE + p,p' -DDD + p,p' -DDT; ^e Σ OCP = Σ HCH + Σ Cyclodienes + Σ DDTs;

Table 6. Comparison of the DDTs concentrations in this study and some sediment quality guidelines

	This study (μ g/kg-dw)	ISQG (μ g/kg-dw)	PLE (μ g/kg-dw)
DDT	< 0.2 – 62.4	1.19	4.77
DDE	< 0.4 – 87.7	1.42	6.75
DDD	< 0.3 – 132.0	3.54	8.51

The highest concentrations in both sample matrices were detected in river Kikavu, whereas water samples from river Kikuletwa were generally free of HCH residues. The low ratio of γ -HCH to α -HCH indicates a past usage of technical grade HCH, which consists principally of the four isomers, α -HCH (60–70%), β -HCH (5–12%), γ -HCH (10–15%) and δ -HCH (6–10%)

(Tomlin, 2000). Technical grade HCH has been intensively used as a broad spectrum insecticide in the sugarcane plantations since 1940s until it was banned all over the county in 1980s. HCH is slightly soluble in water (0.007 g/l) and volatilizes to the atmosphere where it can cause long-range contamination (Guzzella et al., 2005).

Table 7. Mean concentrations and standard deviations of the organochlorine pesticide residues in the four rivers during the two seasons

Water samples (ng/l)								
Site	Σ HCH		Σ DDT		Σ Heptachlor		Σ Cyclodienes	
	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
Karanga	20.1 \pm 26.7	3.3 \pm 7.4	10.9 \pm 20.1	14.2 \pm 16.0	Bdl	7.9 \pm 11.1	0.2 \pm 0.6	2.6 \pm 4.7
Kikavu	26.5 \pm 41.2	7.4 \pm 11.3	41.3 \pm 46.6	13.9 \pm 13.3	Bdl	Bdl	4.6 \pm 12.1	1.6 \pm 3.7
Weruweru	3.8 \pm 5.8	2.1 \pm 3.9	6.8 \pm 10.4	4.2 \pm 7.1	Bdl	Bdl	Bdl	Bdl
Kikuletwa	Bdl	Bdl	22.8 \pm 21	Bdl	Bdl	Bdl	Bdl	Bdl
Sediment samples (ng/g d.w)								
Karanga	Bdl	Bdl	16.3 \pm 38.4	Bdl	11.8 \pm 16.7	Bdl	Bdl	Bdl
Kikavu	8.5 \pm 10.3	3.9 \pm 4.9	53.7 \pm 49.3	23.4 \pm 23.0	16.4 \pm 23.1	Bdl	9.1 \pm 14.3	6.7 \pm 9.4
Weruweru	1.5 \pm 2.3	0.9 \pm 1.3	14.8 \pm 28.9	1.6 \pm 3.8	Bdl	Bdl	Bdl	Bdl
Kikuletwa	3.8 \pm 5.9	1.6 \pm 3.0	14.6 \pm 35.8	0.9 \pm 2.1	Bdl	Bdl	Bdl	Bdl

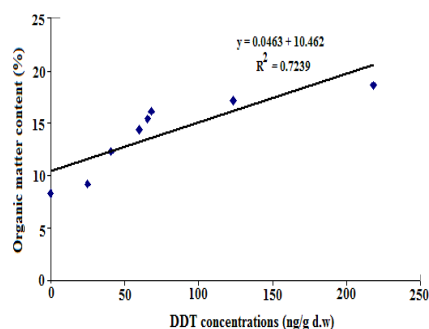


Figure 2: Relationship between DDT concentrations and organic matter content of the sediments

The β -isomer was the most dominant isomer, comprising more than 50% on average of the total HCHs in the analysed samples. These results were consistent with other findings which reported the dominance of β -HCH isomer in environmental samples (Concha-Grañ et al., 2006). This can be attributed to the fact that β -HCH has the lowest water solubility and vapour pressure among the HCH isomers, and relatively resistant to microbial degradation, consequently, it is the most stable HCH isomer in the environment. Furthermore, α -HCH is easily converted to β -HCH in the environment,

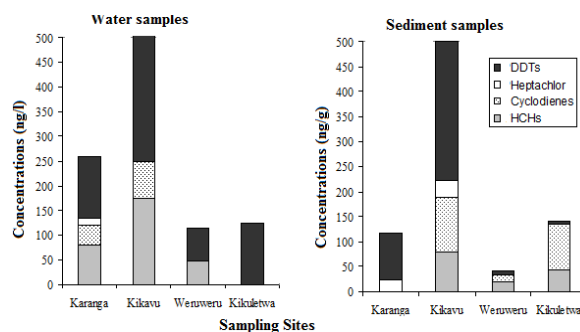


Fig 3: Concentration profiles of the detected OCPs in the four rivers. The OCP concentrations are the sum of the two sampling times.

increasing its concentration (Zhang et al., 2002). These concentrations were lower than those reported by Zhou et al (2006) in a study of surface water and sediments from a similarly intensive agricultural area of Qiantang River, East China, where the HCH residues ranged from 0.74 to 202.8 ng/l in water and 8.22 to 152.1 ng/g-dry weight in sediments, and γ -HCH was the most dominant isomer among the HCHs. However, HCH residues in the Qiantang River were associated with a more recent use of lindane, which is almost pure γ -HCH (Zhou et al., 2006)

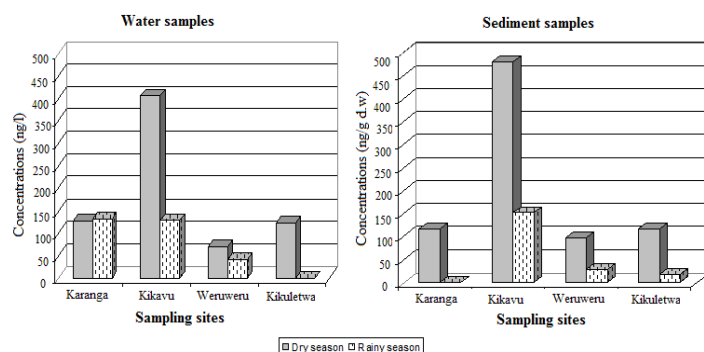


Figure 4: Concentrations of the total OCPs in the four rivers during the two seasons

When comparing the HCH residues concentrations in the four rivers investigated, with results from other African rivers, it was observed that the residue levels reported in this study are lower than those recorded at the Eastern Cape, South Africa, where total HCH ranged from trace to 150 ng/l in river water (Awofolu1 & Fatoki, 2003); but they are higher than those reported in the Ouémé River catchment that drains the largest part of the Bénin's cotton belt, which ranged from < 0.1 to 61 ng/l (Pazou et al., 2006). These differences may be due to the different application history and sources of OCPs in the areas, and other environmental factors such as climatic conditions. HCHs concentrations reported in this study are well below the US EPA and WHO guidelines. The US EPA recommends a maximum contaminant level (MCL) of 200 ng/l for individual HCH isomers in drinking water (US EPA, 1998); and

WHO recommends a maximum residual level (MRL) of 300 ng/l (WHO, 2006).

Endrin and dieldrin were detected in measurable concentrations in both water and sediment samples from river Kikavu. The relatively higher concentrations of the two compounds in the sediment samples may be attributed to the fact that both endrin and dieldrin are not very soluble in water and therefore more likely to adsorb in sediments (Konstantinou et al., 2006). Aldrin was detected in water samples from rivers Karanga and Kikavu (2.3 – 10.2 ng/l), and was below the detection limit in water samples from the rest of the stations. It was not detected in any of the sediment samples. Measured concentrations are all below the WHO guidelines for drinking-water quality that recommends a maximum of 30 ng/l for the compounds (WHO, 2006).

Heptachlor epoxide was not detected in any of the water samples, but in sediment samples from rivers Karanga and Kikavu (23.6 – 32.7 ng/g d.w). Heptachlor is normally transformed through both biotic and abiotic processes to heptachlor epoxide (Pandit et al., 2001), as a result it is rarely found in the environment. Endosulfan- α , endosulfan- β and endosulfan sulphate were detected with measurable concentrations in water samples from rivers Karanga and Kikavu, and in sediment samples from rivers Kikavu and Weruweru. The low detection frequencies of these compounds might be due to their relatively shorter half-lives compared to the other organochlorines. These concentrations were all below the US EPA standards for safe drinking water of 200 ng/l (US EPA, 1998).

DDTs were detected in more than 90% of the samples in both water and sediments from the four rivers investigated. Their concentrations ranged from trace to 120 ng/l; and from trace to 132 ng/g d.w in water and the sediment samples respectively, the highest concentrations in both matrices were detected at the River Kikavu. Detection of more of the degradation products (DDD and DDE) than the parent compound (DDT) indicates past usage of the DDT pesticide. DDT normally degrades under aerobic condition to DDE and under anaerobic condition to DDD, thus a higher DDE + DDD/ Σ DDT ratio is an indication past usage (Tadeo, 2008). DDT, a general term applied to a variety of commercial pesticide formulations that consist predominantly of *p,p'*-DDT and *o,p'*-DDT and minor amounts of DDE and DDD, was intensively used in the sugarcane plantations before their countrywide ban in 1980s. Residues of these compounds detected in the present study are attributed to this past usage. The use of DDT for agricultural purposes is still banned in Tanzania. The DDTs concentrations in sediments detected in some of the stations are higher than those recommended by the Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for the compounds in freshwater (CEQG, 1999), as shown in Table 6.

Spatial and seasonal variations of organochlorine pesticides residues: The highest OCP concentrations in both water and sediments were detected in river Kikavu, and the lowest levels were at river Kikuletwa. Of the four rivers investigated, sampling stations at River Kikavu (S5 and S6, Figure 1) were the closest to the sugarcane plantations, and thus might be receiving relatively more agricultural inputs from the plantations than the other three rivers. The concentration profiles of the total organochlorine pesticide residues are summarized in Figure 3. It can be observed that the DDTs comprised the highest percentages of the total OCP in all the stations, followed by HCHs, whereas heptachlor epoxide was

the least detected pesticide. Figure 4 illustrates the distribution of total OCPs residues in water and sediments from the four rivers during the two seasons. It clearly reveals a marked variation in the concentrations of the pesticide residues between the two seasons, which were generally higher during the dry season. Table 7 shows that there were large variations of OCP concentrations in the four rivers among the sampling seasons. Significant difference in concentrations of total OCP among the dry and the rainy seasons was observed when the comparison with one way ANOVA ($\alpha = 0.05$) was applied. The decreased concentrations of organochlorine pesticides during the rainy season may be ascribed to the dilution of the river waters brought about by large volume of rainy water added into the rivers during rainfalls. The increased water levels and flow rates during the rain season may tend to lower the concentrations of the chemicals in the water column. Pesticide residues sorbed on the sediments may also be diluted by runoff during the rainy season.

Conclusions: The results obtained in this study show that there still exist a variety of organochlorine pesticide residues in the surface waters and fluvial sediments in the four Kilimanjaro rivers, mostly due to the past applications in the sugarcane plantations. The pesticide residues concentrations detected in water samples were generally below the maximum acceptable concentration of 100 ng/l for individual pesticides set by the European Union (EU) for the protection of human health (EU, 1998). However, some elevated levels of β -HCH and *p,p'*-DDD that exceeded the limits were measured in River Kikavu. Concentrations of individual OCPs detected in the sediment samples did not exceed the maximum levels of the current Canadian sediment quality criteria for organochlorine pesticides in bottom sediments, except for DDTs levels in River Kikavu, suggesting unlikely biological adverse effects due to sediment contamination.

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