LEVELS OF PESTICIDE RESIDUES IN WATER, SOIL AND SEDIMENTS FROM SOUTHERN LAKE VICTORIA AND ITS BASIN

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ABSTRACT
Water, sediment and soil samples collected from Southern Lake Victoria and its basin were analysed for 76 organochlorine, organophosphorous, carbamate and pyrethroid pesticide residues. The samples were collected from sampling stations in nine districts on the Tanzanian side of the lake, namely Mwanza, Sengerema, Geita, Ngudu, Misungwi, Magu, Bunda, Tarime and Musoma Districts. DDT and HCH residues were the only detected pesticides. The concentration of total DDT was up to 1.6 mg/L in water, 600 mg/kg dry mass in sediments and 20 mg/kg dry mass in soil. The concentration of total HCHs were up to 0.2 mg/L in water, 132 mg/kg dry mass in sediments and 59 mg/kg dry mass in soil. Generally, higher levels of the residues were detected during the rainy seasons, than in the dry seasons. These levels are generally low indicating that in Southern Lake Victoria and its basin pesticide pollution has not reached alarming levels. However, the present study shows that despite being banned for use in agriculture in Tanzania since 1992, DDT was still being used in some of the districts at the basin. Worse still, technical HCH, which contains only 10 - 15% of the active isomer, lindane, was commonly used in the area in spite of its being de-registered many years ago.

INTRODUCTION
The use of pesticides in the southern Lake Victoria basin dates back to colonial era (Nyanda 2001). Organochlorines, carbamates, pyrethroids and organophosphorus are the major categories of pesticides used in the area (Anon 2001). These pesticides have been, and most are still used mainly in cotton fields and to a lesser extent in horticultural crops. Despite the fact that the use of pesticides in the region has been reduced in the past decade by over 50% due to removal of subsidies (Anon 2001), the status and extent of pollution of water, soil and sediments by pesticides in Southern Lake Victoria and its basin has remained unknown, despite the lingering suspicions that the lake may be heavily contaminated by these toxic chemicals. The present paper reports on an analysis of water, sediment and soil samples from the Southern Lake Victoria basin, to determine pesticide residue levels and their fate in the environment.

Earlier information on the types of pesticides used in the region revealed that, after the banning of DDT for use in agriculture in the early 1990s, pesticides currently used in cotton fields in the region were mainly pyrethroids such as cypermethrin, deltamethrin, cyfluthrin, cyhalothrin and Fenvalerate. Other pesticides included organochlorines like endosulfan; organophosphorous insecticides (dimethoate profenofos, diazinon and fenitrothion); carbamates (mancozeb, carbaryl and propineb); phenylamides (metalaxyl); and chloronitrites
(chlorothalonil) (Anon 2001). However, some other pesticides like HCH were used on horticultural crops but were not registered by the licensing authority (Anon 1996-2002). The study was undertaken with the objective of determining the levels of pesticide residues and their chemodynamics, both in the lake and its basin.

**METHODS**

Waster, soil and sediment samples were collected from sampling stations in nine districts on the Tanzanian side of Lake Victoria, namely Mwanza, Sengerema, Geita, Ngudu, Misungwi, Magu, Bunda, Tarime and Musoma Districts (Fig. 1). Sampling was done using standard methods as described by Åkerblom (1995).

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**Fig. 1:** Map of Southern Lake Victoria showing sampling stations for pesticide residues

All the reagents and solvents used were of analytical grade. Eighty (80) different pesticide standards ordered from Dr. Ehrenstorfer GmbH (Augsburg, Germany) were used. Working standard solutions were made by dilution of these stock standards and mixtures of standards of different concentrations were used in most cases for the screening of the pesticide residues. All glassware used had teflon-stoppers.

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 30 g) for drying. Sodium sulphate was later rinsed with dichloromethane (2 x 3 ml), the combined extract concentrated in vacuo at 30 °C, and the solvent changed to cyclohexane. Volume was adjusted in a stream of air to 2 ml in 9:1 cyclohexane:acetone (v/v) ready for GC analysis. Water extracts appeared clean and were not subjected to further clean up. However, on injection into GC, the peaks for dieldrin and DDE-p,p’ in the SE 30 column may overlap, and hence to remove any ambiguity, sulphuric acid treatment was employed to destroy dieldrin (Mwathi 1998).

Extraction and clean up of sediment samples

Sediment samples (10 g) were mixed with anhydrous sodium sulphate (ca 30 g) and ground to form free flowing powder. The powder was extracted successively, using (50 ml, then 3 x 20 ml) cyclohexane/acetone (1:1 v/v) by manual shaking (5 min) and extracting in an ultra-sonic bath for about 5 min. The contents were then filtered through a plug of wool containing anhydrous sodium sulphate (ca 15 g) and transferred to a separating funnel. The flask was rinsed with 5 ml cyclohexane/acetone (1:1 v/v) that was also filtered through sodium sulphate and added into the separating funnel. The extract was mixed and shaken well with saturated sodium chloride (200 ml). LLE by 50 ml dichloromethane/cyclohexane (15:85 v/v), gave an organic phase that was filtered into a round-bottomed flask through a plug of glass wool containing anhydrous sodium sulphate (ca 5 g), and subsequently subjected to a clean-up process.

Filtered extract was concentrated to near dryness and the solvent changed to cyclohexane/ethyl acetate (1:1 v/v) (2 ml). The extract (1 ml) was injected into a gel permeation chromatograph (GPC) and appropriate fraction collected. The fractions were subsequently evaporated to near dryness and dissolved in cyclohexane: acetone (9:1 v/v) in 2 ml ready for GC analysis.

Extraction and clean up of soil samples

Soil samples (20 g each case) were mixed with saturated ammonium chloride (14 ml), swirled, and allowed to stand for 15 minutes. The mixture was extracted with cyclohexane/acetone (1:1 v/v, 100 ml) by shaking vigorously for a minute, less vigorously about every 10 minutes for 1 hour, followed by treatment by ultrasound in an ultrasonic bath for 30 minutes. The sample was further shaken intermittently for another two hours and allowed to settle, after which distilled water was added cautiously along the side until an organic phase rose to the neck of the bottle. The organic phase was pasteur-pipetted into an E-flask containing about 15 g of anhydrous sodium sulphate. The organic extract was well-swirled and more sodium sulphate added whenever necessary so as to obtain a water free extract, which was then filtered through a plug of glass wool containing...
anhydrous sodium sulphate (5 g) that was subsequently rinsed with acetone/cyclohexane (1:1 v/v), (2 x 4 ml). Clean up of soil samples was done in the same way as for sediment samples.

Blanks and recoveries for samples

Blanks and recovery experiments were run for all three matrices using standard methods (Åkerblom 1995). Recoveries of the detected pesticides ranged between 70-120% and hence needing no correction to recoveries. The average method detection limits in water, sediments and soil were 0.1, 0.6 and 0.2 ppb for g-HCH, 0.2, 1.4 and 0.1 ppb for DDE-p,p’ and 0.3, 2.1 and 0.6 ppb for DDT-p,p’, respectively.

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 63Ni Electron Capture, (EC) and Nitrogen-Phosphorous, (NP) detectors were used for analysis. Nitrogen was used as both a carrier and make up gas in the ECD at a flow rate of 30 ± 1 ml/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°C held for 1 min, 30°C/min to 180°C, 4°C/min to 260°C held for 12 min. The injector and detector temperatures were 250°C and 300°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 subsequently sent abroad and analysed on a GC-MS for confirmation of the results.

RESULTS AND DISCUSSION

Pesticide residues in water

Water samples indicated low residue levels both in the dry and wet seasons. The detected pesticides in water included DDT and its metabolites DDE and DDD, and HCH isomers. Levels of total DDT and g-HCH in water were up to 1.6 and 0.05 mg/L in individual samples, respectively (Fig. 2). These levels were far below the maximum residue limits (MRLs) set by the government of Thailand for surface water quality criteria for toxic and deleterious substances set at 50 mg/L, for both DDT and HCHs (Siriwong 1999).

DDT residues

Dry season water samples had low levels (below 0.2 and 0.3 μg/L, the average method detection limits, respectively) of DDT-p,p’ and DDD-p,p’ residues in samples from River Mwilima in Sengerema only. More residues were detected during the wet season (Fig. 2). River Simiyu, whose samples had no residues during the dry season, had DDT-p,p’ (0.9 μg/L) and DDD-p,p’ (0.6 μg/L) during the wet season. Likewise, River Rubana samples were found to contain relatively high levels of DDT-p,p’ (0.85 μg/L) and DDT-o,p’ (0.24 μg/L) residues during the wet season, whereas the dry season samples had no detectable levels of residues. DDT-p,p’ and DDD-p,p’ were the most frequently detected residues in water samples, a finding that suggests use of DDT in the catchment areas of rivers Mwilima and Rubana; and some being deposited into sediments in which anaerobic degradation is favoured (Falandyisz et al 2001). However, the very low levels of DDT and its metabolites suggest that the use of DDT in the districts had been reduced.
**HCH residues**

The isomers a-HCH and g-HCH were detected in dry season samples collected from Rivers Mwilima in Sengerema, and Rubana along the Mwanza-Musoma Road, at low levels which were below the method quantification limits. All the four HCH isomers (α, β, γ and δ) were detected in samples from a few sites at varying concentrations during the wet season. Samples from rivers Simiyu and Nyaruhwe had concentrations of β-HCH of 0.2 μg/L and 0.16 μg/L, respectively. Occurrence of high 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 active isomer, γ-HCH, commonly known as lindane (Takeoka et al 1991). The main route of loss of HCHs is through volatilisation which is reported to account for about 99.6% of removal of the total applied HCH in the soils (Takeoka et al 1991). The β-isomer has been reported to persist more in the soils where it is applied than α-isomer, due to its lower volatility (Sang et al 1999) and high resistance to microbial degradation (Willet et al 1998). On the other hand, the α-isomer is reported to be the fastest dissipater, followed by the g-isomer (Singh et al 1991).

**Pesticide Residues in Sediment**

**DDT Residues**

Significant concentrations of DDT and its metabolites DDE and DDD were detected in sediments collected during both the dry and wet seasons. The first (1999) dry season samples had total DDT levels of 4.4μg/kg dry mass at Mwilima and 12 μg/kg dry mass at Mwaloni in Mwanza City. The two stations were the only
sites in which DDT residues were detected during the dry season. During the wet season most of the sediment samples had DDT residues (Fig. 3).

Samples from Mwaloni sampling station at Kirumba in Mwanza City had the highest levels of DDT residues. Figure 4 shows the variation of DDT residues in sediments for the three consecutive samplings at the station. Mwaloni is the city’s premier fish-landing site where fish cleaning, drying and packaging are undertaken in earnest. The relatively high residue levels might be caused by washing of pesticide containers at the shore.

![Graph showing variation of DDT residues in sediments](image)

**Fig. 3:** Variation of DDT residues in sediments of southern Lake Victoria and its basin during wet season

Shirati * refer to sediment collected from Shirati off-shore samples.

The trend at Mwaloni neither reflects the degree of contamination of the lake nor its basin. The levels were far higher than those found in sediments taken from other points of the lake and also those taken from different sites in the basin. Surprisingly, the DDT-p,p’ levels at Mwaloni increased sharply from 1.2 µg/kg dry mass in 1999 to 170 µg/kg dry mass in 2000, and then decreased to 60 µg/kg dry mass in 2001 (Fig. 4). The first sampling at Mwaloni in 1999 indicated levels of DDE-p,p’ greater than DDT-p,p’ a pattern that was completely reversed in the other two samplings, indicating high discharge of fresh DDT at the shore.
Fig. 4: Levels of DDT in sediments at Mwaloni - Mwanza City, Tanzania (1999-2001)

The ratio of fresh DDT to sum of its metabolites, DDD and DDE has been used as an indicator of time since the use of DDT (Strandberg and Hites 2001). Detection of higher levels of DDT than its metabolites suggests a recent use or spill of DDT (with no appreciable time for degradation). At Mwaloni the ratios of DDT to sum of its metabolites (DDD and DDE), were ca 0.1, 4.0 and 3.0 respectively for the three consecutive samplings. This indicates the deposition of high quantities of fresh DDT on the shore around the second sampling time, suggesting some dissipation at the last sampling. All water samples from Mwaloni station indicated no DDT residues, probably due to its low water solubility. DDT being lipophilic (log K_{ow} = 6) finds a reserve in the sediment where it accumulates with time. The long residence time it has in the sediments favours the anaerobic conversion of DDT to DDD as opposed to the aerobic conversion to DDE, hence resulting to higher concentrations of the DDD than of DDE (Falandysz et al. 2001) that is distinct in most sediments. Obviously, high dilution and the hydrophobicity of DDT account for the non-detection of its residues in the water samples.

Sediment samples from Rivers Simiyu and Rubana showed relatively high levels of DDT-p,p' (163 and 361 µg/kg dry mass, respectively), with significant levels of DDT-o,p' (69 and 245 µg/kg dry mass, respectively). Technical DDT contains ≤ 30% DDT-o,p' and about 70% of DDT p, p' isomers (Tomlin 2000). The DDT residues detected at the two stations indicate the use of technical DDT with faster dissipation/degradation of DDT-p,p' than DDT-o,p' hence giving a composition of more than 30% DDT-o,p' in the residues. A comparison of sediments obtained at Shirati along the shore and 2 km offshore, show that more DDT was found off shore than on-shore. This suggests further that DDT, being lipophilic, is found more in the offshore sediment that has a high organic content. There
were levels of up to 87 μg/kg dry mass of total DDT in the off shore samples, while on the shoreline samples only 51 μg/kg dry mass of total DDT was quantified.

**HCH residues**

In the dry season samples, only the γ -HCH isomer at a concentration of 1.0 μg/kg dry mass was detected in samples from River Nyaruhwe in Sengerema District. This was not the case for wet season samples in which all four HCH isomers were detected more frequently and at higher concentrations (Fig.5). Levels of lindane (γ-HCH) ranged from 4 to 18 μg/kg dry mass whereas those of the a- and b- isomers were more abundant with concentrations ranging from 15 to 70 μg/kg dry mass for the a-isomer and from 17 to 75 μg/kg dry mass for the b-isomer. The domination of a and b-isomers as compared to the g-isomer clearly indicates the use of technical HCH rather than lindane (99% γ-HCH) (Strandberg and Hites 2001).

Occurrence of high levels of HCH during the wet season suggests significant use of technical HCH in the catchment area, a clear indication of breach of the law because whereas lindane (γ-HCH) is still allowed by law, technical HCH was deregistered in Tanzania since the early 1990s (Anon. 1996). α-HCH is usually transported from the land on which it has been applied by water and occurs mostly in sediments due to its low water solubility (log Kow 3.5) (Tomlin 2000). This implies the possibility of detecting higher levels of these isomers in deeper sediments due to accumulation of these pollutants with time. In a recent study along the Dar es Salaam coast, only lindane (γ-HCH) was detected and not the other isomers, implying the use of lindane rather than the technical HCH, as a pesticide (Mwevura et al. 2002).

Lindane is transformed to other isomers depending on the environmental conditions. In sediments, soil and water, γ-HCH is broken down by algae, fungi and bacteria to less toxic compounds. HCHs are one of the widely dispersed and most readily detected organochlorine pesticides in environmental samples (Willet et al. 1998). Due to its undesirable environmental and public health effects, technical HCH has been banned in a number of countries. Hence its global use declined from 40,000 tonnes in 1980 and to 29,000 tonnes in 1990 (Willet et al. 1998). The study area in the present study, lindane and other HCH isomers were not intended for cotton pests, but for horticultural pests.

**Pesticide residues in soils**

The levels of DDT and HCHs, the only pesticide residues detected in soil samples displayed much variation between sampling sites, thus indicating that individual farmers in the different districts, were using varying amounts of pesticides per unit area.

**DDT residues**

Dry season samples were found to contain DDT and its metabolites DDD and DDE at low concentrations. The observed concentrations were up to 12, 9 and 2 mg/kg for DDT-p,p’, DDE-p,p’ and DDD-p,p’, respectively all being from Mwamajiro sampling station in Ngudu District. In most soil samples DDE-p,p’ was the dominant metabolite, accounting for more than 55% detection frequency. Relatively high levels of DDT were detected in samples from a few sites. Mean levels of up to 3.1 mg/kg, 2.3 mg/kg and 0.8 μg/kg for DDT, DDE and DDD, respectively, were detected. In most sites, DDT was not detected in the dry season samples while DDE was detected at low concentrations reflecting an elapse of appreciable time since the use of the pesticide (Strandberg and Hites 2001). The wet season samples showed relatively higher levels of DDT residues than the dry season ones (Fig. 6). DDT-p,p’ was found in most samples with levels of up to 59, 43, 69 and 60 μg/kg dry mass at Sagani,
Mwamajiro, Isagala and Ibanda, respectively. Levels of DDD-p,p’ and DDE-p,p’ were relatively low, indicating recent use of DDT in Ngudu district.

![Graph](image)

**Fig. 5:** HCH residues in sediments of southern Lake Victoria and its basin during wet season

**HCH residues**

Dry season samples indicated the presence of very low levels of HCH isomers up to only 2.3 μg/kg dry mass in the soil (Fig. 7). Lindane and β-HCH were the most frequently detected isomers during the dry season with concentrations of up to 2.3 and 1.2 μg/kg dry mass, respectively. The wet season samples showed a similar pattern as that observed in sediments, thus, the α- and β- isomers were dominant (Fig. 8).

Lindane is known to be adsorbed onto the soil particles, volatilised to the atmosphere, or leached into groundwater. The half-life of lindane in soil is temperature dependent. In higher temperatures, lindane’s residence time in soil decreases considerably. The mean half-life for lindane in treated soils is estimated to be 120 days (Sang et al. 1999). In soils and sediments, lindane is degraded primarily by bio-transformation although the major removal mechanism of lindane from soil is volatilisation (Sang et al. 1999). In the environment, lindane is transformed into a variety of chemicals, most of which are volatile. These include γ-pentachlorocyclohex-1-ene, γ-3,4,5,6-tetrachlorocyclohex-1-ene, α-HCH, β-HCH, and δ-HCH (Sang et al. 1999). It is further reported that lindane and other HCH isomers
stay on the upper layer of the soil and generally, there is very little movement of HCHs to lower soil layers (Sang et al. 1999). It has also been found that the rates of dissipation of HCH isomers were much faster from the soil under crop conditions than from un-cropped soil (Fig.8).

Fig. 6: Mean total DDT in the soil at four sampling stations of southern Lake Victoria and its basin during dry and wet seasons
Endosulfan residues
Analysis of ground water from a pump-well at Igaka, in Sengerema district, indicated some trace concentrations of endosulfan sulphate (0.02 µg/L). This metabolite was not detected in any of the other samples. Endosulfan is among the pesticides reported to be intensively used in cotton and horticultural crops in the region (Nyanda 2001). Levels of up to 1.7 mg/kg dry soil were reported in the soil samples at Mabuki (Stephens 1987). Detection of endosulfan sulphate in water highlights the long life of most organochlorines and their contamination risk to ground water. The absence of endosulfan isomers (α- and β-) in the other samples indicates long term past use of the pesticide in that area, thus allowing sufficient time for degradation. Moreover, endosulfan degrades faster when compared to DDT and HCH isomers. Endosulfan is degraded in soils with DT_{50} values of 30-70 days. The major metabolite is usually the cyclic sulphate, that is degraded more slowly than the parent pesticide. In the field, the DT_{50} for total endosulfan (α, β and sulphate) is 5-8 months (Roberts and Hutson 2000).
Henry and Kishimba- Levels of pesticide residues in water...

![Graph showing concentrations of various pesticides at different sampling stations.]

- HCH-alpha  
- HCH-beta  
- HCH-gamma  
- HCH-delta  
- HCH-total

Fig. 8: Mean HCH residues in soils of southern Lake Victoria and its basin during wet season.

CONCLUSION

The results show that organochlorines are by far the most persistent of the pesticides in the environment. This is highlighted by the fact that although in recent years other classes of pesticides such as pyrethroids, organophosphorous and carbamate, were the ones predominantly used in the basin no residues of these pesticides were detected. The present study has also highlighted the fact that there was little respect for the law when it came to pesticides. DDT and technical HCH had been banned and not allowed for use in agriculture for at least a decade. But they were still being imported, sold and used. Nevertheless, the overall levels of the residues of these pesticides were so low that there is no cause for alarm.

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