Bull. Environ. Contam. Toxicol. (2005) 75:960–967
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DOI: 10.1007/s00128-005-0843-4

Bulletin of Environmental Contamination and Toxicology

Organochlorine Pesticide Contamination in Surface Water, Sediment, and Air Precipitation of Lake Victoria Basin, East Africa

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Received: 24 January 2005/Accepted: 16 August 2005

Pesticides use has increased worldwide because of the need of increasing agricultural productivity required to meet the swelling world population. Especially in tropical regions where pests can survive well, agricultural intensification has led to higher pesticides consumption (Racke et al 1997). This practice has brought about problems due to the presence in water and air of pollutants dangerous at levels lower than ppb. Although it is true that pesticides are essential in modern agriculture, there is growing concern about possible environmental contamination from agrochemicals. Consequently extensive studies have been conducted to assess the pollution of rainwater (Goolsby et al 1997), sediments (Bester and Huhnerfuss 2000; Daniels et al 2000) and surface waters (Pereira and Hostettler, 1993, Thurman et al 2000) with pesticides. In comparison with temperate regions, studies on pesticides in environment of tropics are very scarce and focus mainly on organochlorine pesticides (Caldas et al 1999, Botcells et al 2000) which have supposedly been curtailed in their use. Also the patterns of regional and local variation, have been only superficially investigated, and detailed pathways of residues within ecosystem networks are poorly understood.

A recent study of currently used pesticides in river ecosystems (Castillo et al 2000) demonstrated that aldrin, heptachlor, lindane and dieldrin are important contaminants in the aquatic environment. Since water and land temperatures are higher in tropical environment than in temperate regions, an increased pesticides loss to the atmosphere by volatilization has to be expected. Air precipitation contamination by pesticides in tropical environments has not been given due consideration. Pesticides present in the water bodies and sediments originate from several sources, including precipitation, land run-off, industrial and municipal waste discharges and accidental spills. The sediments of water bodies are generally considered as ultimate sinks for pesticides and the persistent residues accumulated in the sediments are thought to be inactive. However, several processes may redistribute pesticides from the sediment to the water. These processes include adsorption (Halter & Johnson, 1977), re-suspension of particles from the sediment (Olsson et al 1978), pH changes (Plonke Chesters, 1974) and the activity of benthic macro invertebrates (Sodergren & Larsson, 1982). Rivers Katonga, Simiyu and Nyando drain farmed areas of Lake Victoria basin in which organochlorine pesticides have been used. Due to their relative chemical and biological stability, residues of these pesticides are expected to persist in these river ecosystems for several years. At present, almost nothing is

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known about the existence of these pesticides and their related compounds, in the basin. The aim of the study was to determine the levels of persistent organochlorines in sediment, water, and air precipitation samples collected from Katonga, Simiyu and Nyando wetlands of Lake Victoria basin. The data will help in the subsequent studies to identify the source and routes of transport of the pollutants and assess the risk of human exposure to pesticides and in implementing integrated pesticides management. The results are the first of their kind for the region and should provide valuable information for forthcoming studies.

MATERIALS AND METHODS

Water sampling was undertaken at Katonga, Simiyu and Nyando wetlands of Lake Victoria basin. Sampling for surface water was done in May, 2004 and June, 2004 in the three study areas. The river water samples were taken from about 10 cm below the water surface with 1-L glass bottles that had been thoroughly cleaned and rinsed with ethylacetate and heated at 250°C for 3 h before use. For sampling, turbulent positions of water bodies were chosen to approximate mean concentrations of the river water. After collection, water samples were stored on ice during transport to the laboratory and were kept at 4°C in the laboratory until solid-phase extraction.

Sediment samples were taken from river positions where an accumulation of fine-textured substrate took place, with a van veen sampler. Composite samples were pooled from four sub-samples, homogenised and wrapped in aluminium foil. These samples were stored on ice during transportation to the laboratory and stored at -20°C in the laboratory until analysis.

Air precipitation samples were collected using sampling device for bulk precipitation as a modified NILU – sampler (Norwegian Institute for Air research) consisting of a glass funnel with a 66 cm opening, connected to 5 – litre glass bottles which had been wrapped with aluminium foil to reduce solar heating, and containing 500 ml of distilled water. The sampling devices were exposed for 30 days and then the samples were taken to the laboratory with precautions to give minimum contamination. In the laboratory the air precipitation samples were immediately stored at -20°C until extraction.

Portions of water samples (IL) were filtered through 0.4µm filter to prevent clogging of the sorbet, acidified with hydrochloric acid to pH 3, potassium chloride (20 g) added, and then solid-phase extracted with Sep – Pak silica gel cartridges which had been conditioned by elution with 5 ml each of ethylacetate, methanol and water. After extraction of the water sample, the cartridges were dried in a filtered air stream. Pesticides were eluted by n-hexane (8 ml) and ethyl acetate (12 ml) and the combined eluates were reduced to approximately 10 ml by passing nitrogen over the surface of the extract.

Sediment sample (10 g) was ground with anhydrous sodium sulphate in the mortar till a free- flowing powder was obtained. The sample/sodium sulphate powder was then extracted in the beaker by shaking with 50, 20 20, 20 ml acetone: Cyclohexane 1:1 mixture. This was then filtered into a separatory funnel and the filtrate shaken

Table 1. Recovery of pesticides using different materials and the same extraction/analysis process.

Pesticides	Recovery percentage							
	Surface water			Sediment		Air precipitation		
Endosulfan alpha	96±10	93±11	94±10	84±9	88±10	93±12	97±11	90±10
Endosulfan beta	89±7	90±8	91±9	85±7	89±6	89±9	93±8	91±7
Endosulfan sulphate	94±11	92±10	93±12	77±9	81±10	80±11	87±9	87±10
DDD-pp	87±5	85±6	86±7	81±5	79±7	90±5	96±6	95±5
DDT-op	88±4	87±6	90±6	80±5	80±6	89±5	90±4	91±5
DDT-pp	74±7	80±8	77±6	76±7	79±7	80±7	88±7	87±6
Parathion methyl	75±11	77±8	79±10	78±8	80±10	77±8	79±10	80±10
DDE-pp	93±4	90±5	89±5	84±6	81±3	88±60	90±4	94±5
Lindane	90±4	89±10	93±11	84±10	82±8	92±8	90±4	91±5
Dieldrin	77±6	80±8	78±7	79±6	77±6	77±8	78±6	80±9
Heptachlor	83±7	80±11	85±10	84±9	87±6	83±5	87±5	86±10

with 200 ml of saturated sodium chloride solution. The organic and aqueous phases were separated and the aqueous phase was extracted with dichloromethane: acetone, 85:15 mixture. The organic phases were then combined together with 10 g sodium sulphate in a conical flask. The conical flask was shaken and each time adding sodium sulphate until sodium sulphate flowed freely. The organic phase was decanted into a small flask for the clean up step by flash chromatography.

Cleanup of the extracts prior to gas chromatographic analysis eliminates inter alia, the many volatile constituents of the samples, thus improving resolution and prolonging column life. This was done with an 8-ml glass column packed with 1.0 g of aluminium oxide (deactivated with 0.06 g water g^{-1} sorbent) on top of 1.0 g Florisil(deactivated with 0.1 water g^{-1} sorbent). The extract was changed to the column, and the pesticides consecutively eluted from the column with 6% and 15% diethyl ether in n-hexane. The combined eluants were evaporated to about 10 ml by a rotary evaporator, then to exactly 10.0 ml by passing over a stream of purified nitrogen.

The cleaned up extracts were analysed for the pesticides of interest, endosulfan alpha, endosulfan beta, endosulfan sulphate, DDD-pp, DDT-op, DDT-pp, parathion methyl, DDE-pp, lindane, dieldrin and heptachlor, using gas chromatography instrument, varian model 3800 – CP equipped with electron capture detector (ECD) and a DB-1 capillary column. Operating Conditions: Column: 0.53 mm x 50 m i.d. Temperature program, 90°C; hold for 1 min; raised to 260 at 4°C per min.

The quality of the analytical procedure was assessed by pesticide recovery experiments with water, sediments and air precipitation matrices. The efficiency of the water extraction procedure was tested by spiking 1 – L samples of water sample with 0.1 μg each of pesticide standards dissolved in acetone. Afterwards the samples were extracted and analysed according to the procedure outline above.

Table 2. Concentration of organochlorine compounds in surface water Samples.

Concentration, $\mu g L^{-1}$						
Compound	Katonga		Simiyu		Nyando	
	Range	Mean	Range	Mean	Range	Mean
Endosulfan alpha	0.002-0.004	0.003	0.040-0.042	0.041	0.030-0.038	0.034
Endosulfan beta	0.011-0.013	0.012	0.048-0.052	0.050	0.030-0.032	0.031
Endosulfan sulphate	0.034-0.042	0.038	0.073-0.075	0.074	0.015-0.019	0.017
DDD-pp	0.280-0.320	0.030	0.033-0.037	0.070	0.012-0.016	0.014
DDT-op	0.026-0.03	0.028	0.027-0.081	0.054	0.020-0.022	0.021
DDT-pp	0.026-0.028	0.027	0.079-9,985	0.087	0.024-0.026	0.025
Parathion methyl	0.051-0.053	0.052	0.026-0.028	0.027	0.023-0.025	0.024
DDE-pp	0.007-0.009	0.008	0.004-0.006	0.005	0.003-0.005	0.074
Lindane	0.088-0.092	0.09	0.024-0.034	0.029	0.120-0.148	0.124
Dieldrin	0.078-0.082	0.08	0.030-0.032	0.031	0.034-0.038	0.036
Heptachlor	0.049-0.051	0.05	0.036-0.042	0.039	0.020-0.024	0.002

Similarly, uncontaminated sediment and air precipitation samples were spiked with known quantities of pesticides before extraction (2.5 μg per 25 g of sediment dry mass and 0.1 μg per 500 ml of air precipitation) and processed and analysed as described above.

RESULTS AND DISCUSSIONS

Table 1 shows the percentage of recovery for a 0.1 μg solution of pesticides in water, sediment and air precipiltation. As it can be seen, recovery results indicated that the recovery efficiency exceeded 74% for all compounds measured.
In general, recoveries from sediments were somewhat lower at 76 to 89%, while those from air precipitation and water ranged from 77 to 97% and 74 to 96% respectively.
The multi-residue extraction procedure employed in the present study, followed by gas chromatographic determination, should screen most of the common organochlorine pesticides. High resolution gas chromatography has confirmed the residues of: endosulpan alpha, endosulfan beta, endosulfan sulphate, DDD-pp, DDT. Op, DDT-pp, parathion methyl, DDE-pp, lindane, dieldrin, and heptachlor in the studied wetland ecosystems of Katonga, Simiyu and Nyando.

In an analysis of the input and output of chlorinated hydrocarbon residues in the wetland ecosystems of Lake Victoria basin, the amount entering the study areas by means of precipitation and airborne particles was estimated by gas chromatography (Laabs et al, 1999). The identity of the more important peaks in the chromatograms were for DDT metabolites (pp – DDD, p.;-DDE and DDT – pp), endosulfan, lindane, parathion, dieldrin, as well as heptachlor. The results from analysis of surface water sediment, and air precipitation are presented in Tables 2, 3 and 4 for samples

Table 3. Concentration of organochlorine compounds in surface sediments.

Concentration, µg kg^{-1}						
Compound	Katonga		Simiyu		Nyando	
	Range	Mean	Range	Mean	Range	Mean
Endosulfan alpha	0.010-0.014	0.120	1.456-1.75	1.550	0.41-0.45	0.430
Endosulfan beta	0.370-0.41	0.390	0.70-0.80	0.750	0.42-0.48	0.450
Endosulfan sulphate	0.25-0.29	0.270	0.80-0.84	0.820	0.39-0.45	0.420
DDD-pp	0.55-0.66	0.580	0.75-1.05	0.900	0.40-0.43	0.415
DDT-op	0.656-0.702	0.679	2.20-2.30	2.250	0.471-0.483	0.477
DDT-pp	0.44-0.48	0.460	2.60-2.62	2.610	0.301-0.467	0.384
Parathion methyl	0.480-0.508	0.494	0.80-0.90	0.850	0.73-0.73	0.715
DDE-pp	0.060-0.070	0.065	0.81-0.93	0.870	0.402-0.444	0.423
Lindane	0.380-0.322	0.401	0.61-0.71	0.660	0.590-0.592	0.586
Dieldrin	0.190-0.220	0.205	0.50-0.66	0.580	0.140-0.160	0.150
Heptachlor	0.250-0.264	0.257	0.48-0.52	0.500	0.340-0.350	0.345

collected from Katonga, Simiyu and Nyando wetlands.

Concentrations of organochlorines generally decreased from Simiyu through Katonga to Nyando indicating decreasing input of anthropogenic contaminants to the wetland ecosystems of the investigated areas. At Katonga, relatively low levels of endosulfan alpha and endosulfan beta were observed. This suggests a relatively minor use of these chemicals in agriculture in nearby areas. In Simiyu, very high concentrations of DDT and its metabolites were detected and this might be explained by the historical use of DDT or its present use under disguised

Table 4. Concentration of organochlorine compounds in rainfall.

Concentration, µg m^{2-} day^{-1}						
Compound	Katonga		Simiyu		Nyando	
	Range	Mean	Range	Mean	Range	Mean
Endosulfan alpha	0.011-0.013	0.012	0.037-0.043	0.040	0.016-0.018	0.017
Endosulfan beta	0.008-0.01	0.009	0.041-0.045	0.013	0.018-0.022	0.020
Endosulfan sulphate	0.010-0.014	0.012	0.043-0.047	0.015	0.025-0.029	0.027
DDD-pp	0.030-0.032	0.031	0.058-0.062	0.130	0.026-0.050	0.028
DDT-op	0.041-0.043	0.042	0.048-0.052	0.150	0.028-0.032	0.030
DDT-pp	0.032-0.038	0.035	0.052-0.056	0.244	0.027-0.031	0.029
Parathion methyl	0.048-0.052	0.05	0.037-0.043	0.080	0.024-0.026	0.025
DDE-pp	0.033-0.045	0.034	0.024-0.026	0.025	0.020-0.022	0.021
Lindane	0.024-0.026	0.025	0.048-0.022	0.020	0.022-0.026	0.020
Dieldrin	0.035-0.039	0.037	0.038-0.092	0.040	0.023-0.025	0.024
Heptachlor	0.032-0.034	0.033	0.032-0.036	0.034	0.024-0.032	0.26

formulations. High DDT/DDE ratios in the Simiyu area and Nyando area in comparison with Katonga indicate, recent use of DDT for agriculture and vector control.

The differences between Katonga study area and Nyando study area are small, inspite of their different locations. Nyando study area is situated on lake shore in an agricultural area and shows higher levels of lindane than Katonga and Simiyu study areas located far away from agricultural operations but near enough to receive emissions from daily incineration of garbage. It might be expected that waste products containing lindane is burnt with the varied refuse. Being volatile under heat, lindane escapes to the atmosphere and contaminate the wetlands. A local source is presumably responsible for the relatively high amount of lindane recorded at Nyando study area, although the origin of these deposits is still unknown. The origin and general routes of transport of pesticide compounds to the environment are however, not fully understood.

The regional distribution of $\sum$DDT was similar to that of lindane in the study area. DDT has been used in moderate quantities mainly for controlling tsetse flies in the past. In 1970, the use of DDT was restricted but kept coming in under different formulations. It has been shown that nearly half the amount of DDT applied to the soil surface may volatilize, thus making a slow, long term contribution to the atmosphere (Racke et al., 1997). In a study of chlorinated hydrocarbon residue in urban rain water, it was demonstrated (Dubus et al., 2000) that the higher levels of DDT in urban rainwater, compared with that from a rural area, could be attributed to urban air having a higher content of particulate matter, for which DDT has affinity. This can easily account for different pesticides level in the three studied areas.

Dieldrin is considered to be the most toxic of all commercial insecticides. Appreciably high residue levels were detected in Simiyu study area compared to Katonga and Nyando study areas. Hence dieldrin followed a similar distribution pattern described earlier for $\sum$DDT and may thus be explained accordingly. Generally, dieldrin concentrations in water are low, which may be due to the fact that this insecticide is relatively short-lived and has been used on few occasions in the study areas and also not very water soluble. Dieldrin residues were confirmed in the sediments of the study area coverage concentration was 0.31 μgKg^{-1} dry weight) which may thus act as a reservoir giving traces of dieldrin to the water.

Some of the pesticides used to replace DDT have been the chlorinated cyclodiene hydrocarbons. Some of these compounds are more toxic than DDT itself, but most biodegrade more rapidly. Example of this type of pesticides is heptachlor.
Although heptachlor use has been officially restricted in East Africa, its residues are expected to persist owing to its long use for agricultural and public health purposes. Relatively high concentrations were observed at Simiyu study area coverage concentration was 0.05 μgKg^{-1}) which may be due to the fact that heptachlor is being used in this location. Analysis has shown that the Simiyu wetland sediments contained appreciable amounts of parathion methyl (average concentration was 0.870 μgKg^{-1} dry weight). Thus, parathion methyl may have been absorbed to suspended soil particulate matter carried by the run-off and subsequently deposited in the Simiyu wetland.

The highest pesticides levels in the water of rivers entering lake Victoria (highest value, 0.624 μg L^{-1}) tend to exceed equivalent values in temperate rivers (Frank et al, 1981), and also exceeds the US environmental protection Agency Criterion for water safe to aquatic life. Since the acute toxicity of DDT to different fish species lies between 0.3 and 110 μg litre, and residues bound to particulates are relatively unavailable to fish, it is unlikely that adults are at risk of acute poisoning, but damage to fry is possible.

The wetland ecosystem, some components of which we have analysed, does not seem to store chlorinated hydrocarbon residues in a very simple way. In order to acquire a detailed picture of the pathways and points of storage for these substances in the ecosystem it is obviously necessary to examine the mechanisms of uptake and elimination for each major ecosystem component. A fuller comprehension of this important problem also seems to require much more detailed information about the food ecology of different animal groups than has been hitherto available. Finally, the results should serve as a warning to avoid generalisation from one ecosystem to another.

In the light of the above, the following conclusions may be drawn:

1. Concentrations of organochlorine pesticides were relatively low in both water and sediments from the wetlands
2. There are no direct inputs of organochlorine pesticides to the studied wetlands and transportation via the natural processes seems to be the sole source.
3. Low pesticides levels were detected in the water and this was attributed to both limited application of these insecticide.
4. Pesticides concentrations were relatively high in the sediments of the three wetlands and are probably adsorbed onto suspended particulates.

As chemists we must recognise that following synthesis of new pesticides which are moderately kinetically stable, no matter how carefully they are controlled, they will eventually become quite widely dispersed in the environment. This is a natural consequence of the second law of thermodynamics which ensures that eventually, traces of those pesticides may be found in any environmental sample taken, provided the analytical detection limit is low enough.

On the other hand with many tens of thousands of synthetic pesticides in use, many of which have the potential to cause environmental damage and some of which have fulfilled this potential, action is clearly necessary. Since it is not possible to control everything at once, some prioritization is required. This project has attempted to summarise the current state of pollutant prioritization in Lake Victoria basin and has illustrated the kinds of pesticides involved with some specific examples.

Acknowledgments. The research was financially supported by SIDA-SAREC through Lake Victoria Research (VicRes) Initiative and partially by Makerere University, Dar es Salaam University and Moi University. The invaluable support with logistics by Professor Ogutu is greatly acknowledged. We also thank Mr Waswa J and Mr Mulinda for the analysis.

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