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CHLORINATED INSECTICIDE RESIDUES IN TANZANIAN ENVIRONMENT. TANZADRIN

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ABSTRACT

Sediment, water plant and fish samples in Nyumba ya Mungu Reservoir in Tanzania have been analysed for organochlorine insecticide residues and PCB. PCB was not found (< 0.5 ng/g in dry weight). Also the levels of other chloroinsecticide residues were low (0.1-21 ng/g) except dieldrin (4-36 ng/g) and especially its photometabolite TANZADRIN (appr. 10-250 ng/g). Tanzadrin was found to be product of chlorine-hydrogen exchange at olefinic carbon 9 of dieldrin and could be prepared by UV-irradiation of dieldrin in hexane.

INTRODUCTION

The use of pesticides in Tanzania has been increasing fast in the past ten years. For example, in rose from 5 960 tons in 1977/78 to more than 12 000 tons in 1982/83 - a 100 % increase in five years. Most of the pesticides are used in cash crops (coffe, cotton, sugarcane) as well as in subsistence crops (wheat, maize, beans, bananas). Up to today, a majority of the pesticides used are persistent organochlorines such as DDT, lindane, dieldrin, aldrin, heptachlor and endosulphan /1/.

Nyumba ya Mungu is a small man-made lake situated in North-East Tanzania (Fig. 1). The lake resulted from the construction of a dam on the River Pangani in 1968 with view to generating hydropower and regulation the flow of Pangani River (Fig.2).

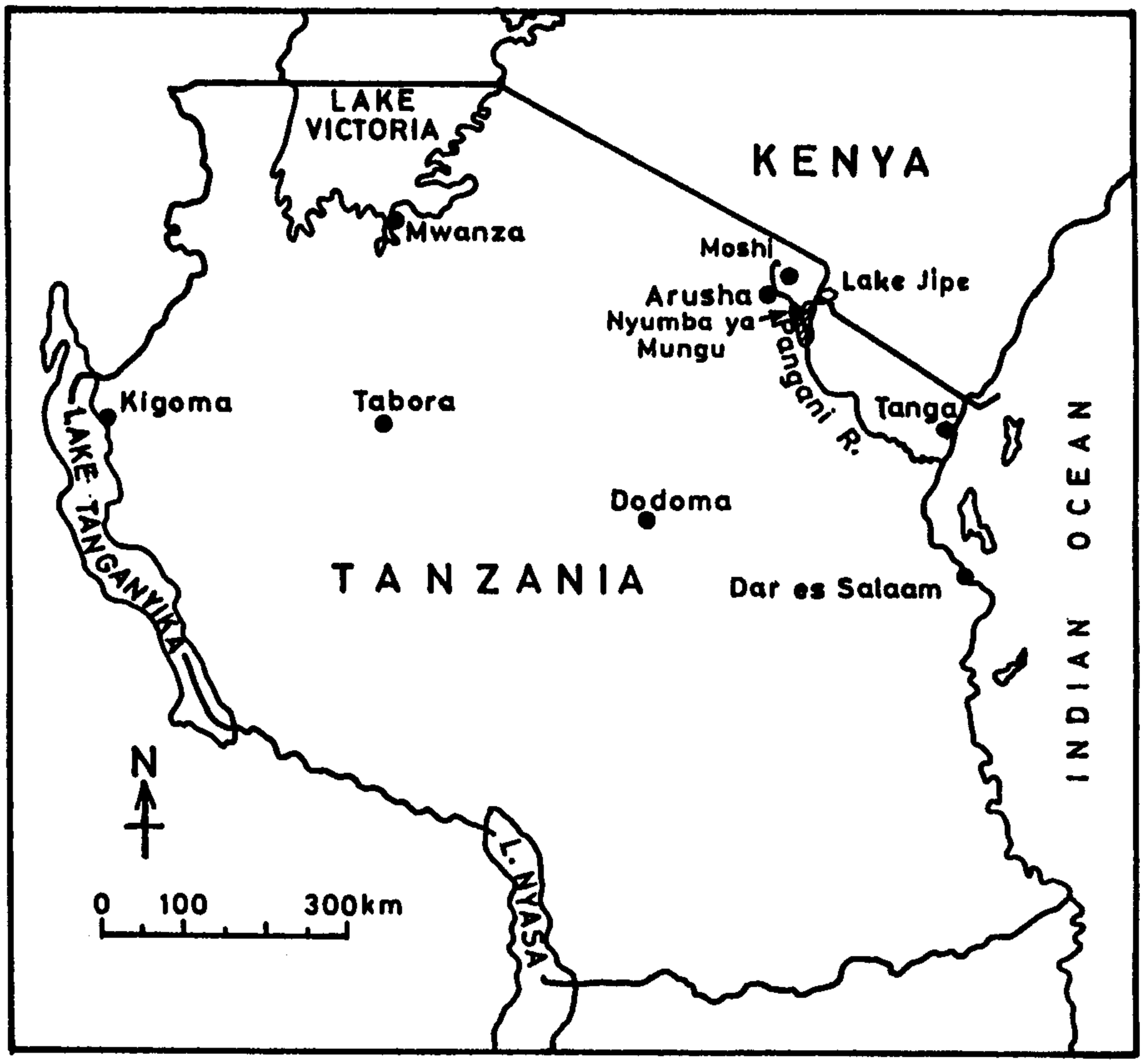


Fig. 1. Location of Nyumba ya Mungu Lake

Although fishing was not included in the original feasibility studies, this activity has grown up very fast. By 1970, the lake had attracted up to 25 000 fishermen, who settled in about 26 villages surrounding the lake, and did manage to catch more than 28 500 tons of fish in 1970-71 /2/.
People around lakes Jipe and Nyumba ya Mungu as well as Ruvu River grow maize, beans, sugarcane, cassava, coconuts, bananas, rice and fruits (peaches, avocado etc.). They also keep cattle and goats /3/. In carrying out this mixed farming, the farmers use a lot of pesticides, especially persistent organochlorines, which finally find their way into Nyumba ya Mungu Lake.

Therefore, environmental samples from there are studied for possible persistent residues.

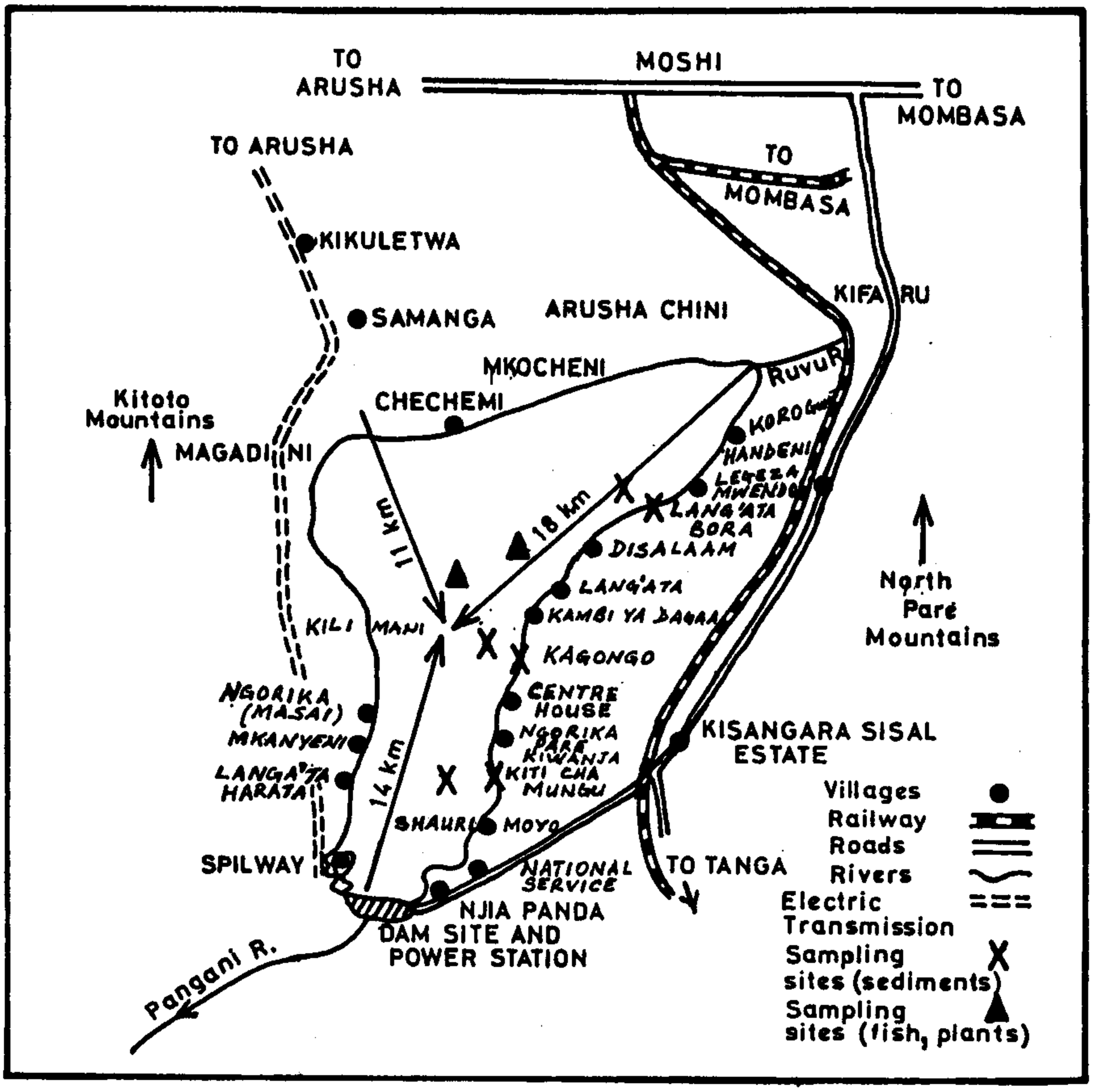


Fig. 2. Nyumba ya Mungu Lake (showing fishing villages and sampling points).

SAMPLING

The following samples were collected 15.12.1986 from Nyumba ya Mungu Lake:

Sample 1. Sediment, Lang'ata Bora - out on the edge
Sample 2. Sediment, Lang'ata Bora - inside the lake
Sample 3. Sediment, Kagongo - inside the lake
Sample 4. Sediment, Kagongo - out on the edge
Sample 5. Sediment, Kiti Cha Mungu - out on edge
Sample 6. Sediment, Kiti Cha Mungu - inside the lake
Sample 7. Roots of Pistia straoites from the lake
Sample 8. Leaves of Pistia straoites from the lake
Sample 9. Fish sample, Tilapia sp., grounded in toto

The milled and dried samples were transported personally from Tanzania to Jyväskylä, Finland, in January 1987 for analysis.

ANALYSIS PROCEDURE

For chlorohydrocarbon analysis measured amount of 2,4,6-trichlorobiphenyl was added to make an internal standard. Samples were extracted by Soxhlet with a solvent mixture hexane-acetone-diethyl ether-petroleum ether (bp. 40-60) 2.5:5.5:1:9 (v/v/v/v) for 6 hours.

A clean up column was constructed as follows: Aluminium oxide was heated at 700°C for 8 hours and after cooling deactivated by adding 5 % of water. The column was made by pouring 6 cm layer of aluminium oxide to a Pasteur pipette. The solvent extract of the samples was rinsed to the column and chlorohydrocarbon fraction eluted down with hexane (10 ml). The hexane eluate was evaporated with nitrogen gas stream to a small volume. Samples were analyzed with a gas chromatograph (MICROMAT HRGC) equipped with two EC-detectors and quartz capillary columns coated with SE-54 and OV-1701.

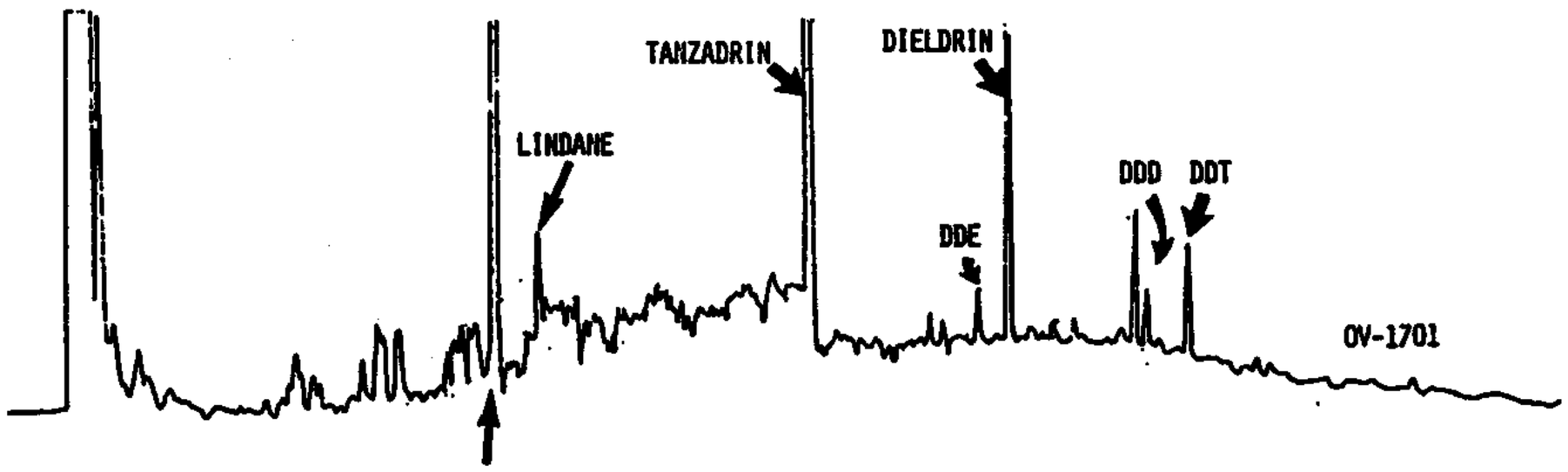
Chlorohydrocarbon peaks in gas chromatograms were identified with the following authentic reference compounds:

1. Hexachlorobenzene (HCB)
2. PCB
3. Alfa-hexachlorocyclohexane (alfa-HCH)
4. Lindane
5. Oxy-chlordane
6. Gamma-chlordane
7. Alfa-chlordane
8. Trans-nonachlor
9. DDT
10. DDE
11. DDD
12. Aldrin
13. Endrin
14. Dieldrin
15. Heptachlor
16. Heptachlorepoxide
17. Alfa-endosulfan
18. Beta-endosulfan

RESULTS

A representative chromatogram is illustrated in Fig. 3. Three insecticides, DDT, lindane and Diedrin, two known metabolites DDE and DDD and one previously unexpected metabolite TANZADRIN (name given by us) were measurable. Quantitation was based on response factors of the internal standard and authentic models except for tanzadrin, whose response was assumed the same as that of dieldrin. Results are shown in Table 1.

Fat content of the fish sample (Nr 9) was measured to be 18.3 % (in dry weight). Consequently, chlorohydrocarbon contents in fat were for DDE 76.5 ng/g, DDD 21.9 ng/g, DDT 32.8 ng/g, lindane 16.4 ng/g, dieldrin 54.6 ng/g and tanzadrin 60.1 ng/g.



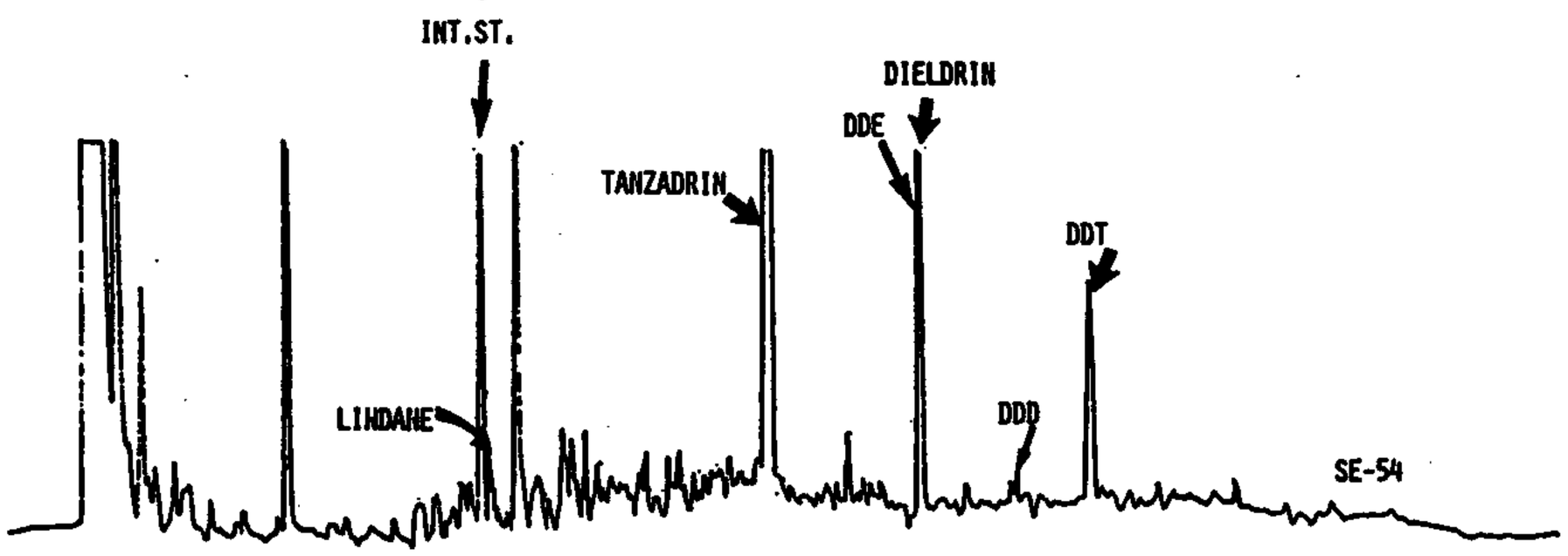


Fig. 3. GC/ECD trace of the Sample 5 (sediment from Kiti Cha Mungu).

TABLE 1. Contents of known polychlorinated insecticide residues and a major previously unknown residue TANZADRIN ng/g in dry weight of environmental samples from Nyumba Ya Mungu lake, Tanzania 1986.

SAMPLE	DDE ng/g	DDD ng/g	DDT ng/g	LINDANE ng/g	DIELDRIN ng/g	TANZADRIN ng/g
1.	+	3	+	1	4	160
2.	1	+	2	+	5	83
3.	1	ND	2	ND	3	110
4.	1	ND	7	4	6	ND
5.	1	+	4	+	5	251
6.	1	+	2	1	3	182
7.	13	ND	15	5	18	35
8.	17	ND	21	4	36	14
9.	14	4	6	3	10	11

\+ = peak below the limit of determination 0.5 ng/g
ND = no observable peak (limit of detection ca. 0.1 ng/g except for PCB mixture ca. 0.5 ng/g; no PCB peaks were detected)

Contamination of the present samples by organochlorine residues was very low, about on global baseline level. In the present case, only dieldrin/tanzadrin contamination can be considered to represent some local pollution. Backround levels of chlorohydrocarbons in Finland are of the same order or higher than in the present Tanzanian samples /4-6/. For example, dry phytoplankton in a pure lake in Finland 1981 contained 125 ng/g DDE and 1379 ng/g PCB and roach fat 1397 ng/g DDE and 6504 ng/g PCB /5/. Aldrin and dieldrin were found in Finnish freshwater fish only occasionally at very low levels /4/.

PREPARATION AND STRUCTURE OF TANZADRIN

Tanzadrin was readily identified with some minor impurity of dieldrin. It could be prepared as a major product by irradiation of dieldrin in hexane. Irradiation was done with a 10 W low pressure mercury lamp (254 nm) employing outside ice-water cooling. The main (85 %) product was identified with the environmental tanzadrin with GC/ECD and indicated by GC/MS to be a product of exchange of one chlorine to hydrogen atom in dieldrin molecule. Its non-identity with the well known dieldrin isomer, photodieldrin /7/, was obvious from the mass spectrum (Fig. 4).

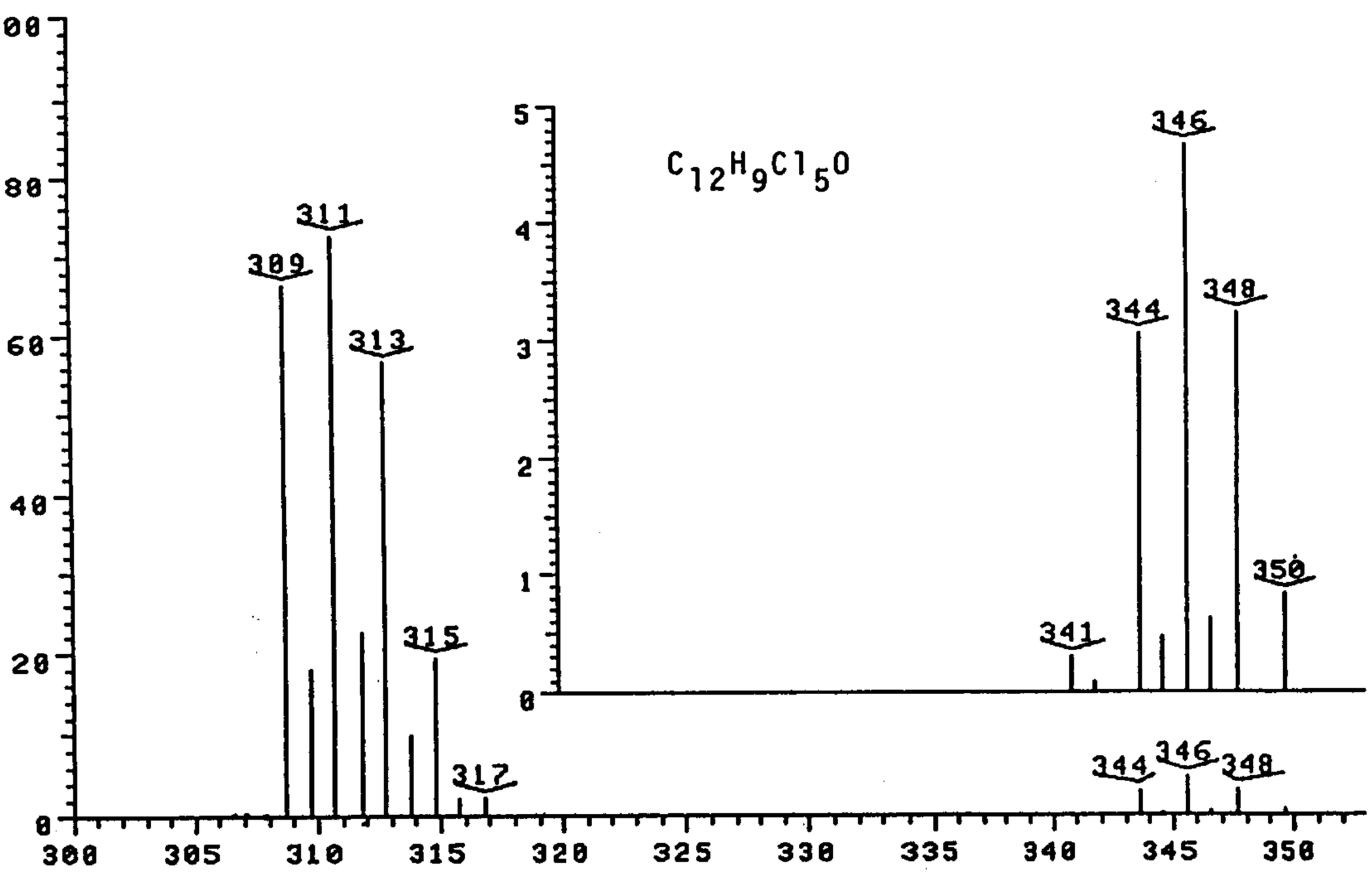
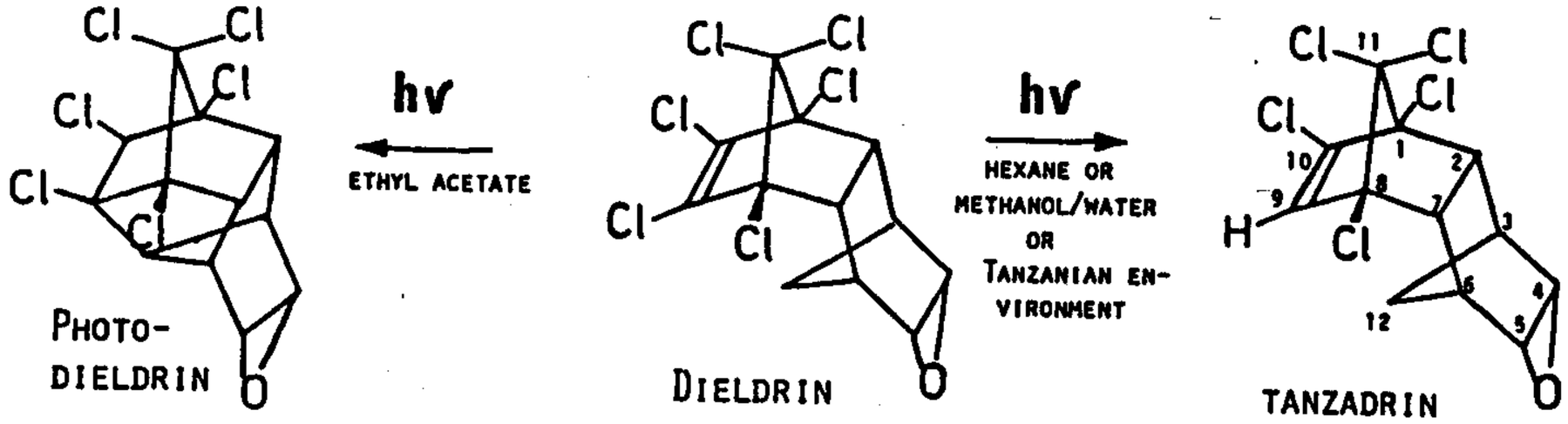


Fig. 4. Mass spectrum of tanzadrin done with spectrometer Finnigan MAT 212 from main GC peak of the grude product of UV irradiation of dieldrin in hexane.

Tanzadrin could be identified with CAS Nr 18417-21-5 reported as the irradiation product of dieldrin in n-hexane and in methanol-water /8,9/ which also appeared as minor product in photolyses of dieldrin in solid phase /10/ and as minor product of gamma-radiolysis of dieldrin /11/, but has not previously reported to occur in environmental samples. The compound has also a name 9-dehydrodieldrin and the present von Baeyer/IUPAC name of tanzadrin is 1,8,10,11,11-pentachloro-4,5-exo-epoxy-2,3-7,6-endo-2,1-7,8-exo-tetracyclo 6.2.1.$1^{3,6}$.$0^{5,9}$ dodec-11-ene /12/.



NMR spectra of tanzadrin could be done from the grude product while the impurities gave only small signals which did not interferre. 270 MHz Proton NMR (instrument JEOL GSX 270) of tanzadrin in $CDCl_3$ showed chemical shifts for proton H2 2.73 ppm (Lit. /9/ 2.72 ppm), H3 2.67 ppm (2.72), H4 3.09 ppm (3.12), H5 3.13 ppm (3.12), H6 2.68 ppm (2.72), H7 2.76 ppm (2.72), H9 6.03 ppm (6.0), H12a 1.19 ppm (1.20) and H12s 1.58 ppm (1.60). Signals 12a and 12s formed an AB spectrum with splitting from the geminal coupling $J_{12a-12s}$ = 12.4 Hz (Lit. /9/ 12.5 Hz).

Proton decoupled carbon-13 NMR spectra of tanzadrin were recorded with GSX 270 in both $CDCl_3$ and in acetone-d_6. Chemical shifts are compared in Table 2.

TABLE 2. Carbon chemical shifts of tanzadrin ppm from TMS.

Carbon Nr	in $CDCl_3$	in acetone-d_6	Lit. /13/ (in $CDCl_3$)
1	80.47	82.14	80.3
2	53.26	54.43	53.1
3	37.11	38.29	37.0
4	51.03	51.61	50.9
5	51.36	51.96	51.2
6	37.56	38.79	37.5
7	54.07	55.22	53.9
8	*	78.24	76.5
9	131.52	133.74	131.2
10	135.74	136.18	135.4
11	106.09	107.25	105.9
12	21.10	21.97	21.0

* Peak obscured by the solvent triplet

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