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Time Trends of Chlordane, DDT, and PCB Concentrations in Pike (*Esox lucius*) and Baltic Herring (*Clupea harengus*) in the Turku Archipelago, Northern Baltic Sea for the Period 1971–1982

Raija Moilanen,[1,2] Heikki Pyysalo,[1] Kim Wickström,[1] and Reino Linko[2]

[1]*Food Research Laboratory, Technical Research Centre of Finland, Biologinkuja 1, SF-02150 Espoo 15, Finland and* [2]*Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku, Finland*

The concentrations of PCB- and DDT-compounds in Baltic wildlife have been extensively studied during the last decade.

Since the use of DDT was banned in the early 70's in many countries, including those in Baltic area, the level of DDT-compounds has decreased in the Baltic environment by PAASIVIRTA and LINKO (1980). The use of PCB-compounds is now banned in Sweden and is practically nonexistant in Finland. In EC countries the use of PCB is widespread, however and we have very little information on their use in eastern European countries.

It has been proved that the concentrations of PCB's in Baltic wildlife is now decreasing (PAASIVIRTA and LINKO 1979). So far less attention has been paid to toxaphenes and chlordanes in Baltic environment. These compounds are, however, in use in eastern European countries, their use being banned in Sweden and Finland.

Chlordanes and toxaphenes have been found in seals, birds and fish in the Baltic area (JANSSON et al. 1979, WICKSTRÖM et al. HELLE et al. 1982), but so far no time trend analysis on their concentrations has been reported.

The analysis of toxaphenes and chlordanes being mixtures of tens of compounds is laborious and needs sophisticated instrumentation like high resolution GLC-selected ion monitoring mass spectrometry. Toxaphenes were suspected to be found in most Baltic animals at low levels, however, the concentrations of these compounds in the samples analysed in this work were too low for exact quantitative and time trend analysis. Chlordanes which are mainly a mixture of α- and γ-chlordanes, oxychlordane (chiefly by metabolism) and trans-nonachlor, were, however, determined

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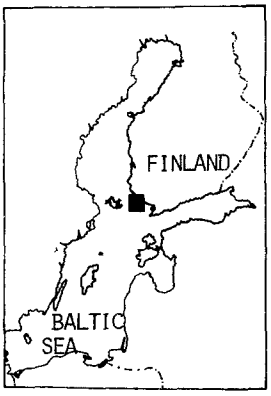
with higher accuracy. The fish studied were pike (Esox lucius), averaging 1 kg in weight and baltic herring (Clupea harengus), economically the most important fish in the northern Baltic area.

The first pike samples were collected in 1971 and the latest in winter 1982. Samples were deepfrozen until 1982. The Baltic herring samples covered only the years 1978-82, but the time trends analysis of PCB's and DDT's in Baltic herring in 1972-78 has been published before (PAASIVIRTA and LINKO 1980).

EXPERIMENTAL

Two grams of the fish sample were homogenized with ten grams of anhydrous sodium sulphate. Heptachlor was added as an internal standard (1 mg/kg). The homogenate was extracted at 25°C once with 35 ml of acetone-hexane (25 + 10 ml) and twice with 20 ml of hexane-diethyl ether (18 + 2 ml) for 30 minutes in an ultrasonic bath. The extracts were filtered, combined and shaken in a separatory funnel with 0.9 % sodium chloride in 75 ml of water. The aqueous layer was extracted with hexane (10 ml), whereas the organic layers were combined and 10 ml of absolute ethyl alcohol was added. The solvents were evaporated at 40°C in vacuo, the solid residue was dissolved in 2 ml of hexane and 2 ml of concentrated sulphuric acid was added. After shaking, the mixture was centrifuged and the organic layer separated. The sulphuric acid was added. After shaking, the mixture was centrifuged and the organic layer separated. The sulphuric acid cleaning procedure was repeated until the acidic layer was colourless.



The purified hexane concentrate was fractioned using a Silica gel column (10 mm x 300 mm, Kieselgel 60, 0,063 - 0,200, Merck). The silica was first heated at 360°C for 16 hours after which 3 % water was added. The column was eluted with 60 ml hexane then 60 ml hexane-diethyl ether (75:25 v/v). The fractions collected were combined and evaporated at 25°C in vacuo to 200 µl.

Figure 1. Sampling area

The sample was further cleaned by thin layer chromatography using Silica gel plates (Kieselgel 60, Merck) and a dichloromethan-hexane (1:3 v/v) solvent

system. The analyzed compounds were removed from the plates, the silica material (R_f= 0.3-1.0) was packed in a Pasteur pipette with a glass wool plug and eluted from this column with 4 ml of cyclohexane-diethylether (6:4 v/v). The eluate was subsequently concentrated in a gentle flow of nitrogen to 200 µl.

The final concentrate was analysed with the aid of high resolution gas chromatography/selective ion monitoring (HRGLC-SIM, mass fragmentography), A 30 m (i.d:0.25 mm) OV-101 glass capillary column. The GLC oven was temperature programmed from 120 to 240°C, 15°C per minute.

The monitored ions were m/e = 237 (particularly for determining p,p'-DDT, p,p'-DDD, oxychlordane, α- and γ-chlordane and trans-nonachlor), 248 (p,p'-DDE), 263 (aldrine, oxychlordane, α- and γ-chlordane and trans-nonachlor), 272 (heptachlor), 283 (trans-nonachlor), 324 (PCB), 341 (chlorinated terpenes and chlordanes), 343 (chlorinated terpenes), 358 (PCB) and 377 (α- and γ-chlordane and chlorinated terpenes).

In ambiguous cases the identifications were confirmed by selective ion monitoring of the six most prominent ions in the mass spectrum of an individual compound.

The retention times of the identified compounds were identical with those of reference compounds supplied by the U.S. Environmental Protection Agency.

The quantitative determinations were based on comparisons of the peak areas obtained from the samples with those obtained from reference standard solutions. The peak area of the internal standard heptachlor was taken into account in calculating the final concentrations by use of appropriate response factors.

The sensitivity of the method was about 10 µg per kilo for the studied compounds, when no interferring compounds were present, even higher sensitivity was occasionally obtained.

Fat content of the samples was analysed according to method of AOAC (1980).

The regression models were computed using stepwise regression analysis using the SCSS-programm (NIE 1980).

The essential results are presented in tables 1-2 and figures 2-3.

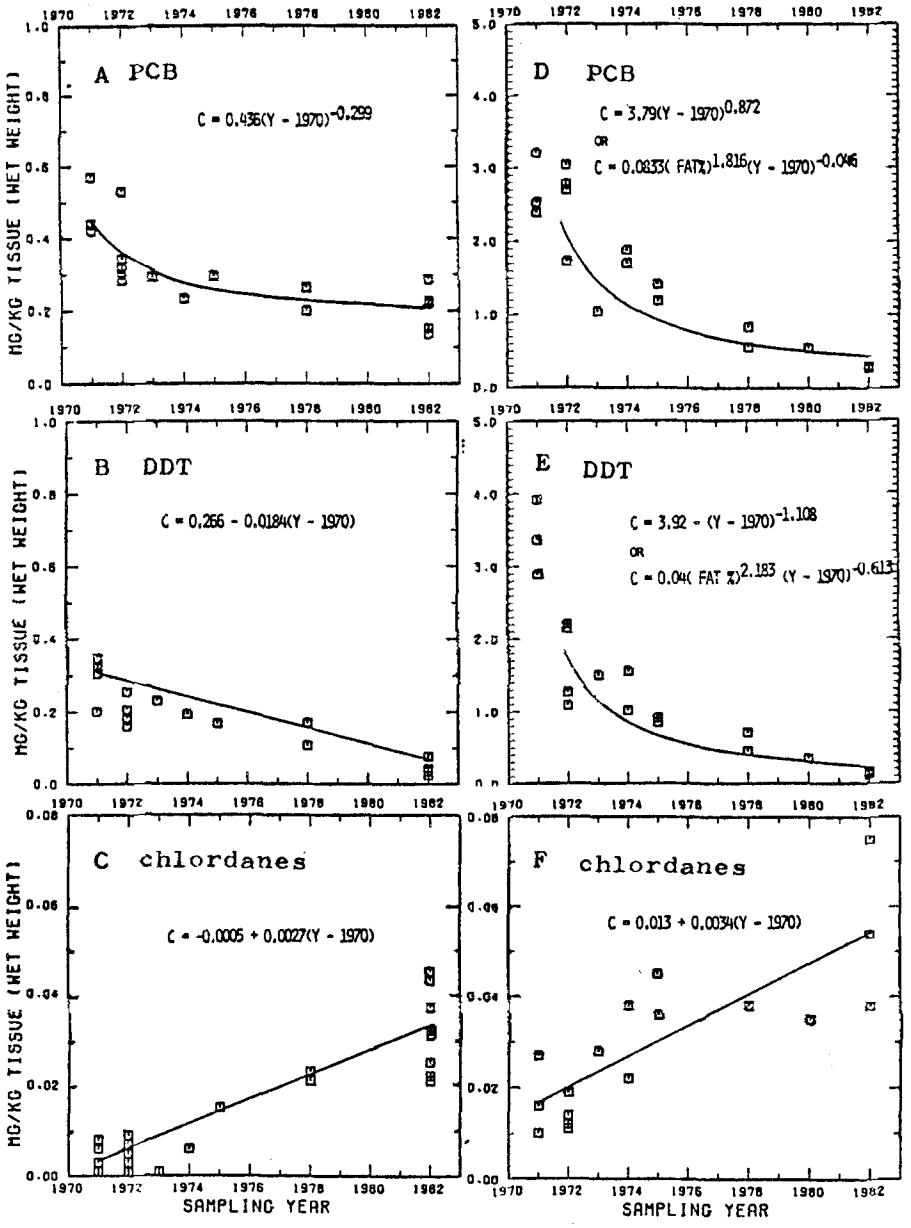


Figure 2. Concentrations of ∑PCB-, ∑DDT- and chlordane-compounds in pike tissue 1971-82 (A,B,C) and in pike liver (D,E,F) and the corresponding equations (C = concentration, mg/kg, Y = year)

Table 1. ΣPCB-, ΣDDT- and chlordane-concentrations (mg/kg) on the basis of fat content in the pike samples.

weight g	sex	sampling time	tissue fat %	fat % liver	in muscle tissue ∑PCB	∑DDT	Chlordanes	in liver tissue ∑PCB	∑DDT	Chlordanes
920	f	1971	0.80	8.08	71.2	40.3	0.38	39.6	35.8	0.20
1170	m	1971	0.78	7.75	56.4	25.8	0.13	31.9	50.4	0.13
1100	m	1971	0.70		59.1	49.7	0.86			
1035	m	1971	0.77	7.25	54.7	39.6	1.04	34.8	46.4	0.36
1070	f	1972	0.73	6.75	72.6	21.9	0.96	25.6	16.2	0.21
920	m	1972	0.69		43.8	30.2	1.30			
1100	m	1972	0.67	6.83	47.5	27.6	0.75	39.5	31.4	0.16
700	m	1972	0.75		45.6	21.5	0.13			
900	f	1972	0.69	7.00	49.9	25.8	0.44	43.4	31.5	0.27
800	m	1972	0.71	6.93	40.1	28.2	0.14	40.1	18.3	0.17
650	m	1973	0.74	6.05	39.7	31.2	0.14	17.3	24.8	0.46
1200	m	1974	0.78	6.81	30.0	24.9	0.77	27.6	22.9	0.56
1110	f	1975	0.77	6.39	38.6	21.8	1.95	22.2	14.3	0.70
1100	m	1978	0.80	6.11	33.0	21.3	2.63	9.2	11.7	0.62
1190	f	1978	0.74	5.88	27.0	14.6	3.11	14.2	7.76	0.65
950	m	1982	0.72		21.1	4.86	5.14			
1200	m	1982	0.75	3.43	29.9	5.87	4.13	7.84	3.56	1.11
1125	f	1982	0.75	3.52	30.7	3.52	2.39	8.21	4.38	2.13
895	m	1982	0.70	4.53	31.6	3.43	6.28	6.78	3.91	1.19
1100	m	1982	0.71		30.9	10.8	3.52			
750	f	1982	0.70		19.6	5.28	6.43			
950	m	1982	0.75		38.1	10.4	5.73			
960	m	1982	0.73		31.2	4.93	4.38			

Sampling time	Weight g	Fat %	∑PCB	∑DDT	Chlordanes
1978	78.1	3.7	16.6	6.3	0.49
1978	65.5	3.6	18.5	5.3	0.58
1978	80.2	3.6	18.8	7.2	0.28
1978	79.7	5.5	12.0	8.9	0.22
1978	63.2	3.2	19.2	5.2	0.53
1978	80.9	4.8	16.0	6.1	0.21
1978	79.4	5.7	12.4	7.6	0.37
1978	78.2	4.4	14.2	7.5	0.61
1982	77.2	7.0	6.7	2.4	0.56
1982	79.7	7.6	3.0	2.4	0.51
1982	60.3	5.3	5.2	1.7	0.83
1982	65.5	7.0	4.4	1.8	0.54
1982	61.6	6.7	4.6	2.2	0.39
1982	63.2	6.0	4.4	1.9	0.42
1982	75.5	7.7	3.5	2.6	0.69

Table 2. ∑PCB-, ∑DDT- and chlordane-concentrations (mg/kg) on the basis of fat content in Baltic herring.

The time trends of PCB and DDT compounds during the years 78-82 are in accordance with and are the logic continuation of the results from 72-78 presented earlier by PAASIVIRTA and LINKO (1980): the concentrations of DDT- and PCB-compounds is decreasing in Baltic fishes. It seems, however, that the decrease in PCB levels is not any more rapid than that presented for the years 72-78. Conversely the increase of chlordane concentrations in fish is clearly seen in the figures and tables.

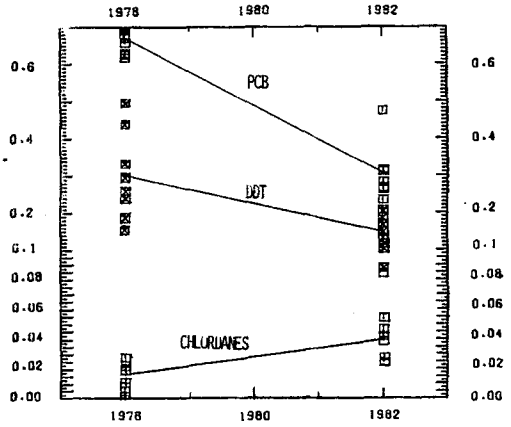


Figure 3. Concentrations of ∑PCB-, ∑DDT- and chlordane-compounds in Baltic herring muscle tissue 1978-82.

In the mixture of different DDT compounds the proportion of p,p'-DDE dominates. The mixture of chlordanes is more complicated. In this work the sum of oxychlordane, α- and γ-chlordane and trans-nonachlor was calculated. The ratio of these compounds varied considerably in muscle and liver tissues, as seen in Table 3.

Table 3. The relative concentration of chlordanes in pike

	muscle tissue	liver tissue
oxychlordane	14.8 %	35.1 %
γ-chlordane	33.9	28.4
α-chlordane	36.6	22.2
trans-nonachlor	14.7	14.3

The results in Table 3 give an indication that oxychlordane is formed in living organisms via metabolism.

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