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# Chlorinated Hydrocarbons and Mercury in Aquatic Vascular Plants of Lake Päijänne, Finland

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This paper is a part of a study of the chlorinated hydrocarbons and mercury residues in the food webs of Lake Päijänne. The purpose was to search differences in the residue levels between the regions, years (1972-1974), species and trophic levels. Mercury has been discharged into the lake near to stat. 1 and 2 (Figure 1) till year 1968 as slimicides of the wood-processing industry. PCB and DDT have not been used in particularly great amounts in the drainage area flowing into this lake. The total use of PCB in Finland was in 1969 about 240 tons (RAUTAPÄÄ 1972) and of DDT from 1953 to 1971 229 tons (MARKKULA 1972) and the use of DDT has been nearly totally prohibited since 1971.

## MATERIALS AND METHODS

### Sampling

Samples were taken by diving, with a dredge or by picking from four areas (Figure 1) and the material consisted of the regionally most abundant species of which parts were gathered from both above and below the water surface. No roots or other subterranean parts were taken. Sampling was done mainly in August. Species growing above the shore-line were not taken. Epiphytic algae growing on plants were not removed but their portion in the whole biomass was extremely small in other species but Utricularia and Myriophyllum. The plants were frozen in 1-3 l plastic bags which did not contain PCB.

### Analyses of chlorinated hydrocarbons

The plants were dried in 75°C for 10 hours and homogenized in Sorvall Omnimixer and applied for the extraction.

The fat extraction was carried out as described by HATTULA (1974) and the solvent system used was the mixture of n-hexane, acetone, diethylether and petroleumether (bp. 40-60°) 2.5 : 5.5 : 1 : 9 (v/v). The clean up was carried out by three methods, treatment with sulphuric acid and chromic acid, TLC and column chromatography (HATTULA 1973).

The final analysis was carried out by GLC with Varian Model 600 with EC-detector. The column was 1.5 m x 1.5 mm and the filling was the mixture of 65 parts 8% QF-1 and 35 parts 4% SF-96

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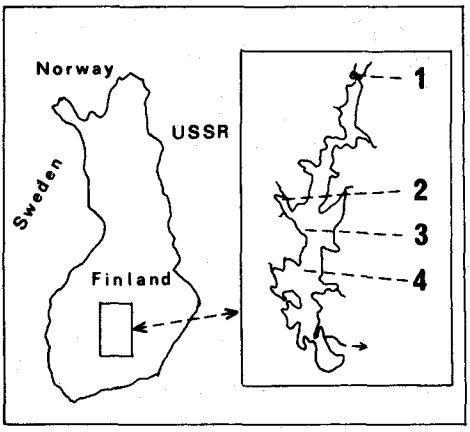


FIGURE 1. Lake Päijänne and the sampling stations.

on Chromosorb W 100-120 mesh. Pure nitrogen (99.99%) was used as carrier gas and the column temperature was 180°C, the detector and injector 190 and 225°, respectively. Clophen A 60 (Bayer) was used as PCB standard and the pesticide standards were from Analytical Standards (100% purity). The quantitative determination of the chlorinated hydrocarbons was carried out as described by HATTULA (1973).

Analyses of mercury

The total mercury determination was made by flameless atomic absorption with Coleman MAS-50 mercury analyzer. 1-2 g wet tissue was homogenated in an erlenmeyer flask in 0.5 ml water and 10 ml concentrated sulphuric acid (Merck, p.a.) was added. The flask was kept in an ice-bath. The flask was then covered with a plastic film and kept in 60°C for 4 hours. After cooling 15 ml $KMnO_4$ (6%) was added from a burette and the flask was stirred in the ice bath. The sample was diluted to 100 ml and 2 ml hydroxylaminhydrochloride (20%) and 1 ml $SNCl_2$ (40% in 5% sulphuric acid) were added and the measuring was carried out immediately. $HgCl_2$ (Merck, p.a.) was used as a standard.

## RESULTS

In Table 1 are presented the results of the whole material. As seen from Table 2, the average concentration of mercury was higher than the average of chlorinated hydrocarbons of which the value of PCB was highest. In ΣDDT (DDE+DDD+DDT) DDE is the main component. As to DDD, lindan and dieldrin the concentrations in no case exceeded the lowest measurable contents, 0.5 µg/kg dry

weight. The wet weight of the plants was on an average 5.8 times the dry weight.

TABLE 1

Contents of different residues as µg/kg dry weight in the plant samples. Stations as in Figure 1. Species:

1 Isoetes lacustris L.
2 Equisetum fluviatile L.
3 Alisma plantago-aquatica L.
4 Sagittaria sagittifolia L.
5 Potamogeton perfoliatus L.
6 P. natans L.
7 Typha latifolia L.
8 T. angustifolia L.
9 Sparganium angustifolium Michx.
10 S. simplex (L.) Huds.
11 S. erectum L.
12 Iris pseudacorus L.
13 Scirpus lacustris L.
14 Eleocharis palustris (L.) RBr.
15 Carex acuta L.
16 Phragmites communis Trin.
17 Glyceria maxima (Hn) Holmb.
18 Polygonum amphibium L.
19 Nymphaea candida Presl.
20 Nuphar luteum (L.) Sm.
21 Myriophyllum alterniflorum DC.
22 Utricularia vulgaris L.
23 Lobelia dortmanna L.

| Species | Mercury | PCB | DDE | DDT | ΣDDT | Aldr. |
|---|---|---|---|---|---|---|
| | Stat. 1 8.IX.1972 | | | | | |
| 6 | - | 76 | 0 | 0 | 0 | 0 |
| 10 | 139 | 244 | 0 | 0 | 0 | 0 |
| 11 | 52 | 52 | 0 | 0 | 0 | 0 |
| 16 | 35 | 267 | 0 | 0 | 0 | 0 |
| 17 | 122 | 331 | 0 | 0 | 0 | 0 |
| 18 | 17 | 46 | 0 | 0 | 0 | 0 |
| | Stat. 2 1.VIII.1972 | | | | | |
| 2 | 12 | 8 | 1 | 0 | 1 | 0 |
| 4 | - | 105 | 7 | 0 | 7 | 0 |
| 5 | 8 | 7 | 4 | 1 | 5 | 0 |
| 6 | - | 9 | 4 | 1 | 5 | 0 |
| 13 | 15 | 6 | 7 | 1 | 8 | 0 |
| 16 | - | 8 | 1 | 1 | 2 | 0 |
| 17 | 62 | 5 | 8 | 1 | 9 | 0 |
| 19 | - | 7 | 6 | 0 | 6 | 0 |
| 20 | 11 | 5 | 3 | 0 | 3 | 0 |
| 22 | 122 | 44 | 2 | 0 | 2 | 0 |
| | Stat. 3 30.VIII.1972 | | | | | |
| 2 | - | 12 | 0 | 0 | 0 | 0 |
| 44 | - | 17 | 0 | 0 | 0 | 0 |
| 6 | - | 12 | 0 | 0 | 0 | 0 |
| 10 | - | 12 | 0 | 0 | 0 | 0 |
| 16 | - | 29 | 0 | 0 | 0 | 0 |
| 18 | - | 12 | 0 | 0 | 0 | 0 |
| 20 | - | 12 | 0 | 0 | 0 | 0 |

TABLE 1 continued:

| Species | PCB | DDE | DDT | ΣDDT | Aldr. |
|---|---|---|---|---|---|
| Stat. 4 2.VIII.1972 | | | | | |
| 1 | 41 | 6 | 4 | 10 | 0 |
| 2 | 9 | 3 | 1 | 4 | 0 |
| 3 | 21 | 6 | 1 | 7 | 0 |
| 4 | 17 | 7 | 7 | 14 | 0 |
| 6 | 8 | 2 | 2 | 4 | 0 |
| 7 | 12 | 2 | 3 | 5 | 0 |
| 10 | 12 | 9 | 2 | 11 | 0 |
| 16 | 7 | 1 | 2 | 3 | 0 |
| 18 | 6 | 4 | 0 | 4 | 0 |
| 20 | 7 | 1 | 2 | 3 | 0 |
| 21 | 23 | 4 | 3 | 7 | 0 |
| 23 | 10 | 9 | 5 | 14 | 0 |
| Stat. 1 4.IX.1973 | | | | | |
| 7 | 13 | 0 | 0 | 0 | 0 |
| 10 | 22 | 11 | 0 | 11 | 10 |
| 11 | 15 | 1 | 0 | 1 | 3 |
| 13 | 12 | 4 | 0 | 4 | 10 |
| 14 | 30 | 2 | 0 | 2 | 2 |
| 16 | 12 | 1 | 1 | 2 | 0 |
| 17 | 11 | 1 | 0 | 1 | 0 |
| 18 | 16 | 2 | 0 | 2 | 17 |
| 20 | 21 | 1 | 0 | 1 | 36 |
| Stat. 2 17.VIII.1973 | | | | | |
| 2 | 10 | 8 | 0 | 8 | 0 |
| 6 | 11 | 6 | 0 | 6 | 0 |
| 13 | 7 | 3 | 1 | 4 | 15 |
| 16 | 7 | 3 | 2 | 5 | 1 |
| 17 | 8 | 5 | 1 | 6 | 11 |
| 20 | 5 | 6 | 0 | 6 | 0 |
| 22 | 1 | 4 | 0 | 4 | 0 |
| Stat. 3 18.VIII.1973 | | | | | |
| 2 | 7 | 1 | 1 | 2 | 0 |
| 4 | 45 | 3 | 0 | 3 | 0 |
| 5 | 24 | 2 | 0 | 2 | 1 |
| 6 | 11 | 2 | 3 | 5 | 0 |
| 9 | 14 | 8 | 0 | 8 | 0 |
| 12 | 6 | 1 | 0 | 1 | 1 |
| 16 | 6 | 4 | 1 | 5 | 4 |
| 18 | 13 | 6 | 2 | 8 | 0 |
| 21 | 10 | 7 | 1 | 8 | 0 |
| 21 | 18 | 12 | 6 | 18 | 0 |
| Stat. 4 6.VIII.1973 | | | | | |
| 3 | 16 | 1 | 1 | 2 | 0 |
| 6 | 9 | 7 | 0 | 7 | 9 |
| 7 | 8 | 1 | 0 | 1 | 0 |
| 9 | 20 | 12 | 0 | 12 | 17 |
| 11 | 11 | 8 | 0 | 8 | 13 |
| 13 | 7 | 5 | 1 | 6 | 0 |
| 16 | 13 | 3 | 4 | 7 | 0 |
| 18 | 8 | 6 | 0 | 6 | 0 |
| 20 | 10 | 10 | 0 | 10 | 9 |
| 21 | 11 | 3 | 3 | 6 | 0 |
| Stat. 1 13.IX.1974 | | | | | |
| 10 | 14 | 2 | 0 | 2 | 0 |
| 11 | 4 | 0 | 0 | 0 | 0 |
| 13 | 5 | 1 | 0 | 1 | 0 |
| 15 | 4 | 1 | 0 | 1 | 0 |
| 16 | 9 | 1 | 0 | 1 | 0 |
| 17 | 12 | 2 | 0 | 2 | 0 |
| 18 | 10 | 1 | 0 | 1 | 0 |
| 19 | 9 | 1 | 0 | 1 | 0 |
| 20 | 4 | 1 | 0 | 1 | 0 |
| Stat. 2 7.VIII.1974 | | | | | |
| 2 | 0 | 0 | 0 | 0 | 0 |
| 6 | 0 | 0 | 0 | 0 | 0 |
| 8 | 5 | 0 | 0 | 0 | 2 |
| 10 | 3 | 0 | 0 | 0 | 0 |
| 13 | 0 | 0 | 0 | 0 | 0 |
| 17 | 3 | 0 | 0 | 0 | 0 |
| 19 | 0 | 0 | 0 | 0 | 0 |
| 20 | 0 | 0 | 0 | 0 | 0 |
| 22 | 0 | 0 | 0 | 0 | 0 |
| Stat. 3 6.VIII.1974 | | | | | |
| 2 | 4 | 0 | 0 | 0 | 0 |
| 3 | 5 | 0 | 1 | 1 | 0 |
| 4 | 102 | 0 | 0 | 0 | 0 |
| 5 | 4 | 0 | 0 | 0 | 0 |
| 6 | 11 | 0 | 0 | 0 | 0 |
| 10 | 8 | 0 | 0 | 0 | 0 |
| 12 | 0 | 0 | 0 | 0 | 0 |
| 16 | 7 | 0 | 2 | 2 | 0 |
| 18 | 3 | 0 | 0 | 0 | 0 |
| 20 | 2 | 0 | 0 | 0 | 23 |
| 21 | 7 | 0 | 0 | 0 | 0 |
| Stat. 4 8.VIII.1974 | | | | | |
| 1 | 0 | 0 | 0 | 0 | 0 |
| 3 | 5 | 1 | 0 | 1 | 0 |
| 6 | 4 | 1 | 0 | 1 | 0 |
| 7 | 4 | 0 | 0 | 0 | 0 |
| 9 | 10 | 2 | 0 | 2 | 0 |
| 10 | 9 | 1 | 0 | 1 | 0 |
| 13 | 0 | 0 | 0 | 0 | 0 |
| 16 | 0 | 0 | 0 | 0 | 0 |
| 18 | 0 | 0 | 0 | 0 | 0 |
| 19 | 2 | 0 | 0 | 0 | 0 |
| 20 | 2 | 0 | 0 | 0 | 0 |

TABLE 2

Means, standard deviations (S.D.), n, minimums and maximums of contents of different residues as µg/kg dry weight.

| | Mean | S.D. | n | Min. | Max. |
|---|---|---|---|---|---|
| Mercury | 54 | 51 | 11 | 8 | 122 |
| PCB | 20 | 47 | 112 | 0 | 331 |
| DDE | 2 | 3 | 114 | 0 | 12 |
| DDT | 1 | 1 | 114 | 0 | 7 |
| ΣDDT | 3 | 4 | 114 | 0 | 18 |
| Aldrin | 2 | 5 | 114 | 0 | 36 |

The differences between the years were significant in the contents of PCB, ΣDDT and aldrin (Table 3) when the whole material from each year was compared ($p < 0.001$, analysis of variance). The contents of PCB showed to be decreasing from 1972 to 1974. The mean of ΣDDT of 1974 was significantly ($p < 0.001$) smaller than in two preceeding years when tested by t-tests. However, the differences in regional distribution of the samples may have an effect on these annual differences. When annual differences were considered in the contents of PCB and ΣDDT in each of the species separately some differences with significance of $p < 0.05$ or $p < 0.01$ were found. However, due to the small size of these test groups and the regional differences these differences must not be much emphasized.

Some regional differences could be found (Table 4) if the whole material were considered without noticing the annual differences. The contents of PCB was highest in stat. 1, the contents of ΣDDT in stat. 4 and the contents of aldrin in stat. 1 (in 1973). The differences were in some cases significant ($p < 0.05$) but also the effect of annual differences may cause confusion, as well as the differences between the species. Within the species no remarkable regional differences, however, could be shown.

When the differences between the plant species were considered, significant ($p < 0.05$) paired differences in the PCB contents were found in a few cases, in the ΣDDT contents only one time. Because of the small sample number of every species and because of the effect of the regional and annual variation clear differences in the contents between the species could not be shown.

The species were also divided into life-forms: isoetids (species no 1 and 23, Table 1), elodeids (5, 21, 22), nymphaeids (6, 9, 18-20) and helophytes (2-4, 7, 8, 10-17) the average residue contents of which are presented in Table 5. The differences between these groups were, however, not significant according to the analyses of variance. The contents of ΣDDT was according to t-tests in isoetids significantly higher than in nymphaeids and helophytes ($p < 0.05$).

Of the correlations between mercury, PCB and ΣDDT only that between mercury and PCB was significant ($r = 0.610$, $df = 9$, $p < 0.05$). This fact may due to the small number of mercury

analyses and to the regionally uneven material. The correlation between fat contents and lipid-soluble chlorinated hydrocarbons was not significant.

TABLE 3

Annual means, standard deviations (S.D.) and n of the residue contents as µg/kg dry weight.

| | Year | 1972 | 1973 | 1974 |
|---|---|---|---|---|
| Mercury | Mean | 9 | - | - |
| | S.D. | 8 | - | - |
| | n | 11 | | |
| PCB | Mean | 43 | 13 | 7 |
| | S.D. | 78 | 8 | 16 |
| | n | 36 | 37 | 41 |
| ΣDDT | Mean | 4 | 5 | 0 |
| | S.D. | 4 | 4 | 1 |
| | n | 36 | 37 | 41 |
| Aldrin | Mean | 0 | 5 | 1 |
| | S.D. | 0 | 8 | 4 |
| | n | 36 | 37 | 41 |

TABLE 4

Regional means, standard deviations (S.D.) and n of the residue contents as µg/kg dry weight.

| | Stat. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| Mercury | Mean | 73 | 38 | - | - |
| | S.D. | 54 | 46 | - | - |
| | n | 5 | 6 | - | - |
| PCB | Mean | 52 | 10 | 15 | 10 |
| | S.D. | 91 | 21 | 19 | 8 |
| | n | 24 | 26 | 28 | 33 |
| ΣDDT | Mean | 1 | 3 | 2 | 5 |
| | S.D. | 2 | 3 | 4 | 4 |
| | n | 24 | 26 | 28 | 33 |
| Aldrin | Mean | 3 | 1 | 0 | 2 |
| | S.D. | 8 | 4 | 1 | 4 |
| | n | 24 | 26 | 28 | 33 |

TABLE 5

Means, standard deviations (S.D.) and n of the residue contents in different life-forms as µg/kg dry weight.

| | | Isoetids | Elodeids | Nymphaeids | Helophytes |
|---|---|---|---|---|---|
| Mercury | Mean | - | 65 | 14 | 62 |
| | S.D. | - | 81 | 4 | 50 |
| | n | - | 2 | 2 | 7 |
| PCB | Mean | 17 | 13 | 11 | 27 |
| | S.D. | 21 | 13 | 14 | 62 |
| | n | 3 | 11 | 37 | 61 |
| ΣDDT | Mean | 8 | 4 | 3 | 3 |
| | S.D. | 7 | 5 | 3 | 3 |
| | n | 3 | 11 | 37 | 61 |
| Aldrin | Mean | 0 | 0 | 3 | 1 |
| | S.D. | 0 | 0 | 8 | 3 |
| | n | 3 | 11 | 37 | 61 |

## DISCUSSION

The regional differences which are shown indicate that PCB has been discharged near stat. 1 but its origin in town of Jyväskylä is unknown. Because the regional differences in the contents of other residues but PCB are comparatively small, the contents of ΣDDT and aldrin can be assumed to indicate the background level at this region. The temporal decreasing direction in the concentration of PCB and ΣDDT may due to their decreased usage. The regional and annual differences and differences between species generally are very small and the results can be considered mainly to show the order of magnitude of the contents of the residues studied.

The comparisons with other corresponding investigations which are small in number, show that the mean of mercury (9 µg/kg w.w. = wet weight, 54 µg/kg d.w. = dry weight) and even the maximum value in Päijänne (24 µg/kg w.w., 139 d.w.) are small if compared with the values reported by CUMONT & MONTIEL (1972) and JOHNELS et al. (1967) (28-3700 µg/kg). The mean contents of PCB in Päijänne, 20 µg/kg d.w., is much smaller than obtained by VAQUER (1973) but the maximum 331 µg/kg d.w. is of the same order. In a polluted marine region PARKER & WILSON (1975) found PCB in algae 30-340 µg/kg w.w. which corresponds dry weight values of about 150-1700 µg/kg, and these values are much higher than the values found in Päijänne. The mean 3 and maximum 18 µg/kg d.w. of ΣDDT in Päijänne are much smaller than the values in the region of Camarque according to VAQUER (1973).

The ratio ΣDDT/PCB which has been considered in some studies, is on an average 0.15 (cf. e.g. RISEBROUGH et al. 1968, NELSON et al. 1972).

As possible sources of errors and causes of variation can be mentioned the algae fastened on the plants which possibly can absorb the residues. This fact has been observed in the studies of mercury e.g. by HANNERZ (1968). Variations can also be due to differences between the different parts of the plants which has been proved e.g. by HANNERZ (1968) and VAQUER (1973). Also the fat contents can vary between the species and cause variations in lipid soluble residues, which was not, however, observed in the present study.

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