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Chlorinated Hydrocarbons in the Lake Ontario Ecosystem (IFYGL)

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CHLORINATED HYDROCARBONS IN THE LAKE ONTARIO ECOSYSTEM (IFYGL)

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ABSTRACT

Lake Ontario fish, water, sediment, net plankton, Cladophora, and benthos were examined for DDT group pesticides, dieldrin, and PCBs. Endrin, BHC group pesticides, and heptachlor were also identified in some fish samples. Average concentrations ranged from 28 ng/l (t-DDT, e.e., sum of DDT, DDE, and DDD), 4.8 ng/l (dieldrin), and 55 ng/l (PCBs as Aroclor 1254 equivalent) for water to 1.40 µg/g (t-DDT), 0.07 µg/g (dieldrin), and 5.15 µg/g (PCBs) for whole fish. DDE levels were generally similar to t-DDT levels, except for sediments where DDD and DDT contributed significantly to t-DDT values. PCB/t-DDT ratios averaged 2.6 for all samples except for sediment (7.0) and benthos (5.3).

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ACKNOWLEDGEMENTS

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SECTION I

CONCLUSIONS

Lake Ontario fish, water, sediment, net plankton, Cladophora, and benthic fauna contained significant concentrations of DDT group pesticides, dieldrin, and PCBs. Endrin, heptachlor, and BHC group pesticides (especially lindane, γ BHC) were also identified in some fish.

Lake-wide concentrations of t-DDT, dieldrin, and PCBs (Arochlor 1254 equivalent) for fish (alewives, smelt, and slimy sculpin) ranged from 0.95 to 1.40 µg/g, 0.04 to 0.07 µg/g, and 2.35 to 5.13 µg/g, respectively.

Lake Ontario water was found to contain "total" concentrations (dissolved + particulate) of 28 ng/l, 4.8 ng/l, and 55 ng/l for t-DDT, dieldrin, and PCBs. Water collected off Oswego contained comparatively high levels of DDT group pesticides, dieldrin, and PCBs, while waters off Hamilton contained higher t-DDT levels, and waters off the mouth of the Niagara River showed higher PCB concentrations.

Average sediment t-DDT, dieldrin, and PCB concentrations were 22, 1.2, and 120 ng/g, respectively. Sediment off the mouth of the Welland Canal showed higher levels of all three contaminants while sediments off the mouth of the Niagara River contained higher levels of PCBs and dieldrin. Sediments off Oswego and at an eastern mid-lake site showed higher levels of PCBs and dieldrin, respectively.

Average concentrations in net plankton were 3.5 µg/g (t-DDT), 0.12 µg/g (dieldrin), and 7.2 µg/g (PCBs). Corresponding concentrations in Cladophora were 229, 13, and 515 ng/g for t-DDT, dieldrin, and PCBs, respectively. Lake Ontario benthic fauna were found to contain 99, 6.9, and 471 ng/g t-DDT, dieldrin, and PCBs, respectively, with benthos taken off Hamilton exhibiting levels approximately four times benthos off Rochester and Oswego.

High concentrations of PCBs in waters and sediments off the mouth of the Niagara River and Oswego indicate the importance of the Niagara and Oswego Rivers as inputs of PCBs associated with settlable particulates. In most cases, t-DDT concentrations were similar to concentrations of the DDT metabolite, DDE, except in sediments where DDT and DDD contributed much larger fractions.

PCB/t-DDT ratios for all samples fell in the range of 1.9 to 3.1 except for sediment (7.0) and benthos (5.3).

Relative chlorinated hydrocarbon concentrations for various segments of the Lake Ontario ecosystem were about 1; 2,500; 10,000; 150,000; and 300,000 for water, sediment, benthos, net plankton, and fish, relatively. Although these concentration differences indicated large accumulation factors for chlorinated hydrocarbons in fish, considerable additional information is required to elucidate mechanisms of chlorinated hydrocarbon transport and accumulation that will allow an assessment of the probable impact on the aquatic ecosystem when contaminant inputs to the lake are altered.

SECTION II

RECOMMENDATIONS

Although Lake Ontario fish contained accumulated chlorinated hydrocarbons at levels several orders of magnitude higher than amounts in their food organisms and the lake water, processes of uptake and elimination of these contaminants by fish are uncertain. The mechanisms controlling these processes should be determined and their relative importance evaluated to aid in understanding the relationships between contaminant concentrations in water and in the associated biota. The elucidation of these relationships will allow an assessment of the probable impact on the aquatic ecosystem when contaminant inputs to the lake are altered.

Since chlorinated hydrocarbons associated with the dissolved and particulate (organic and inorganic) fractions of lake waters may interact differently within the lake ecosystem, analytical methods should be developed to separate and quantitate the contaminant concentrations in these fractions.

Lake Ontario waters and sediments near the mouths of the Niagara and Oswego Rivers were found to contain significantly higher concentrations of PCBs than the other waters and sediments sampled. This indicated the necessity to determine the levels and forms (dissolved or associated with particulates) of PCBs in these rivers to allow an assessment of their importance as sources of PCBs to the Lake Ontario ecosystem.

Since fish are capable of accumulating chlorinated hydrocarbon concentrations several orders of magnitude higher than the surrounding water, Lake Ontario fish should be extensively examined for halogenated hydrocarbons not previously identified or confirmed in fish. Some compounds, although present in lake waters at undetected levels, may be of considerable importance due to their toxicities even at very low levels.

SECTION III

INTRODUCTION

Measurements of pesticide residues in the Great Lakes have shown excessive levels of several chlorinated hydrocarbons. Polychlorinated biphenyls (PCBs) and DDT group pesticides (i.e., DDT, DDE, DDD, and related isomers) have been confirmed in Lake Michigan fish at levels exceeding U.S. Food and Drug Administration action limits, and dieldrin has been found at levels approaching the action limit (Veith, 1970; Reinert, 1970). The pesticide contamination problem in Lake Ontario has received less attention than in Lake Michigan where residue concentrations in several segments of the ecosystem may be higher (Reinert, 1970; Veith, 1973). Although studies of chlorinated hydrocarbon contamination in Lake Ontario fish have been conducted (Reinert, 1970; Kaiser, 1974), information concerning other segments of the ecosystem is incomplete.

This study was conducted as a part of the International Field Year for the Great Lakes to provide baseline information on the levels of DDT group pesticides, dieldrin, and PCBs in Lake Ontario fish, water, sediment, net plankton, Cladophora, and benthic fauna. This information will allow a more complete assessment of the chlorinated hydrocarbon problem in Lake Ontario and contribute to an understanding of chlorinated hydrocarbon transport in aquatic ecosystems.

SECTION IV

METHODS

SAMPLING

Alewives (Alosa pseudoharengus), smelt (Osmerus mordax), slimy sculpin (Cottus cognatus), water, sediment, net plankton, Cladophora, and benthos samples were obtained from several near-shore and mid-lake sites on Lake Ontario during the summer of 1972. Sampling was more intensive near Rochester, Oswego, and Hamilton. Samples were also collected off Cobourg and Olcott, at the eastern end of the lake, and at four mid-lake sites. Figure 1 shows the locations of the sampling stations. Water samples were taken (Van Dorn type sampler) just below the surface, at 10 m below the surface, and at 10 m above the sediment at each station. Fish were trawl-netted at 18 to 73 m and mixed plankton netted (64 um mesh opening) at 5 to 10 m. Cladophora was gathered at 1 to 2 m depths. Sediments were sampled with a Ponar grab, and benthos were captured using a epibenthic sled. All samples were transported and stored frozen or near $4^{o}C$ in glass or metal containers to minimize chemical changes and contamination.

EXTRACTION AND CLEANUP

Fish

Extraction and cleanup of whole fish were conducted according to the procedures described by Veith (1970). Frozen fish (a combined sample of at least eight individuals for each species captured at each site) were ground twice to homogenize the flesh before weighing out six 10 g sub-samples. Each sub-sample was blended with 70 g anhydrous Na_2SO_4 and extracted for at least 4 hr with 170 ml of 1:1 ethyl ether-hexane (v/v) in an all-glass Soxhlet extractor. The extracts were concentrated to 20 ml in an air stream and 2 ml aliquots were removed for analysis of non-volitile fats and oils (residue after evaporation at $150^{o}C$ for 20 min). The remaining extracts were subjected to liquid chromatographic cleanup and fractionation. The extracts were placed on 20 g columns of florisil (Fisher F-100, 60-100 mesh washed

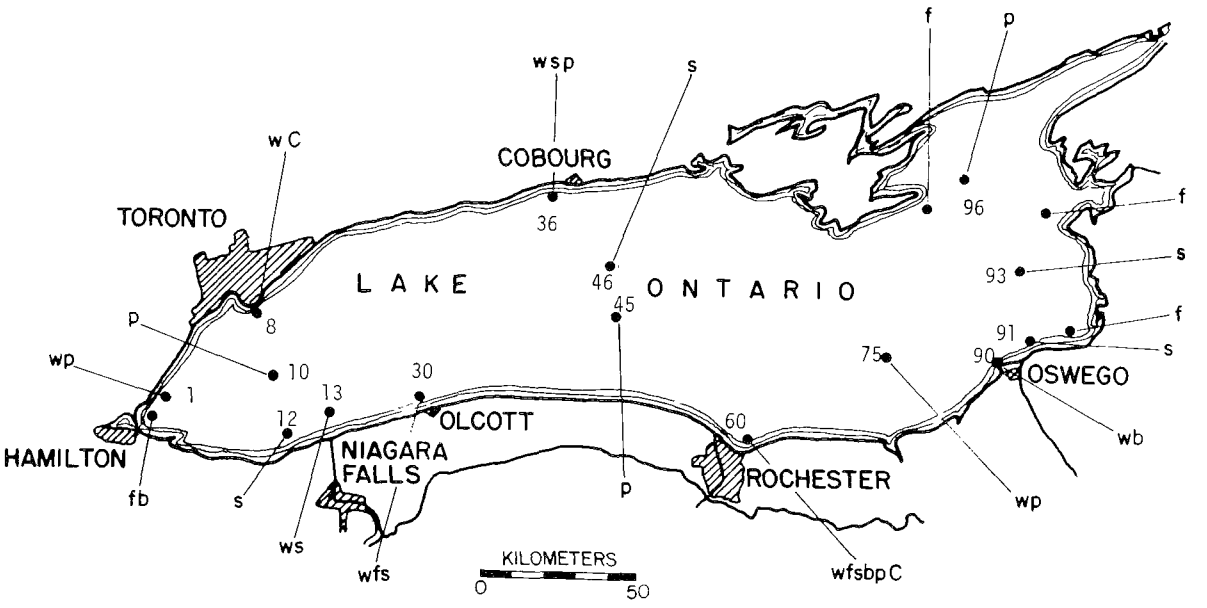

Figure 1. Lake Ontario sampling sites for chlorinated hydrocarbon analysis. Notations are: f-Fish, w-Water, s-Sediment, p-Net Plankton, C-Cladophora, b-Benthos. Station numbers are IFYGL station identifiers.

with hexane and activated by heating to 650°C for 2 hr) and topped with anhydrous Na_2SO_4 to prevent deactivation of the florisil by water. The columns were sequentially eluted with 200 ml each of 6, 12, and 50% ether in hexane (v/v). Since preliminary gas chromatographic analysis of the 12 and 50% eluates failed to provide identification of compounds of interest, notably dieldrin and endrin, which were identified in the 6% eluates, only the 6% eluates were considered for subsequent examination. The presence of dieldrin and endrin in the less polar fractions likely resulted from some deactivation of the florisil by water vapor prior to use. The 6% eluates were concentrated (air stream) to 50 ml before removing 5 ml aliquots for preliminary gas chromatographic determination of DDE (generally the largest peak on the chromatogram). The remaining portions were concentrated to less than 10 ml before placing on 20 g columns of silicic acid (washed with hexane, dried at 130°C overnight, and partially deactivated with 2.1% water). Elution with 250 ml hexane produced the PCB fractions. Further elution with 200 ml 3:1 dichloromethane-hexane (v/v) allowed elution of the chlorinated pesticide fractions. These fractions were evaporated in an air stream, hexane was added, and the fractions were re-evaporated. This process was repeated several times to insure complete removal of the dichloromethane.

Water

Each water sample (10 l) was extracted at the collection site by passage through a column of six polyurethane foam plugs at a flow rate of 250 ml/min using the procedure described by Uthe et al. (1972). Preparation of the plugs involved Soxhlet extractions (at least 4 hr) with 1:1 ethyl ether-hexane (v/v) to remove contaminants followed by coating the plugs with a 1% solution of DC-200 silicone oil in hexane and air-drying. Following extraction of water samples, the plugs were removed from the column and again extracted (4 hr) with 1:1 ether-hexane (v/v). The columns were rinsed several times with acetone. The combined extracts from the plugs and column rinsings were reduced to about 5 ml in an air stream before cleanup by liquid chromatographic procedures similar to those for cleanup of fish extracts.

Sediment

Samples were allowed to air dry at room temperature before weighing out six 25 g sub-samples for analysis. The sub-samples were thoroughly ground by mortar and pestle, mixed with anhydrous Na_2SO_4, and extracted with 170 ml 1:1 ether-hexane (v/v) in all-glass Soxhlet extractors for 4 hr. The extracts were concentrated to about 10 ml before liquid chromatographic cleanup in a manner similar to that used for fish extracts.

Net Plankton and Cladophora

Net plankton and Cladophora samples were transferred to tared centrifuge tubes and sub-divided into sub-samples of about 1 g where appropriate. After centrifuging at 2000 rpm for 25 min, the supernatant was decanted rapidly into separatory funnels, 2 ml acetone was added to each tube, and the samples were allowed to air-dry. The tubes were weighed and sample dry weights were determined by difference. Water decanted from each tube was extracted twice with 25 ml of hexane to recover materials released from the cells. A 35 ml portion of the extract was added to the corresponding sample tube and the tube was shaken periodically over a 36 hr period. The extract was decanted and the residue extracted a second time with a 35 ml portion of fresh hexane. The combined extracts were concentrated to 5 ml for cleanup by procedures similar to those for fish extracts.

Benthos

Mixed benthic fauna (largely Pontiporeia affinis) were dried at room temperature and separated into at least three 10 g aliquots before extraction and cleanup by procedures identical to those used for sediment samples.

PESTICIDE DETERMINATION

Qualitative Determination

Pesticide fractions of all fish and several water, sediment, plankton, Cladophora, and benthos extracts from silicic acid cleanup were

chromatographed (Varian Aerograph 1500 or 1700) on four gas chromatographic (GC) columns eluting into electron capture detectors (^{3}H or ^{63}Ni) to allow multiple column peak-matching identification of fraction components. The GC columns and column conditions utilized are listed in Table 1. To facilitate peak matching, peak retention times were converted to relative retention times (relative to the retention time of p,p'-DDE) for each set of column and conditions. A file of relative retention times of many chlorinated pesticides and metabolites was compiled from chromatograms of single- and multi-component pesticide standard solutions and from retention time data reported by Thompson et al. (1969). Positions of significant peaks on chromatograms of pesticide fractions on the four columns were converted to relative retention times for comparison with the relative retention times of standards in the file. Peak identity assignments were made based on four matched relative retention times for peaks of similar height.

Several pesticide and PCB fractions from silicic acid liquid chromatographic cleanup of fish extracts were examined by gas chromatography/mass spectrometric (GC/MS) limited mass range scan techniques for DDE, dieldrin, and DDT. The fractions were chromatographed (Varian Aerograph 1400) on a 1.8 m x 4 mm ID glass column of 3% DC-200 on 60-80 mesh Gas-Chrom Q, with column and injector temperatures of 175°C and 200°C, respectively, eluting (by a helium flow of 10 ml/min) directly into the ion source of a quadrupole mass spectrometer (Finnigan 1015C) focused on narrow m/e ranges characteristic of the degradation patterns of DDE, dieldrin, or DDT. DDE and DDT were monitored by focusing on m/e ranges of 246-250 and 235-239, respectively, adapting procedures described by Bonelli (1972). Dieldrin was detected by monitoring the m/e range of 261-267. Identities were based on the response of this selective detector consistent with appropriate retention times.

Quantitative Determination

For determination of DDE in fish, the 5 ml aliquots taken from extracts after florisil cleanup were diluted to 10 ml and chromatographed on a 1.5 m x 2 mm ID glass column of 3% DC-200 on 80-100 mesh Chromasorb W, and

Table 1. GAS CHROMATOGRAPHIC COLUMNS AND CONDITIONS.

Stationary Phase[a]	1.5% OV-17/1.95% QF-1	2% OV-101/3% QF-1	1% QF-1	3% OV-17
Column Length (m)[b]	2.1	1.5	3	2.1
Column Temperature (^{o}C)	185	150	185	185
Detector Temperature (^{o}C)	210	190	210	210
Injector Temperature (^{o}C)	210	210	210	210
Carrier Gas (N_2) Flow (ml/min)	15	12	36	24

[a]Solid support was 100-120 mesh Gas-Chrom Q.

[b]All columns are 2 mm ID coiled glass tubes.

eluted with N_2 carrier flow of 40 ml/min into an electron capture detector (^3H). The column, detector, and injector temperatures were 200, 210, and 225°C, respectively. The relatively large p,p'-DDE peak of the chromatograms allowed its determination through peak height comparison with standards.

Pesticide fractions from silicic acid cleanup of fish, water, sediment, net plankton, Cladophora, and benthos extracts were chromatographed on a 3 m x 2 mm ID glass column of 1% QF-1 on 100-120 mesh Gas-Chrom Q to determine the DDT group pesticides and dieldrin. Column, detector, and injector temperatures were 180, 200, and 215°C, respectively, and the N_2 flow was 30 ml/min. An electron capture detector (^3H or ^{63}Ni) was used. All fractions were diluted to 2 ml (with hexane) before determination except for fish extracts which were diluted to 25 ml. Areas of peaks identified as DDT group pesticides and dieldrin were measured by a disc integrator and compared with standards. Since DDE is not fractionated cleanly into the pesticide fraction during silicic acid chromatography of extracts of water, net plankton, Cladophora, and benthos, the PCB fractions were also chromatographed as above to determine their DDE content. Sediment PCB fractions could not be similarily examined because of severe interferences.

The DDE content of several fish PCB fractions from silicic acid cleanup was determined by GC/MS limited mass range scan techniques. Chromatographic conditions were similar to those described for the qualitative determination of DDE. Peak heights were compared with those of standards.

PCB DETERMINATION

Perchlorination

PCB fractions from silicic acid cleanup of fish, water, sediment, net plankton, benthos, and Cladophora extracts were perchlorinated by procedures described by Veith (1973). Fractions were evaporated to dryness in glass vials, $SbCl_5$ (0.2 ml) was added to each vial, and the vials were sealed with teflon-lined screw caps before heating to 180°C

for 6 hr. After cooling to near $0^{o}C$ in an ice bath, 1 ml of 6N HCl was added to each vial to destroy the residual $SbCl_5$. The reaction solutions were extracted with five 1 ml portions of hexane. The hexane extracts were combined and passed through a disposable pipet containing anhydrous Na_2SO_4 to remove traces of water. Some highly colored extracts from sediment PCB fractions were washed with 1 ml of 10% KOH in anhydrous methanol to remove interfering inorganics. All perchlorinated extracts were reduced to 2 ml for GC determination of decachlorobiphenyl (DCB) except fish extracts which were analyzed at 25 ml.

Determination of Decachlorobiphenyl

Perchlorinated PCB fractions were chromatographed on a 1.5 m x 2 mm ID glass column of 1.5% OV-17/1.95% QF-1 on 100-120 mesh Gas-Chrom Q with N_2 flow rate of 50 ml/min into an electron capture detector (^{3}H or ^{63}Ni). Column, detector, and injector temperatures were 200, 210, and $230^{o}C$, respectively. Peak heights of DCB in the extracts were compared with those of standards and the DCB content was converted numerically to equivalent concentrations of Aroclor 1254.

The results of these analytical methods are reported without correction with respect to recovery during sample extraction and extract cleanup. The number of significant digits of the data reported reflects only analytical precision. Sampling precision was also considered in judgement of the significance of differences between sampling rates.

SECTION V

RESULTS AND DISCUSSION

FISH

All pesticide fractions from silicic acid cleanup of fish extracts contained DDT group pesticides and dieldrin, based on identification by multiple column GC and peak-matching techniques. In addition, several other common chlorinated hydrocarbon pesticides were identified in the extracts of fish from some sampling sites using this technique. Notably, endrin was identified in all fish taken off Prince Edward Point and from Mexico Bay, but was apparently absent in fish from a transect between Galloo Island and Stoney Island, the other eastern lake sampling site. Endrin was not identified in fish collected from western lake sites off Hamilton, Olcott, and Rochester. The BHC family pesticides were identified in fish taken off Olcott, Rochester, Prince Edward Point, and in Mexico Bay, with lindane (γ BHC) generally the major constituent. Heptachlor was identified in slimy sculpin taken off Rochester. Although identity assignments from a limited file of compounds were based on peak-matching which is subject to some of the ambiquity inherent in complex chromatograms, the use of a four-column system tended to decrease the incidence of these ambiguities.

The GC/MS limited mass range identity assignments of extract components provided positive identification of chlorinated hydrocarbons in fish. Using this technique, all fish pesticide fractions examined were shown to contain DDE, DDD, DDT, and dieldrin. In addition, the PCB fractions of extracts from most fish contained significant levels of DDE, while DDD, DDT, and dieldrin were undetectable (less than 2 ng/g on a whole fish basis).

Concentrations of t-DDT (sum of DDT, DDE, and DDD), dieldrin, and PCBs (expressed as Aroclor 1254 equivalent) found in whole fish (i.e. wet weight basis) and the extractable fat contents of the fish are shown in Table 2. The DDE values shown resulted from preliminary DDE

Table 2. CHLORINATED HYDROCARBONS AND FAT IN LAKE ONTARIO FISH[a]

Species	Location	Fat %	DDE	DDD	DDT	Total DDT	Dieldrin	PCB
			µg/g whole fish					
Alewife	Hamilton	3.6	0.46	0.07	0.14	0.67	0.04	3.12
Alewife	Olcott	5.2	0.77	0.07	0.16	1.00	0.03	1.73
Alewife	Rochester	3.4	0.71	0.10	0.18	0.99	0.04	4.36
Alewife	Mexico Bay	3.1	0.79	0.07	0.13	0.99	0.03	0.94
Alewife	Prince Edward Pt.	1.2	0.81	N.D.	N.D.	0.81	0.03	0.14
Alewife	Galloo-Stoney	2.4	0.96	0.08	0.18	1.22	0.04	3.81
Smelt	Hamilton	4.9	1.36	0.06	0.23	1.65	0.04	2.47
Smelt	Olcott	3.0	0.85	0.05	0.20	1.10	0.02	2.62
Smelt	Rochester	4.1	1.37	0.13	0.29	1.79	0.03	3.25
Smelt	Prince Edward Pt.	6.7	0.86	0.10	0.23	1.19	0.06	3.49
Smelt	Galloo-Stoney	6.0	0.91	0.10	0.24	1.25	0.07	1.40
Slimy Sculpin	Hamilton	9.8	0.94	N.D.	N.D.	0.94	N.D.	2.89
Slimy Sculpin	Olcott	5.1	1.10	0.15	0.29	1.54	0.06	9.17
Slimy Sculpin	Rochester	4.3	1.11	0.10	0.26	1.41	0.05	4.32
Slimy Sculpin	Mexico Bay	5.7	1.28	N.D.	0.26	1.54	0.10	6.49
Slimy Sculpin	Prince Edward Pt.	7.6	0.83	0.15	0.25	1.23	0.11	1.58
Slimy Sculpin	Galloo-Stoney	8.6	0.60	0.12	0.17	0.89	0.04	3.33

[a]N.D. indicates that no determination was made.

determinations on the extracts following florisil liquid chromatographic cleanup, while the DDD and DDT levels were obtained from determinations on pesticide fractions following silicic acid cleanup. DDE was also determined on the silicic acid pesticide fractions by electron capture GC and on the silicic acid PCB fractions by limited mass range GC/MS techniques. The sum of DDE in the silicic acid pesticide and PCB fractions was considerably less than the amount in the preceding florisil eluate, in some cases as much as 50% less. However since DDE was the largest peak for chromatograms of extracts after florisil cleanup, PCB contribution to the DDE peak was probably small. In most cases, the major contribution to t-DDT values was from DDE. Quantitatively, DDT and DDD were minor constituents, making up less than 26% and 14% of the total, respectively. Although dieldrin concentrations shown (Table 2) are of interest, the low levels observed do not allow evaluation of possible station-to-station or species-to-species relationships. The higher levels of t-DDT observed provide a better basis for comparisons.

Individual variation in the chlorinated hydrocarbon contents of the fish were decreased by sampling an aggregate of ground whole fish of several age-weight classes for each species collected at each site. Because chlorinated hydrocarbon levels have been related to the fat content of the fish (Veith, 1973), these variations likely are further decreased by examining chlorinated hydrocarbon concentrations in relation to the extractable fats contents of the whole fish. Table 3 shows t-DDT and PCB levels in fish based on fat content. This data indicates that the more migratory alewives and smelt accumulate higher t-DDT levels on a fat basis (averages of 36.2 μg/g and 30.5 μg/g) than the less migratory slimy sculpin (16.9 μg/g) (Scott and Crossman, 1973). Relative standard deviations for t-DDT levels (fat basis) for the species are 53, 36, and 66% for alewives, smelt, and slimy sculpin, respectively. Comparison of these variations with the average relative deviation for analytical replicates for extracts of an aggregated sample (14%) suggests that these variations are partly related to differences in chlorinated hydrocarbon levels among the sampling sites.

Table 3. DDT AND PCBs IN LAKE ONTARIO FISH FAT

(μg/g)

Species	Location	Total DDT	PCB	PCB/Total DDT
Alewife	Hamilton	18.6	86.7	4.7
Alewife	Olcott	19.2	33.3	1.7
Alewife	Rochester	29.1	128.2	4.4
Alewife	Mexico Bay	31.9	30.3	0.9
Alewife	Prince Edward Pt.	67.5	11.7	0.2
Alewife	Galloo-Stoney	50.8	158.8	3.1
Smelt	Hamilton	33.7	50.4	1.5
Smelt	Olcott	36.7	87.3	2.4
Smelt	Rochester	43.7	79.3	1.8
Smelt	Prince Edward Pt.	17.8	52.1	2.9
Smelt	Galloo-Stoney	20.8	23.3	1.1
Slimy Sculpin	Hamilton	9.6	29.5	3.1
Slimy Sculpin	Olcott	30.2	179.8	6.0
Slimy Sculpin	Rochester	32.8	100.5	3.1
Slimy Sculpin	Mexico Bay	27.0	113.9	4.2
Slimy Sculpin	Prince Edward Pt.	16.2	60.3	3.7
Slimy Sculpin	Galloo-Stoney	10.4	38.7	3.7

This is supported by the highest relative standard deviation for the slimy sculpin. Considering the slimy sculpin data shown in Table 3, the waters off Olcott, Rochester, and of Mexico Bay may contribute to greater accumulaion of DDT group pesticides by slimy sculpin than water off Hamilton, Prince Edward Point, and between Galloo and Stoney Islands. The lake bottom characteristics of these areas may also be important factors in the chlorinated hydrocarbon accumulation in the bottom-feeding sculpin.

The lake-wide average for t-DDT (whole fish) in smelt (1.40 µg/g) for 1972 compares favorably with that reported by Reinert (1970) for Lake Ontario fish captured from 1965 to 1968 (1.58 µg/g) although the alewife value (0.95 µg/g) is less than half that reported in 1970 (1.99 µg/g). Reinert (1970) did not report on Lake Ontario slimy sculpin. Dieldrin levels reported by Reinert (1970) for alewives and smelt caputred from 1967 to 1968 (0.11 µg/g and 0.06 µg/g, respectively) are comparable to levels in fish for 1972 (0.04 µg/g for alewife and smelt).

PCB concentrations (2.65 µg/g) found in smelt (Table 2) were similar to those reported by Veith (1973) for Lake Michigan smelt (2.7 µg/g). However, concentrations found in alewives (2.35 µg/g) were considerably lower than values reported for Lake Michigan alewives (4.6 µg/g). For both lakes, PCB levels were expressed as Arochlor 1254 equivalent. Slimy sculpin were not included in the Lake Michigan report.

Lake Ontario slimy sculpin exhibited highly variable PCB and t-DDT concentrations on a fat basis. The relative standard deviation for PCB levels in slimy sculpin (fat basis) was 65% about a mean of 97.1 µg/g. Corresponding relative standard deviation values for alewives and smelt were about 80% (mean = 74.8 µg/g) and 44% (mean = 58.5 µg/g), respectively. This indicates greater station-to-station variation for PCB accumulation in slimy sculpin and alewives than in smelt. Furthermore, the waters near Olcott, Rochester and in Mexico Bay contributed to greater accumulation of PCB concentrations by sculpin than waters off Hamilton,

Prince Edward Point, and between Galloo and Stoney Islands, which is in agreement with the trend for DDT accumulation.

A large variation was observed in PCB/t-DDT ratios for fish (Table 3). Average values, however, (2.5 for alewives, 1.9 for smelt, and 4.0 for slimy sculpin), were comparable to those reported by Veith (1973) (1.4 for alewives and 2.6 for smelt) for Lake Michigan fish. PCB/t-DDT ratios were often cited due to chemical similarities between PCBs and persistent DDT metabolites, although their importance has not been well established.

WATER

The t-DDT, dieldrin, and PCB concentrations for water are shown in Table 4. Since there were no apparent relationships between concentrations and depth, with the one exception as discussed below, determinations from different depths were treated as replicates for each site and averaged. Lake-wide averages for t-DDT and dieldrin were 28 ng/l and 4.8 ng/l, respectively. Relative standard deviations for t-DDT and dieldrin were 54% and 85%, respectively, indicating considerable site-to-site variation. Waters off Hamilton, Cobourg, and Oswego showed high levels of t-DDT. Dieldrin levels were highest off Cobourg and Oswego. The anomalously high dieldrin level for waters of Oswego resulted from a very high surface water value (34.9 ng/l) which was averaged with a much lower levels found in samples of deeper waters (1.7 ng/l and 1.1 ng/l). In all waters, except off Oswego, DDE was the major component of the DDT group pesticides. DDD contributed 0 to 19%, while DDT represented 6 to 13% in most cases. The t-DDT in waters off Oswego contained higher proportions of DDD and DDT, 28% and 26%, respectively. Waters from the Deep Hole area of the Rochester Basin showed a t-DDT level of 16 ng/l with DDT contributing over 40%.

Table 4. CHLORINATED HYDROCARBONS IN LAKE ONTARIO WATER

(ng/l)

Location	IFYGL Station Identifier	Station Depth m	DDE	DDD	DDT	Total DDT	Dieldrin	PCB
Hamilton	1	33	37.4	2.5	4.5	44	3.1	49
Toronto	8	76	20.5	1.6	1.4	24	3.5	35
Niagara River	13	13	13.9	0.9	2.4	17	2.1	97
Olcott	30	24	26.6	7.1	4.6	38	3.9	44
Cobourg	36	24	45.2	4.5	7.2	57	9.9	45
Rochester	60	25	29.9	< 0.5	2.3	32	2.2	40
Deep Hole	75	229	9.4	< 0.5	6.5	16	1.3	56
Oswego	90	21	22.4	13.8	12.8	49	12.6	77

PCB concentrations for Lake Ontario waters were between 35 and 56 ng/l, except for waters off Oswego (77 ng/l) and the mouth of the Niagara River (97 ng/l). The lake-wide average concentration was 55 ng/l. Neglecting the two highest concentrations, the lake-wide average becomes 45 ng/l with a relative standard deviation of 16%. Other than these south-shore areas, the PCB content of Lake Ontario waters appears relatively uniform. The PCB/t-DDT ratios for Lake Ontario waters averaged 2.1, a value comparable to that for Lake Ontario fish.

Since the water sampling and extraction procedures did not discriminate between dissolved and particulate fractions, the t-DDT, dieldrin, and PCB concentrations shown in Table 4 represent "total" concentrations. The contribution of contaminants associated with net plankton (i.e., particles larger than 64 um) to the "total" levels found in Lake Ontario waters is estimated to be less than 1%. This estimate was calculated from the contaminant concentrations found in net plankton (Table 6) from three areas of Lake Ontario, phytoplankton cell counts determined for these areas during the month these areas were sampled for chlorinated hydrocarbons (Stoermer, 1973), and dry weight per cell values reported for a laboratory algal culture (Lee et al., 1971). Thus DDT group pesticides, dieldrin, and PCBs in the Lake Ontario waters sampled are likely dissolved or associated with particles that will pass through a 64 um net (e.g., nanoplankton and small inorganic particles).

SEDIMENT

Sediment concentrations of t-DDT, dieldrin, and PCBs are shown in Table 5. Lake-wide averages for sediment t-DDT and dieldrin are 22 ng/g and 1.2 ng/g, respectively, with relative standard deviations of 72% and 61%, respectively. These variations are indicative of significant site-to-site differences. Sediments taken off the mouth of the Welland Canal and at the eastern mid-lake site showed higher levels of dieldrin and t-DDT. Sediment from three of the eight sites showed DDE contributions to t-DDT levels of less than 50%. DDD was the major contributor to t-DDT

Table 5. CHLORINATED HYDROCARBONS IN LAKE ONTARIO SEDIMENT

(ng/g dry sediment)[a]

Location	IFYGL Station Identifier	DDE	DDD	DDT	Total DDT	Dieldrin	PCB
Welland Canal	12	12	15	12	39	2.6	245
Niagara River	13	11	3.5	0.7	15	1.4	155
Olcott	30	4.8	5.6	1.2	12	0.9	80
Cobourg	36	8.0	0.9	0.9	10	0.6	43
Mid-lake	46	11	5.4	2.8	19	0.5	79
Rochester	60	8.0	1.5	0.2	10	0.9	84
Oswego	91	9.0	5.1	3.8	18	0.8	158
Mid-lake East	93	16	31	7.4	54	2.1	N.D.

[a]N.D. indicates no determination was made.

in sediments from the eastern mid-lake site and off the Welland Canal. The DDE levels shown in Table 5 must be considered underestimates, however, since it was not possible to measure the DDE contents of sediment PCB fractions due to interferences. Lake-wide t-DDT and dieldrin averages were comparable generally to those found by Leland et al. (1973) for southern Lake Michigan top interval sediments (18.5 ng/g and 2.0 ng/g, respectively). However, the Lake Michigan sediments showed major DDT contributions (ca. 50%) to the t-DDT, while Lake Ontario data showed DDT contributions no greater than 31%. Sediment PCB concentrations averaged 120 ng/g. PCB concentrations in sediments off the mouths of the Welland Canal and Niagara River and off Oswego, (mean = 184 ng/g) averaged more than twic the concentrations found at the four other sites (mean = 72 ng/g). Considering the high PCB contents found for lake water off the mouth of the Niagara River and off Oswego, the Niagara and Oswego Rivers may be important sources to Lake Ontario of PCBs associated with settlable particulates.

The PCB/t-DDT ratios exhibited a low relative standard deviation of 33% about a mean of 7.0. This mean may be too high due to underestimation of DDE levels. It is unlikely, however, that the DDE content of the sediment extracts could be great enough to decrease PCB/t-DDT ratios to levels similar to those for the fish and water.

NET PLANKTON

DDT group pesticides, dieldrin, and PCB levels (dry weight basis) found in mixed net plankton are shown in Table 6. Although the samples were predominantly viable phytoplankton, the sampling method also collects smaller zooplankton, detritus, and suspended inorganic matter. Contributions of these minor components could not be assessed. Lake-wide averages for t-DDT and dieldrin were 3.5 µg/g and 0.12 µg/g on a dry weight basis, respectively, with corresponding relative standard deviations of 42% and 91%. In nearly every case, DDE comprised over 75% of the t-DDT concentrations.

Table 6. CHLORINATED HYDROCARBONS IN LAKE ONTARIO NET PLANKTON

(μg/g dry weight)[a]

Location	IFYGL Station Identifier	DDE	DDD	DDT	Total DDT	Dieldrin	PCB
Hamilton	1	4.00	0.09	0.04	4.1	0.24	3.4
Mid-lake West	10	3.52	0.37	0.12	4.0	0.25	10.6
Cobourg	36	3.26	< 0.05	< 0.05	3.3	< 0.05	7.6
Mid-lake	45	1.49	0.07	0.78	2.3	0.16	3.6
Rochester	60	1.19	< 0.05	< 0.05	1.2	0.02	N.D.
Deep Hole	75	5.89	0.04	< 0.05	5.9	0.02	11.8
Mid-lake East	96	2.45	0.09	0.86	3.4	0.18	6.0

[a]N.D. indicates that no determination was made.

Net plankton PCB levels averaged 7.2 µg/g. Plankton from the Deep Hole of the Rochester Basin and the mid-lake west site, show high PCB levels contributing to a relative standard deviation of 49% for the lake-wide average PCB concentration. The average PCB/t-DDT ratio (3.1) was somewhat higher than for water or fish.

Chlorinated hydrocarbon levels for plankton appeared high compared to concentrations in fish. However, plankton concentrations were expressed on a dry weight basis while fish concentrations were on a whole fish (wet weight) basis. Assuming whole fish are about 20% dry weight (F.D.A., 1969), typical fish t-DDT, dieldrin, and PCB concentrations were 7.0 µg/g, 0.3 µg/g, and 13.2 µg/g dry weight (smelt), respectively. On this basis, net plankton concentrations of these chlorinated hydrocarbons were about 50% less than concentrations in fish.

CLADOPHORA

The results of determinations of DDT group pesticides, dieldrin, and PCB levels in extracts of Cladophora are shown in Table 7. Most samples, except those off Toronto and in the Black River Bay, were from the south shore of Lake Ontario. The exact sampling site locations of four of the samples is uncertain. The average t-DDT, dieldrin, and PCB levels (dry weight basis) were 229, 13, and 515 ng/g, respectively, with relative standard deviations of 40, 64, and 39%, respectively. These concentrations are 10 to 100 times less than for net plankton. The average PCB/t-DDT ratio of 2.3 was near the corresponding averages for fish and water.

BENTHOS

DDT group pesticide, dieldrin, and PCB levels determined for extracts of benthic fauna, largely Pontiporeia, are shown in Table 8. Of the three samples taken, one off Hamilton showed t-DDT, dieldrin, and PCB levels approximately four times those determined for benthos off Oswego and Rochester. Also, DDD made a significantly larger contribution to the t-DDT in benthos off Rochester than other samples. Average t-DDT and PCB levels, 99 ng/g and 471 ng/g on a dry weight basis, respectively,

Table 7. CHLORINATED HYDROCARBONS IN LAKE ONTARIO CLADOPHORA

(ng/g dry weight)

Location	DDE	DDD	DDT	Total DDT	Dieldrin	PCB
Black River Bay	344	4.8	7.4	357	1.9	860
Black River Bay	129	0.45	1.9	131	6.5	333
South Shore[a]	97	19	2.5	119	14	232
South Shore[a]	194	26	4.7	225	14	607
South Shore[a]	347	17	1.1	365	4.0	436
South Shore[a]	192	30	16	238	25	576
Rochester	165	5.2	6.0	176	16	411
Toronto	196	13	8.0	217	21	666

[a]Specific sampling site unknown.

Table 8. CHLORINATED HYDROCARBONS IN LAKE ONTARIO BENTHIC FAUNA

(ng/g dry weight)

Location	DDE	DDD	DDT	Total DDT	Dieldrin	PCB
Hamilton	124	26	59	209	14.8	976
Rochester	34	1.8	6.1	42	2.9	341
Oswego	26	3.4	2.4	32	3.0	97

were quite comparable to levels reported by Flotard (1974) for Pontiporeia of the western shore of Lake Michigan, 130 ng/g and 310 ng/g, respectively. The PCB/t-DDT ratios averaged 5.3. This value is somewhat higher than that calculated from the concentrations reported by Flotard (1974) or ratios calculated for all other samples reported except sediment. Although some sediment contamination may be indicated, the benthos PCB/t-DDT ratio is comparable to that for slimy sculpin (4.0), whose diet is primarily benthic fauna (Scott and Crossman, 1973).

SECTION VI

REFERENCES

Bonelli, E.J. 1972. Gas Chromatograph/Mass Spectrometer Techniques for Determination of Interferences in Pesticide Analysis. Anal. Chem. 44:603-606.

Flotard, R.D. 1974. PCBs in Lake Sediments. Ph.D. Thesis (Water Chemistry), University of Wisconsin, Madison (in progress).

Kaiser, K.L.E. 1974. Mirex: An Unrecognized Contaminant of Fishes from Lake Ontario. Science 185:523-525.

Lee, C.C., R.F. Harris, J.K. Syers, and D.E. Armstrong. 1971. Adenosine Triphosphate Content of Selenastrum capricornutum. Appl. Microbiol. 21:957-958.

Leland, H.V., W.N. Bruce, and N.F. Shimp. 1973. Chlorinated Hydrocarbon Insecticides in Sediments of Southern Lake Michigan. Environ. Sci. Technol. 7:833-838.

Reinert, R.E. 1970. Pesticide Concentrations in Great Lakes Fish. Pestic. Monit. J. 3:233-240.

Scott, W.B. and E.J. Crossman. 1973. Freshwater Fishes of Canada. Fish. Res. Bd. Can. Bulletin 184, Ottawa. 966 p.

Stoermer, E.F. 1973. Analysis of Phytoplankton Composition and Abundance During IFYGL. In: First Annual Reports of EPA Grants Funded for IFYGL. Ecol. Res. Series #EPA-660/3-73-021. U.S. Environmental Protection Agency, Grosse Ile Laboratory, Grosse Ile, Michigan. pp. 90-109.

Thompson, J.F., A.C. Walker, and R.F. Moseman. 1969. Evaluation of Eight Gas Chromatographic Columns for Chlorinated Pesticides. J.A.O.A.C. 52:1263-1277.

U.S. Food and Drug Administration. 1969. Pesticide Analytical Manual, Volume 1. U.S. Department of Health, Education and Welfare, Washington, D.C.

Uthe, J.F., J. Reinke, and H. Gesser. 1972. Extraction of Organochlorine Pesticides from Water by Porous Polyurethane Coated with Selective Absorbent. Environ. Letters 3:117-135.

Veith, G.D. 1970. Environmental Chemistry of PCBs in the Milwaukee River. Ph.D. Thesis (Water Chemistry), University of Wisconsin, Madison. 180 p.

Veith, G.D. 1973. Chlorinated Hydrocarbons in Fish from Lake Michigan. A final report on Project #16020PBE to the U.S. Environmental Protection Agency, National Water Quality Laboratory, Duluth, Minnesota. University of Wisconsin-Madison, Water Chemistry Department, Madison, Wisconsin. 129 p.

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16. ABSTRACT

Lake Ontario fish, water, sediment, net plankton, Cladophora, and benthos were examined for DDT group pesticides, dieldrin, and PCBs. Endrin, BHC group pesticides, and heptachlor were also identified in some fish samples. Average concentrations ranged from 28 ng/l (t-DDT), 4.8 ng/l (dieldrin), and 55 ng/l (PCBs as Aroclor 1254 equivalent) for water to 1.40 µg/g (t-DDT), 0.07 µg/g (dieldrin), and 5.15 µg/g (PCBs) for whole fish. DDE levels were generally similar to t-DDT levels, except for sediments where DDD and DDT contributed significantly to t-DDT values. PCB/t-DDT ratios averaged 2.6 for all samples except for sediment (7.0) and benthos (5.3).

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