

LONG RANGE TRANSPORT OF TOXIC ORGANIC CONTAMINANTS
TO THE NORTH AMERICAN GREAT LAKES

by

W.R. Swain¹
M.D. Mullin²
J.C. Filkins²

ABSTRACT

Studies of persistent organic contaminants made for the Upper Lakes Reference Group of the International Joint Commission in 1974-1976 indicated increased levels of organic contamination in the flesh of fish taken from the vicinity of Isle Royale in Lake Superior. These findings led to a preliminary study of polychlorinated biphenyl (PCB) compounds in atmospheric precipitation deposited in Siskiwit Lake on Isle Royale.

The subsequent studies reported here support the earlier findings but show significant shifts in observed concentrations. Initially, these altered values were thought to be the result of increasing environmental concentrations of PCBs. The use of refined analytical procedures suggests, however, that the apparent changes are a function of the co-occurrence of derivatives of the pesticide Toxaphene within the analytical spectrum of the PCB fraction. A comparison of the older data from Siskiwit Lake with those acquired from contemporary analytical procedures suggests that it is likely that derivatives of Toxaphene may have been enumerated with PCB peaks, thus being inadvertently reported as total PCB. Based on results obtained with high resolution capillary chromatography, apparent increases in concentrations of PCB compounds in 1980 packed column chromatography samples are undoubtedly a function of historic analytical limitation, rather than an absolute change in environmental concentrations of the PCB compounds.

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¹Vakgroep Aquatische Oecologie, Universiteit van Amsterdam, Kruislaan 320, 1098 SM Amsterdam, The Netherlands

²Large Lakes Research Station, U.S. Environmental Protection Agency, Grosse Ile, Michigan 48138 USA

INTRODUCTION

In 1974, studies of the accumulation of selected persistent organic residues in the fish species of the Lake Superior ecosystem were initiated under the auspices of the International Joint Commission's Upper Lakes Reference Group. The findings of these studies indicated substantially increased levels of halogenated organic substances in Lake Superior fish near Isle Royal, particularly in lean lake trout, Salvelinus namaycush, and in fat lake trout, Salvelinus namaycush siscowet.

As a check on contaminant levels in Lake Superior fish, a control site, Siskiwit Lake on Isle Royale, was established. This deep, cold, oligotrophic lake contained indigenous species of fish similar to those in Lake Superior, allowing direct comparison. The island, and hence the lake, was remote from inhabited areas, thus being well removed from the industrial and cultural influences of man's activities. Surprisingly, however, the values for several organic contaminants in the flesh of fish from Siskiwit Lake were significantly higher than corresponding values in fish from Lake Superior. Polychlorinated biphenyl (PCB) compounds were nearly double the Lake Superior mean value, and p,p-DDE showed a more than 10-fold increase in Siskiwit Lake. These findings led to a preliminary study of the transport of PCB compounds in atmospheric precipitation. For a more complete summary of this work, the reader is referred to Swain (1978).

The present study was undertaken as a continuation of the earlier effort, with particular interest in the changes in residue levels in the fish population of this landlocked, remote island lake.

GEOGRAPHICAL SETTING

Isle Royale is a rock-strewn conglomerate of a central island mass with associated irregular reefs. It lies 27.4 km from the closest shoreward margin of Lake Superior at Thunder Cape, Ontario, but it is more than 50 km to Thunder Bay, Ontario, the nearest major population center (Figure 1).

Isle Royale (Figure 2) has an extreme length of 70.8 km, lying on a southwest-northeast axis. Its maximum width, 14.5 km, occurs near the southwest end of the island. The highest point in the island is Mount Desor, 242 m above Lake Superior. The entire island structure, including its associated reefs and islets, constitutes Isle Royale National Park, established in 1940. Efforts from that date have been made to preserve the island's native wilderness character. As a result, the only means of access from one part of the island to another is by means of foot trails. Siskiwit Lake, accessible only in this fashion, provided a remote aquatic ecosystem relatively undisturbed by human activity.

Siskiwit Lake lies 0.6 km inland from Lake Superior in a depression of Precambrian Middle Keweenawan flow of the Portage Lakes Volcanics. The entire watershed of the lake also lies in bedrock of this type. The long axis of Siskiwit lake follows the same direction as the long axis of Isle Royale, i.e., northeast-southwest.

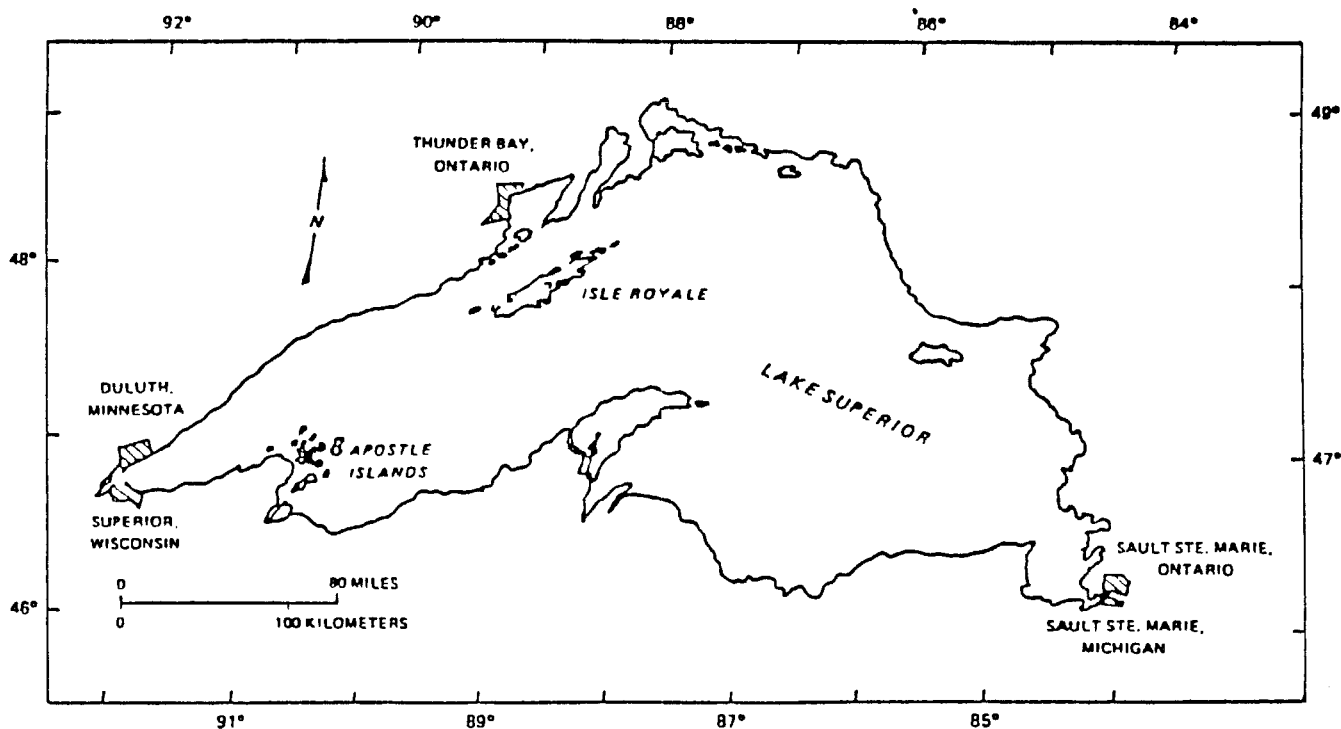


Figure 1. Geographic area of study in Lake Superior.

The length of Siskiwit Lake is 11.10 km, the maximum breadth is 2.25 km, and the mean breadth is 1.40 km (Huber, 1975). The lake area is 15.6 km², exclusive of islands. Shoreline development, calculated from the expression $D_L = L/A$, is typical of subcircular eliptiform lakes, having a value of 2.66. The elevation of Siskiwit Lake above the mean Lake Superior level is 17.37 m, indicating no direct input from Superior to Siskiwit Lake. Siskiwit Lake drains by a single small stream to Lake Superior, the Siskiwit River. The maximum depth of Siskiwit Lake is 36.58 m.

METHODOLOGY

Sample collection from the remote sites at Siskiwit Lake were made in 1980 from a canoe that was portaged to the site from the Superior shoreline. Fish samples were taken by means of a 350-foot (106.68 m) section of 5.72-cm gill net that was backpacked into Siskiwit Lake and set overnight at a depth of 24.4 to 46.5 m at the location shown in Figure 2. For all collections, the catch was exclusively lake trout (*Salvelinus namaycush*), whitefish (*Coregonus culpeaformis*), and bowfin (*Amia calva*). In each case, only lake trout and whitefish were retained, carried out in a clean mesh bag, eviscerated, iced, and after transport to a populated area, immediately frozen in dry ice for transport to the laboratory.

Snow samples were taken from the undisturbed surface of the lake and were transported to the laboratory in sealed teflon containers. Because of prevailing ambient temperatures, further refrigeration was not necessary.

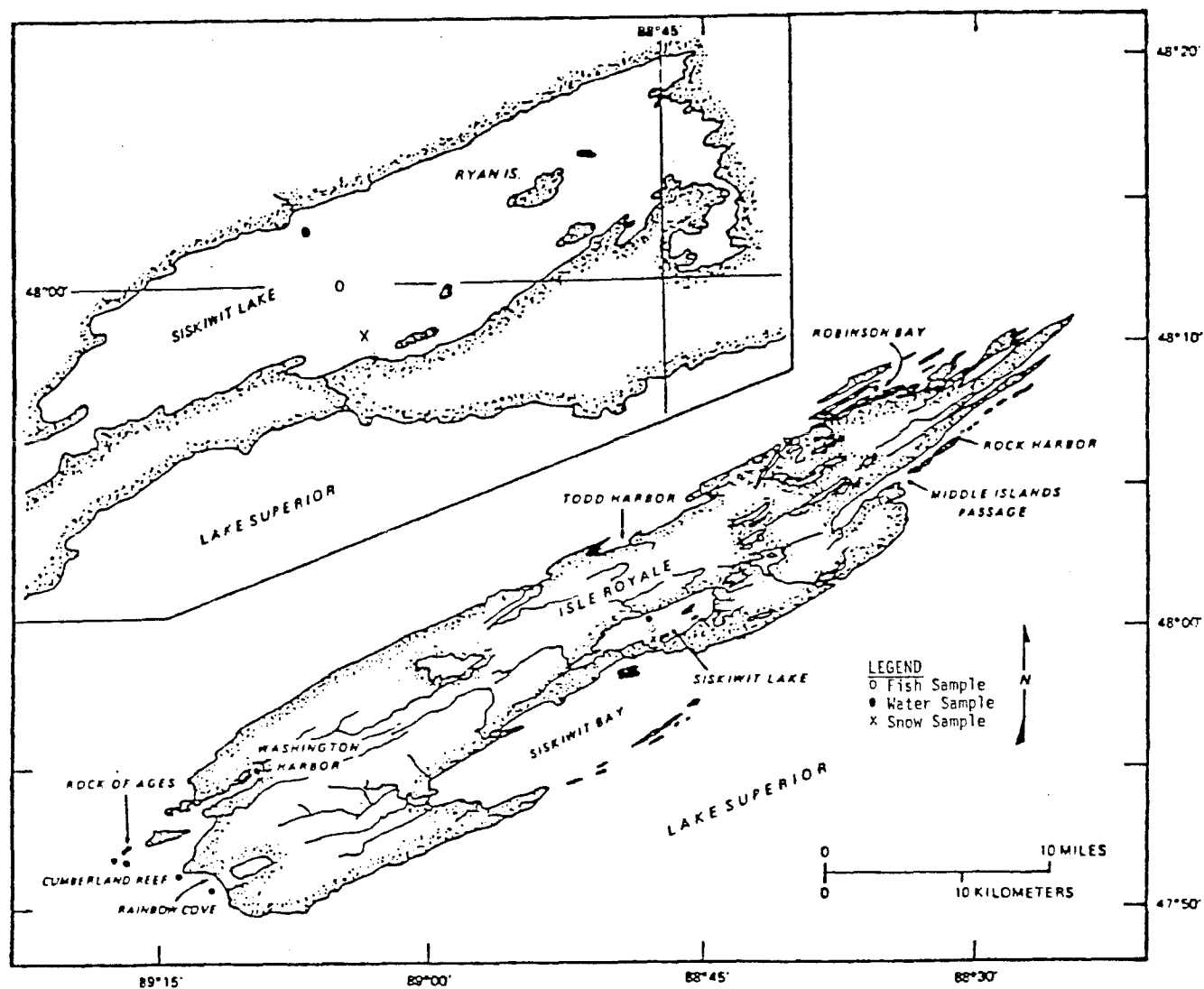


Figure 2. Location of sampling sites for fish, water, and snow in the vicinity of Siskiwit Lake, Isle Royale.

Samples of atmospheric precipitation in the Lake Huron area were taken using both event samplers and bulk collectors lined with thin teflon bags. These bags were suspended within the frame of the bulk collector in such a manner as to minimize evaporation losses from the collected sample. In all but one case, samples were taken from the Michigan side of Lake Huron. The single exception was an August sample taken from the Canadian shore line of Lake Huron below the Bruce Peninsula.

ANALYTICAL PROCEDURES

In an effort to minimize analytical error, samples of fish were submitted to three separate laboratories for analysis. These analytical efforts included the Columbia National Fisheries Laboratory of the U.S. Fish and Wildlife Service at Columbia, Missouri; the Cranbrook Institute of Sciences at Bloomfield Hills, Michigan, and the U.S. Environmental Protection Agency's Large Lakes Research Station at Grosse Ile, Michigan.

Initial packed column gas chromatography studies followed accepted analytical procedure. A detailed description is presented by Swain (1978). When it became apparent that PCB congeners were co-occurring with compounds of Toxaphene, however, subsequent analytical efforts utilized high resolution capillary column chromatography. The procedures associated with this type of analysis are summarized below.

High resolution fused silica capillary gas chromatography was performed on a VARIAN Model 3700 gas chromatograph equipped with a ^{63}Ni electron capture detector. A 50-m fused silica column (0.2 mm i.d.) coated with SE-54 (Hewlett-Packard) was used to separate the PCB congeners and the Toxaphene-like compounds. The oven temperature was programmed at a rate of $1.0\text{ }^{\circ}\text{C min}^{-1}$ from 100 to $240\text{ }^{\circ}\text{C}$. The injector and detector temperatures were 270 and $330\text{ }^{\circ}\text{C}$, respectively. Sample volume, 6.0 μl , was injected by using an automatic sampler with splitting in the injector (10:1 split ratio, vented from 0.75 to 1.75 min.) The hydrogen carrier gas was held at a constant pressure of 2.25 kg cm^{-2} to give the optimized velocity (u) at $100\text{ }^{\circ}\text{C}$ of 45 cm s^{-1} .

ANALYSIS

The interpretation of the chromatograms was complicated by the presence, in all samples, of PCBs as well as the polychlorinated camphene (Toxaphene-like) components. The high resolution chromatography used permitted the evaluation of both groups of compounds together without additional separation procedures. There were more than 110 peaks in the PCB reference standard and 39 of the larger peaks in technical Toxaphene were used in the Toxaphene reference standard. Of these approximately 150 different compounds, only about a dozen co-eluted and, of this number, fewer than six were significant. Where co-eluting compounds existed, the following procedure was used: if other PCB peaks in the same time portion of the chromatogram were present and other Toxaphene-like peaks were absent, the peak in question was assumed to be a PCB; conversely, if other PCB peaks in the same time portion of the chromatogram were absent and other Toxaphene-like peaks were present, then the peak in question was assumed to be a Toxaphene-like compound; if both PCB and Toxaphene-like peaks were present, then the peak was excluded from both the PCB and Toxaphene-like calculations.

PCB data were determined by comparing the relative retention times (RRT) of the individual peaks (octachloronaphthalene as internal standard = 1.000) in the chromatogram to those generated by a mixture of Aroclors 1016, 1254 and 1260. If the RRT were within a narrow window of ca 0.0004 RRT units and the height of the peak was proportionate to other PCB peaks in the same time portion of the chromatogram, then the PCB assignment was made and the amount calculated was based on a comparison of the height of the peak in the standard for which the concentration was known) to the height of the peak in the sample.

Toxaphene-like data were calculated differently because of the lack of individual compound standards against which to compare the sample. The 39 peaks in the Toxaphene reference standard all were assigned the same value--the total concentration of the Toxaphene standard--and relative response factors (RRF) for each peak were calculated. Summing these concentrations and dividing by the number of peaks yields the concentration of the solution. Toxaphene-like compounds from the samples were determined in a similar manner. After making qualitative assignments based on the same ± 0.0004 RRT units exclusion window as used in the PCB determination and comparing the peak height to other Toxaphene-like peaks in the same time portion of the chromatogram to ensure that they were proportionate to the same peaks in the standard, a concentration was calculated for each peak by comparing its height to the height of the same peak in the standard. These concentrations were summed and the sum divided by the number of Toxaphene-like peaks identified in the sample. If fewer than 20 peaks were identified, then the qualitative identification of the peaks as Toxaphene-like was uncertain and reported as questionable.

It should be noted that at the time of preparation of this report, the precise identification of Toxaphene in biologic tissue is still a matter of some analytical discussion. While two laboratories participating in the analytical portion of this study unhesitatingly refer to the material observed as "Toxaphene", a third group is concerned that all of the peaks observed are not entirely co-incidental with pure standards of Toxaphene. This group observes that the sample appears to be "environmentally weathered" as a result of passage through biologic systems. It is their opinion that the substances should be labeled as "chlorinated turpines/camphenes" or as "Toxaphene-like" compounds, suggesting this analytical uncertainty. The latter, more conservative approach has been used for this report.

RESULTS AND DISCUSSION

In 1976, a series of four fresh snow samples was collected, melted, extracted, and analyzed from the Isle Royale site (Figure 2). PCB compounds were expressed as an aggregate of Aroclor 1254, the reference mixture that Veith et al. (1977) reported as most resembling mixtures observed in Lake Superior. This Aroclor mixture was used as an index of airborne movements of persistent organic compounds, and the levels observed at Siskiwit Lake were compared with values at Duluth, Minnesota. The mean value for PCB compounds observed in precipitation samples from the Duluth, Minnesota, metropolitan area was 50.0 ng/l, whereas the mean value from Siskiwit Lake was nearly five times greater, 230.0 ng/l (Swain, 1978). Similar results were reported by Murphy (1976) and by Murphy and Rzeszutko (1978) in the Lake Michigan area,

comparing precipitation in Chicago, Illinois, against that of Beaver Island in Northern Lake, Michigan.

Strachan and Huneault (1979), working in the Province of Ontario adjacent to the Great Lakes found 86 percent of 50 rain samples to contain an average of 21 ng/l PCB, with an observed maximum of 120 ng/l PCB. These workers found an average of 26 ng/l in 14 rainfall samples adjacent to Lake Superior and a mean of 38 ng/l in 4 samples of snow from the Lake Superior area. In their later summary of airborne contaminants to the Great Lakes ecosystem, Eisenreich et al. (1981) report a range of 10 to 100 ng/l PCB in precipitation over the Great Lakes with an average content of 30 ng/l. These workers project total annual PCB deposition of airborne trace organic compounds to Lake Superior at 9.8 metric tons per annum (MTA), 6.9 MTA for Lake Michigan, 7.2 MTA for Lake Huron, 3.1 MTA for Lake Erie, and 2.3 MTA for Lake Ontario.

All of these studies suggested continuing inputs of PCBs to the Great Lakes ecosystem via the atmosphere, even though usage of these materials in North America was drastically curtailed in the early 1970s. For this reason, it was thought that sampling of the remote Siskiwit Lake site should be continued because the only source of contaminants to this system is apparently the atmosphere. Lake trout from Siskiwit Lake were selected for this study because of their well known predisposition to accumulate contaminants and because these fish occur both in Siskiwit Lake and in the upper Great Lakes, thus enabling direct comparison. Further, continued use of this species would permit extension of previous data from the lake and reflect changes in levels of contamination with time.

In the 1976 data set (Swain, 1978), a single composite of two lake trout was reported. These fish averaged 54.5 cm in body length, weighed an average of 1.6 kg, and contained 3.5 percent lipid. Two additional unreported composites of two lake trout each--1.5 kg and 1.7 kg average weight, and 3.2 and 3.8 percent lipid, respectively--contained 0.9 and 1.3 mg/kg PCB on a wet weight basis.

For comparison with these data, 18 lake trout were taken in 1980 and assigned to five composites as indicated in Table 1. These composites were forwarded to three participating laboratories with a request to run standard packed column gas chromatography analysis for PCBs with methods analogous and comparable with those used in the 1976 study. Laboratory 1 reported individual values for each of the five composites. These values were 3.26, 2.27, 1.57, 1.22, and 2.17 mg/kg PCB on a wet weight basis for composites 1 through 5, respectively. The reported mean value was 2.1 mg/kg PCB. Laboratories 2 and 3 homogenized the five individual composite samples and performed the analysis on a single grand composite of 18 fish. Laboratory 2 reported an observed level of 3.85 mg/kg PCB, and Laboratory 3 reported 4.3 mg/kg PCB. This yielded an average value of 3.42 mg/kg PCB for the analysis of the three laboratories. Although there was a rather large range between the three laboratories, both the individual values reported and the mean of the analyses were substantially higher than the average of 1.13 mg/kg observed in 1976.

Because of the individual variation among laboratories and because of the availability of newer, more sensitive methodologies, a blind duplicate

TABLE 1. CHARACTERISTICS OF LAKE TROUT FROM SISKIWIT LAKE, ISLE ROYALE (LAKE SUPERIOR), 1980

Composite sample	Fish per composite	Length (cm)			Avg. weight (kg)	Percent lipid
		Min.	Max.	Avg.		
1	1	71.0	71.0	71.0	4.682	10.41
2	4	54.0	58.0	55.8	1.784	9.82
3	4	54.0	58.0	55.0	1.598	5.85
4	5	35.0	53.0	46.2	1.045	9.06
5	4	52.0	57.0	53.2	1.412	7.20
Sample mean	3.6	53.2	59.4	56.24	2.104	8.486

sample was submitted to each of the three laboratories with a request for analysis of the identical material using high resolution capillary column gas chromatography. The results, shown in Table 2, were surprising. Not only were the analyses in excellent agreement, but the mean of the analyses was well below the levels observed on Siskiwit Lake in 1976, and nearly five times lower than the packed column analyses.

To verify these results, the five Siskiwit Lake lake trout were reanalyzed as individual composites, and in addition, two fillets of lake trout were included from outer Saginaw Bay in Lake Huron. A 1.16-kg fillet was submitted taken from a 62-cm male lake trout containing 13.7 percent lipid, and the second was a 1.9-kg fillet containing 12.5 percent lipid taken from a 75-cm female lake trout. The results of the comparative analyses are shown in Table 3. In all cases, the values determined by packed column chromatography exceeded those observed with high resolution capillary column chromatography by an average of more than three times.

TABLE 2. ANALYSIS OF PCB IN SISKIWIT LAKE COMPOSITE LAKE TROUT SAMPLES BY PACKED COLUMN AS COMPARED WITH HIGH RESOLUTION CAPILLARY COLUMN GAS CHROMATOGRAPHY

Laboratory identification	Sample means total PCB packed column (mg/kg)	Sample means total PCB capillary column (mg/kg)
1	2.10	0.70
2	3.85	0.72
3	4.30	0.70

TABLE 3. ANALYSIS OF PCB BY PACKED COLUMN AS COMPARED WITH
HIGH RESOLUTION CAPILLARY COLUMN GAS CHROMATOGRAPHY

Sample	Sample means total PCB packed column (mg/kg)	Sample means total PCB capillary column (mg/kg)
Lake trout fillet, male Saginaw Bay-Lake Huron	11.08	5.70
Lake trout fillet, female Saginaw Bay-Lake Huron	5.16	2.30
Lake trout-Siskiwit Lake composite number 1	3.26	1.35
Lake trout-Siskiwit Lake composite number 2	2.27	0.91
Lake trout-Siskiwit Lake composite number 3	1.57	0.57
Lake trout-Siskiwit Lake composite number 4	1.22	0.35
Lake trout-Siskiwit Lake composite number 5	2.17	0.41*
		0.39*
Sample means	3.82	1.5

*Duplicate analysis.

To answer the obvious question of the reason for the differences, an intense study of the individual chromatograms was made. It quickly became apparent that a number of non-PCB peaks co-eluted in the same portion of the gas chromatographic spectrum as the PCB congeners. Careful resolution and separation with capillary column chromatography and comparison with known standards revealed that these additional peaks were derived from chlorinated turpene/camphene products characteristic of technical Toxaphene. Although, as noted previously, it was not possible to match all peaks with pure standards of Toxaphene because of biologic "weathering" of environmental samples, a consistent match of more than 20 peaks was normally achieved.

Aliquots of the same samples reported in Table 3 were reanalyzed against Toxaphene reference standards. The results of this effort are reported in Table 4. In all cases, the absolute quantities of Toxaphene-like materials exceeded the levels of PCBs observed by a considerable margin; an average difference of more than 5-fold was seen. A relatively consistent ratio of Toxaphene-like compounds to PCB congeners was observed. Only in one case, composite number 4, did this ratio become excessively large. In this case, the ratio observed was nearly double the mean of the other samples (10.6 as compared with 5.42).

For comparison with the values observed in lake trout, two water samples were taken at 1 meter of depth at the site on Siskiwit Lake indicated in Figure 2. Two additional samples were taken in Lake Superior from the 50-meter strata of water approximately 5 km southwest of Menagerie Light on Siskiwit Bay of

TABLE 4. PCB AND TOXAPHENE-LIKE COMPOUNDS (TOX) OBSERVED IN LAKE TROUT

Sample location	Total PCB (mg/kg)	Number of peaks utilized for PCB	Total TOX (mg/kg)	Number of peaks utilized for TOX	Ratio TOX:PCB
Fillet, Saginaw Bay Lake Huron	5.7	26	25.84	28	4.53
Fillet, Saginaw Bay Lake Huron	2.3	26	12.05	29	5.24
Siskiwit Lake composite no. 1	1.35	25	6.37	31	4.72
Siskiwit Lake composite no. 2	0.91	25	5.14	28	5.65
Siskiwit Lake composite no. 3	0.57	25	3.01	39	5.28
Siskiwit Lake composite no. 4	0.35	25	3.71	27	10.6
Siskiwit Lake composite no. 5	0.41*	25	2.57	30	6.27
	0.39*	25	2.45	30	6.28
Sample means	1.49	25.25	7.64	29	6.07

*Duplicate analysis.

Isle Royale. The means of these samples are compared in Table 5 with the average values of samples collected in Lake Huron by staff of the Cranbrook Institute of Science, and jointly analyzed by this group and the second author. Again, a consistent ratio of Toxaphene-like material to PCB congeners was observed for all samples except those of Siskiwit Lake. Apparently because of its relative size, state of oligotrophy, and the relatively higher inputs of PCBs received, the ratio in this lake was reduced to 1.72, as compared with an average of 3.45 for the other analyses.

To assess the quantity of PCB compounds in atmospheric precipitation, a series of bulk collectors and event samplers had been set out along the Lake Huron shoreline at Hoeft State Park, Michigan, Sturgeon Point, Michigan, and Tawas State Park, Michigan. Additionally, one confirmatory station was established on the Canadian shoreline of Lake Huron below the Bruce Peninsula, and one station was established below Lake Huron at Grosse Ile, Michigan. When the results of the studies of lake water and lake trout became available, the precipitation samples were also analyzed for PCB and Toxaphene-like compounds.

The results of these analyses are shown in Table 6. Again in every case, the values observed for the Toxaphene-like substances exceeded those observed for PCBs. The mean of the ratios observed for all bulk precipitation samples, by far the majority of the data, was 3.24, which compares well with the mean ratio found for open Lake Huron water, 3.51, and with that of Lake Superior, 3.16. As was previously noted, the data points that are derived from peaks of Toxaphene-like substances of less than 20 in number should be regarded with

caution. Although the data have been included for continuity, four such points exist in the data set--one from Hoeft State Park, two from Sturgeon Point, and one from the Tawas State Park sampling station. At best, the values for the Toxaphene-like substances associated with these samples should be regarded as a qualitative estimation of the amount of these substances present.

Although these data are currently being more completely analyzed, it is apparent that Toxaphene-like components make up a currently significant portion of the contaminant burden of Upper Great Lakes water, fish, and precipitation inputs. It may even be necessary to reconsider some of the historic data on PCBs in the Great Lakes in light of this new information to evaluate the possible positive interference of Toxaphene-like compounds in the analysis of these samples.

In keeping with the original purpose of this sequence of studies, a comparison of several other 1980 pesticide levels in lake trout from Siskiwit Lake also was made with the earlier data. The results of the associated analyses are shown in Table 7. In all cases for which comparative data were available, significant reductions in levels of pesticides were observed. Compounds showing such declines included the alpha isomer of benzenehexachloride (BHC, also known as hexachlorocyclohexane), heptachlor epoxide, p,p'-DDE, and p-p'-DDD. A group of new materials also was observed among which were the gamma isomer of BHC (also known as hexachlorocyclohexane, or Lindane), Toxaphene-like compounds, and the family of substances related to chlordane, including oxychlordane, trans-chlordane, cis-chlordane, and cis-ionachlor.

Finally, using a 1-kg homogenate of the 18 lake trout comprising composites 1 through 5 of Tables 1 through 4, negative ionization mass spectroscopy analyses were made for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The results of these analyses are shown in Table 8.

TABLE 5. MEAN VALUES OF ANALYSES OF PCB AND TOXAPHENE-LIKE COMPOUNDS (TOX) IN SELECTED WATER SAMPLES

Location	Total PCB (ng/l)	Total TOX (ng/l)	Numbers of peaks in TOX analysis	Ratio PCB: TOX
Lake Huron				
Southern Lake Huron	0.39	1.50	42	3.85
Middle Lake Huron	0.46	2.14	39	4.65
Northern Lake Huron	0.28	1.23	35	4.39
North Channel	0.77	1.60	25	2.08
Georgian Bay	0.57	1.48	36	2.60
Lake Superior	0.31	0.98	38	3.16
Adjacent to Isle Royale				
Siskiwit Lake, Isle Royale	1.28	2.2	37	1.72

TABLE 6. PCB AND TOXAPHENE-LIKE COMPOUNDS (TOX) OBSERVED IN SAMPLES-
EVENT AND BULK PRECIPITATION, LAKE HURON

Location	Month sample taken	Sample volume (l)	Total PCB (ng/l)	Number of peaks in PCB analysis	Total TOX (ng/l)	Number of peaks in TOX analysis	Ratio TOX:PCB
Hoeft State Park sampling station	1	12.65	7.7	23	36.3	15	4.73
	2	5.86	11.1	60	21.0	31	1.88
	6	11.76	19.9	40	55.9	26	2.80
	8	15.25	1.8	40	14.5	38	8.13
	9	36.05	2.7	60	5.0	31	1.89
	10	9.85	22.9	40	51.4	32	2.24
	12	12.10	108.0	71	112.0	26	1.03
Sturgeon Point sampling station	1	5.53	87.0	65	99.0	22	1.14
	2	7.83	6.9	54	16.7	25	2.42
	5	31.05	4.3	40	17.7	23	4.11
	6	30.20	7.3	47	13.1	19	1.79
	6*	5.65	8.6	59	17.8	38	2.07
	7	30.44	1.4	35	5.58	33	3.96
	8	30.91	2.2	37	14.6	34	6.59
	8*	5.79	21.0	42	37.0	41	1.75
	9	36.75	7.6	40	16.3	34	2.15
	10	9.00	19.9	54	51.5	15	2.59
	10*	1.65	31.6	65	40.4	29	1.28
	11	18.30	9.2	41	21.3	28	2.32
Canadian shore station	8	45.72	2.6	35	26.7	22	10.38
Grosse Ile sampling station	6	28.36	5.0	43	16.2	39	3.26
	8	83.73	8.1	55	18.9	39	2.35
	10	10.44	22.9	45	74.2	32	3.24
Tawas State Park sampling station	6	24.72	8.5	42	15.6	37	1.84
	8	24.29	3.5	42	19.9	49	5.73
	9	42.15	5.3	47	11.7	36	2.21
	10	12.26	30.0	51	52.1	17	1.74
	11	24.24	4.9	33	9.7	30	1.99
	12	7.40	46.0	62	80.0	21	1.74
Mean of all samples		21.39	17.9	47.9	33.5	29.7	3.08
Mean of bulk precip. samp.		23.36	17.5	47.1	33.7	29.0	3.24
Mean of event precip. samp.		4.36	20.4	55.3	31.73	36.0	1.7

*Event samples.

TABLE 7. COMPARISON OF RESIDUE-FORMING ORGANIC SUBSTANCES
OBSERVED IN LAKE TROUT (EVisCERATED WHOLE FISH)
FROM SISKIWIT LAKE, 1974-1976 and 1980

Compound	Concentration (ng/g, ppb)	
	1974-76	1980
α BHC	11.0	3.5
γ BHC	-	1.5
HCB	5.0	-
Heptachlor epoxide	8.0	5.2
Oxychlordane	-	5.3
<u>trans</u> -chlordane	-	8.8
<u>cis</u> -chlordane	-	24.4
p,p'-DDE	2370.0	318.0
p,p'-DDD	36.0	25.0
<u>cis</u> -Nonachlor	-	25.0
Toxaphene-like compounds	-	3200.0

Trace amounts of the 7 and 8 chlorine substituted PCDDs were found, but the more toxic 4 chlorine substituted isomers were not observed, nor were the 5 and 6 chlorine substituted groups. Four chlorine substituted PCDFs made up two-thirds of the total PCDFs found, the remaining one-third consisting of the 5 chlorine substituted compounds. The concentration ratio (PCDFs/PCBs) $\times 10^6$ yields a value of 21.4 when the high resolution capillary column PCB values are used. This ratio may be of particular significance when potential impacts of PCBs on human health are considered.

CONCLUSION

The occurrence and distribution of selected persistent organochlorine compounds has been studied in the Siskiwit Lake, Lake Superior, and Lake Huron ecosystems. Although the origins of the more ubiquitous PCB compounds are not clear, historic use patterns of the pesticide Toxaphene suggest major mechanisms for long range transport of derivatives of this material to the Great Lakes. Traditionally, the vast majority of Toxaphene compounds have been used in the deep South of the United States as an agricultural insecticide against pests of cotton crops, specifically the cotton boll weevil Anthonomus grandis (Coleoptera: Curculioninae). Utilization patterns of Toxaphene in other areas closer to the Great Lakes suggest that only in recent years has application of this material been made as a herbicide, or as an insecticide in conjunction with the cultivation of sunflower crops in the mid-western states. Toxaphene has never been registered or approved for use in Canada. Because existing data indicate Toxaphene-like components in fish of the upper Great Lakes as early as 1974 (Swain and Glass, 1984), and because a loading rate of more than a metric ton per year would be required to observe the burdens of these Toxaphene-like materials in each of the Upper Great Lakes, it is highly likely that the majority of these components are derived from extremely long range transport (thousands of kilometers) by way of the atmosphere from areas of major utilization in the southern United States. Recent research (Rice et al., 1984), utilizing air and precipitation samples, and meteorological data, reached the same conclu-

sion, i.e., that the probable source of the Toxaphene-like compounds observed is from the central-southern United States.

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TABLE 8. NEGATIVE IONIZATION MASS SPECTROSCOPY ANALYSIS OF EVISCERATED WHOLE LAKE TROUT FROM SISKIWIIT LAKE (1 kg composite of 18 fish taken in 1980)

Compound	Concentration (ng/kg, ppt) by number of chlorine substitutions					
	4	5	6	7	8	Total
Chlorinated dibenzo-p-dioxins (Detection limit)	ND (1.0)	ND (1.0)	ND (2.0)	Tr. (2.0)	Tr. (3.0)	Trace
Chlorinated dibenzofurans (Detection limit)	10 (0.5)	5 (0.5)	ND (0.5)	ND (1.0)	Tr. (1.0)	15
Ratio of four chlorine PCDFs to total 10:15 = 0.67						
Concentration ratio (PCDFs/PCBs) X 10 ⁶						
Packed column PCBs	.. (15/4.3) X 10 ⁶ = 3.5					
High resolution capillary column PCBs	.. (15/0.7) X 10 ⁶ = 21.4					

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