Lake salmon and trout 'unfit to eat'

By Casey Bukro
Environment editor

ALL LAKE MICHIGAN coho salmon and lake trout tested for PCB content last year were found to be unfit for human consumption, a United States Fish and Wildlife Service expert testified Thursday.

PCB — polychlorinated biphenyl — is an industrial poison found widely scattered throughout the world at levels considered hazardous to public health.

The fish and wildlife expert, Wayne Willford, testified at a three-day conference in the Pick-Congress hotel aimed at focusing attention on the newly emerging environmental hazard.

In sampling done last fall, Willford said, 70 to 80 per cent of Lake Michigan chubs and 100 per cent of the lake's coho salmon and lake trout had PCB levels higher than the 5 parts per million pure foods limit set by the Food and Drug Administration.

Lake Michigan fish are tainted with the highest doses of PCB found in the five Great Lakes, says Francis Mayo, Great Lakes regional director of the U.S. Environmental Protection Agency. The next highest amounts are found in fish in Lakes Ontario and Huron. The lowest PCB levels are found in Lakes Superior and Erie, Mayo said.

"COMMERCIAL USE of Lake Michigan salmon and lake trout cannot even be considered at this time because of the contamination level," Willford said. The fish cannot be sold in interstate commerce, and fishermen who eat them do so at their own risk.

Thirty salmon and thirty trout were tested by Willford.

Medical experts at the conference have testified that PCB poisoning can cause fatigue, numbness, skin disorders, and reproductive failure.

"I recommend that people who eat these fish go by the recommendation of several states, and that is not to eat more than one meal of these fish a week," said Willford.

"Pregnant women and children should avoid it."

The National Fisheries Institute Inc., of Washington, D.C., representing 550 seafood packers and distributors, asked for a nationwide ban on PCB because of "the potential risk to the American food supply."

PCB products are used widely in the electrical equipment industry because of their heat resistant qualities. They also are used for making plastics.

WILFORD SAID sampling shows that PCB levels in Lake Michigan fish have stayed about the same since 1972, despite voluntary efforts to curb PCB pollution.

John Hesse, of the Michigan Department of Natural Resources, testified here that his department is urging a national ban on domestic and imported PCBs, except for those used in the electrical industry. Michigan's legislators introduced a bill on Aug. 14 to prohibit the manufacture, sale, and use of PCBs except for transformers and capacitors.

PCB poison ruins family's fish business

By Casey Bukro
Environment editor

PCB SPELLS THE END of a way of life for the Hermes family of Green Bay, Wis.

A Green Bay commercial fishing family going back 70 to 80 years, the Hermes were shut down by the United States Food and Drug Administration last August because of excessive PCB in the fish they caught.

"We never knew about PCBs until a few months ago," said Jean Hermes, 31.

"It seemed to happen overnight. PCB poisoned the fish so they were inedible. They're dangerous to eat. The FDA shut us down. It means the end of our livelihood."

Mrs. Hermes came to Chicago with her husband, Jim, 33, to tell their story before a national PCB conference in the Pick-Congress hotel, which opened Wednesday.

A lot has been heard about PCB, most of it technical. The Hermes gave a human side of the story.

PCB — SHORT FOR polychlorinated biphenyls — is an industrial poison considered a growing environmental and public health threat. It works like a cross between DDT and mercury, two long-lasting poisons.

"It wrecked our business," said Jim Hermes. "All I know is commercial fishing." He estimates he has $150,000 tied up in fishing equipment, which he used mainly to catch carp.

Re-examine budget, Thompson asks

By Eleanor Randolph

REPUBLICAN GUBERNATORIAL candidate James Thompson Thursday urged the legislature to "re-examine" the state budget to see if extra money for public schools exists.

"If there is money for television studios ... or for an unnecessary political bureaucracy in Springfield or Chicago, there may be money for schools," he told guests at a $125-a-plate fund-raising dinner in the Conrad Hilton Hotel.

"A wise governor and a wise mayor should find it," he said.

Thompson aides said the dinner raised about $200,000 for his campaign. Among the officials at the dinner were State Comptroller George Lindberg, Cook County State's Atty. Bernard Carey, and Atty. Gen. William J. Scott, who only last week attended a dinner for Michael Howlett, expected challenger of Gov. Walker for the Democratic gubernatorial nomination.

THOMPSON INDIRECTLY accused Walker of mismanagment of the state government and campaign improprieties, but did not name him.

"There will be no name-calling (during his campaign)," Thompson told his supporters. "There will be no dark corners — whether for contributions or political favors. No dollars not disclosed. No words whispered in private that cannot be shouted in public."

MDNS 0649589

CHARACTERIZATION OF POLYCHLORINATED BIPHENYLS

J. P. Mieure, O. Hicks, R. G. Kaley and V. W. Saeger

Monsanto Company
800 N. Lindbergh Blvd.
St. Louis, Missouri 63166

CHEMICAL STRUCTURE

Polychlorinated biphenyls (PCBs) are made by direct chlorination of biphenyl. The biphenyl molecule has ten possible sites at which chlorine atoms can be substituted. The numbering system for the biphenyl structure is shown in Figure 1. By convention, the two rings are numbered identically except the ring with the fewest chlorine substituents or substituted in the highest numerical positions is designated as primed. Examples of nomenclature for a tri- and a tetrachlorobiphenyl are included in Figure 1. An excellent discussion of PCB nomenclature can be found in a recent text by Hutzinger, Safe and Zitko (1).

There are 209 possible chlorobiphenyl isomers distributed as indicated in Table I. However, many of these isomers are not likely to occur at significant levels in commercial PCB mixtures. For example, isomers with four or five chlorine atoms on one ring but none on the other ring are not detectable in PCB products.

TABLE I

209 POSSIBLE PCB ISOMERS

Degree of Substitution	Number of Isomers
Mono	3
Di	12
Tri	24
Tetra	42
Penta	46
Hexa	42
Hepta	24
Octa	12
Nona	3
Deca	1
	209

AROCLOR PRODUCTS

The major producer of PCBs in the United States is Monsanto Company, which markets mixtures for closed electrical system applications under the Aroclor® trademark. Aroclor products are identified by a four digit numbering code in which the first two digits, 12, indicate the parent molecule is biphenyl and the last two digits specify the weight percent of chlorine. The exception is Monsanto's newest product, Aroclor 1016 (41% chlorine), which was assigned the 1016 designation by which it was known during development. Aroclor products manufactured in the United States are listed in Table II. Production of the materials listed as discontinued was terminated in or prior to 1971.

TABLE II

AROCLOR PRODUCTS MANUFACTURED IN THE U.S.

Current	Discontinued	Percent Chlorine
1221		21
	1232	32
1016		41
1242		42
	1248	48
1254		54
	1260	60
	1262	62
	1268	68

AROCLOR COMPOSITION

The composition of the four Aroclor products currently marketed in the United States is given in Table III. Aroclor 1221 is primarily monochlorobiphenyl while Aroclor 1016 and Aroclor 1242 are primarily trichlorobiphenyls. The major difference between these two products is the lower penta- and hexachlorobiphenyl content of Aroclor 1016. Aroclor 1254 is primarily pentachlorobiphenyl. The values in Table III were calculated from measurements by gas chromatography with flame ionization detection after component identification by gas chromatography/mass spectrometry. All gas chromatographic separations were made with a high resolution capillary column. Average response factors determined for each degree of chlorine substitution were applied to all components.

Detailed chromatograms of these four products are illustrated in Figures 2-5. Specific isomer identification determined by Webb and McCall (2) and Sissons and Welti (3) are listed for the major Aroclor 1242 components in Figure 4. The complexity of these mixtures was emphasized by amplifying the first and last portions of the Aroclor 1254 chromatogram in Figure 5. Eighty-five components were detected in Aroclor 1254. A .32 mm id X 50 m glass capillary column coated with OV-101 was used for these separations. The flow rate was 2 ml/min helium and the column temperature was programmed from 50° to 230°C at 2°C/min.

High resolution chromatographic conditions are very useful for characterizing PCB products. However, for routine monitoring of environmental materials, it is more appropriate to use gas chromatography with packed columns and electron capture detection. Typical chromatograms of this type for Aroclor 1016 and Aroclor 1242 are compared in Figure 6. The chromatograms are essentially identical for retention times less than 70 relative to p,p'-DDE. However, the higher chlorinated components with relative retention times 70 and greater represent a significantly smaller contribution in the Aroclor 1016 chromatogram. These chromatograms illustrate the feasibility of distinguishing these unaltered products. However, in environmental materials the characteristic features of Aroclor 1242 are frequently obscured by interfering compounds or by component alteration so the distinction is less clear or sometimes entirely lacking. These separations were carried out on a 6 ft. X 4 mm id glass column packed with 3% SE-30 on 80/100 mesh Chromosorb W - HP at 190°C.

TABLE III

TYPICAL PERCENT COMPOSITION OF AROCLOR PRODUCTS

HOMOLOG # Cl/BIPHENYL	AROCLOR 1221	AROCLOR 1016	AROCLOR 1242	AROCLOR 1254
0	11	<0.1	<0.1	<0.1
1	51	1	1	<0.1
2	32	20	16	<0.5
3	4	57	49	1
4	2	21	25	21
5	<0.5	1	8	48
6	ND	<0.1	1	23
7	ND	ND	<0.1	6
8	ND	ND	ND	ND

ND = NONE DETECTED, <0.01%

PHYSICO-CHEMICAL DIFFERENCES

The physical and chemical properties of PCB isomers and commercial mixtures vary greatly depending on the degree and position of chlorine substitution. The effect of chlorine content on several physico-chemical properties is summarized in Table IV. Three of these properties, volatility, water solubility, and biodegradability, are very relevant to the environmental occurance of PCBs. Volatility and water solubility represent potential mechanisms for introduction into and transport within the ecosystem. Biodegradation represents a mechanism for removing PCBs from the environment. Illustrations of the relative significance of these properties for different PCB isomers are evident from the following three examples.

TABLE IV

PHYSICO-CHEMICAL PROPERTIES FOR PCB PRODUCTS

Property	Percent Chlorine 21	42	54
Density (g/ml)	1.19	1.39	1.50
Distillation Range (°C)	275-320	325-366	365-390
Fire Point (°C)	176	None	None
Vaporization Rate ($mg/cm^2/hr$ @100°C)	1.74	.338	.053
Water Solubility (ppm)	>.2	.2	.04
Biodegradability*	81	26	15

*Percent degradation/48 hr cycle with semi-continuous activated sludge

Relative volatilities for the PCB components in Aroclor 1016 are indicated in Figure 7 by comparing chromatograms of liquid and vapor composition. The higher numbered components make successively less contribution to the total vapor composition.

Water solubility of Aroclor 1016 components is illustrated in similar fashion in Figure 8. Water saturated with Aroclor 1016 was extracted with hexane and the extract compared chromatographically to an Aroclor 1016 standard. The numbers above significant peaks express the percentage contribution of that peak area to the total area. Earlier eluting, lower chlorinated components are more soluble and contribute more to the water saturated composition. A related study has shown that PCBs leaching from Aroclor 1016 impregnated soils after the equivalent of forty years annual rainfall consist of lower chlorinated biphenyls (4) (Figure 9).

Microbial degradation also affects PCB isomers to different degrees. For example, Figure 10 shows chromatograms depicting Aroclor 1016 composition after exposure to a naturally occuring mixed microbial population for 1/2 hour (above) and 14 days (below). The number above each GC peak indicates the percent biodegradation for that component. These percentages range from 17 to >98 and in general are higher for lower chlorobiphenyls. The exposure was carried out with activated sludge from a domestic sewage treatment facility. The sludge was previously acclimated to a mixture of industrial organic compounds before addition of 3 ppm Aroclor 1016. PCB composition was determined by extracting a representative aliquot of mixed liquor with hexane followed by analysis by gas chromatography using a glass capillary column and electron capture detection.

It is apparent from these examples that introduction of PCBs into the ecosystem by volatility or water solubility would result in an environmental composition skewed in favor of lower chlorinated components. PCB removal from the environment by microbial degradation would lead to the opposite effect because lower chlorobiphenyls are significantly more degradable than higher chlorobiphenyls. These and related factors combine to make assessment of PCB environmental impact a very complex problem.

In view of the recognized complexity in studying commercial PCB mixtures, it would seem expedient to substitute for the mixture a single isomer product having the desired electrical and physical properties. The environmental properties of this isomer would be much simpler to

characterize and control. However, no such PCB isomer exists. Most PCB isomers are solid crystalline materials when isolated at 25°C. Commercial products are liquids only because of the mutual melting point depression exerted by the PCB components of the mixture.

CONCLUSIONS

Commercial PCB products are mixtures of many different isomers with varying chlorine content. The properties of these isomers, and hence the products, are vastly different and are complex to study. The environmental impact for each product must be accurately assessed and compared to the functional benefit before we fully understand the significance of PCBs.

REFERENCES

1. O. Hutzinger, S. Safe and V. Zitko, "The Chemistry of PCBs", CRC Press, Cleveland, 1974.
2. R. G. Webb and A. C. McCall, J. Assoc. Offic. Anal. Chem., 55, 746(1972).
3. D. Sissons and D. Welti, J. Chromatog., 60, 15(1971).
4. E. S. Tucker, W. J. Litschgi and W. M. Mees, Bull. Environ. Contam. Toxicol., 13, 86(1975).

MONS 064598