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PCB'S AND OTHER ORGANOCHLORINE COMPOUNDS IN SHARKS AND TUNAS

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ABSTRACT

A number of organochlorine compounds were identified by GCMS in livers of sharks and bluefin tunas. In addition to the commonly determined PCB's, hexachlorobenzene, and the DDT group, chlordanes and nonachlors were generally present. Several components of toxaphene and other organochlorine compounds were detected in some samples.

RÉSUMÉ

Un nombre de composés organochlorés ont été identifiés par la chromatographie gazeuse-spectrométrie de masse dans les foies de requins et de thons rouges. En plus des composés ordinairement présents tels que les concentrations de PCB, hexachlorobenzine, et le groupe de DDT, chlordanes et nonachlores sont communément présents. Plusieurs composants de toxaphène ont été trouvés dans quelques échantillons.

This work was undertaken to identify by GCMS organohalogen compounds that might have escaped attention under conventional analytical conditions (GC with an EC detector). The work was focused on samples containing high levels of the usual organochlorine compounds. Livers of sharks are obtained occasionally by this laboratory. The levels of organochlorine compounds in livers of bluefin tunas caught off Nova Scotia, Canada, have been monitored for 3 yr. The results of the monitoring study will be reported later. This work concentrates on three specimens with higher-than-average levels of contamination. One specimen is particularly interesting. This fish was noticeably "sick" on landing and contained several times the average levels of organochlorine compounds.

Literature data on organochlorine compounds in sharks are limited. Two basking sharks (Cetorhinus maximus) and a white shark (Carcharodon carcharias) were analyzed (Zitko and Choi 1971). The levels of PCB's and DDE were quite low in the former species. The white shark contained very high levels of organochlorine compounds and was re-analyzed in this work. The liver of a silky shark (Carcharhinus falciformis) caught off the US east coast (31N-78W) was used in an IDOE intercalibration program (Harvey and

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Miklas 1972). The sample contained PCB's, DDE, DDD, and DDT at about 13, 9, 1, and 5 µg/g lipid, respectively. PCB's in spotted sharks (Mustellus manazo) were studied by Shimma and Shimma (1974). The levels of PCB's in livers of juvenile fish were from 22 to 250 µg/g lipid. Liver of a mature female contained PCB's at 770 µg/g lipid.

Early analyses of tuna were reviewed by Zitko and Choi (1971). The levels of organochlorine compounds varied with species and location. Highest levels were detected in bluefin tunas (Thunnus thynnus) and skipjack tunas (Euthynnus pelamis) from the northwest Atlantic. Sims et al. (1977) analyzed a number of bluefin tunas and noted generally elevated levels of PCB's and of the DDT group.

Of the somewhat less commonly measured organochlorine compounds, chlordanes and nonachlors (Zitko 1978; Miyazaki et al. 1979; Jansson et al. 1979) were observed also in this study. In addition, several other components of chlordane as well as oxychlordane, a metabolite of chlordane, were detected.

Until recently, the contamination of aquatic fauna by toxaphene appeared localized (Pollock and Kilgore 1978). Components of toxaphene were since detected in fish from the North Sea and from the Baltic (Jansson et al. 1979), and a number of chlorinated terpenes, presumably components of toxaphene, were detected in this study, particularly in the "sick" fish.

Atmospheric concentrations of toxaphene are generally higher than those of other commonly measured organochlorine compounds (National Research Council 1978; Billings and Bidleman 1980). Analytical difficulties are probably the main reason for the relative lack of data on toxaphene in marine fauna.

MATERIALS AND METHODS

Sharks. A sample of white shark liver, stored at -20°C since 1971 was extracted and analyzed in 1977. Porbeagle (Lamna nasus) was caught off Deer Island, New Brunswick, Canada in 1976. The liver sample was extracted and analyzed within a month.

Tunas. Bluefin tunas were sampled in 1976-78 from an enclosure in St. Margaret's Bay, Nova Scotia, Canada. Liver samples were stored at -20°C, extracted and analyzed within 6 months of collection. Livers of two fish from 1976 and one from 1978 were analyzed by GCMS.

Extraction and cleanup. Liver samples (5 g) were ground with anhydrous sodium sulfate (30 g) and extracted in a Soxhlet with hexane for 1 h. A portion of the extract was cleaned-up on alumina and silica, and analyzed as described (Zitko et al. 1974). For GCMS analysis, a portion of the extract, corresponding to 2 g lipid, or as much as available, was cleaned on a preparative column with alumina (40 g/g lipid). The effluent from this column was concentrated in a rotatory evaporator to about 2 mL and cleaned-up further on a small column with alumina.

GCMS. The analyses were performed on a Finnigan 1015 mass spectrometer coupled to a Finnigan 9500 gas chromatograph and a Finnigan 6100 data system. The GC column (I.D. 2 mm) contained 3% OV-1 on Chromosorb W 60/80. As the analyses were performed occasionally over several years, columns

varying in length from 120 to 180 cm were used. Column temperature was programmed, usually from 100 to 280°C at 8°C/min, but some separations were carried out from 190 to 280°C at 4°C/min. The injector and separator temperatures were 220 and 290-305°C, respectively. EI mass spectra were scanned from 100 to 500 or, on occasions, 50-500 or 200-500 daltons, every 3 sec. For most samples, the instrument response was calibrated by an external standard of trans-nonachlor.

RESULTS AND DISCUSSION

Levels of routinely quantitated organochlorine compounds. Levels of PCB's, the DDT group and, in some cases, dieldrin (D), in livers of sharks and tunas studied in this work are very high (Table 1). The specimens of tuna contain considerably higher-than-average levels of organochlorine compounds. For example, the mean concentration and standard deviation of PCB's and DDE in six other specimens of bluefin tuna sampled in St. Margaret's Bay in 1976 were 14 (9) and 2.3 (1.5) µg/g lipid, respectively (Zitko, unpublished).

Table 1
Levels of routinely quantified organochlorine compounds (µg/g lipid) in livers of sharks and tunas

Species, year	Lipid, %	HCB	PCB's	DDE	D	DDD	DDT
White shark, 1971	78.6	nq	290	450	nq	57	84
Porbeagle, 1976	66.5	nq	44	19	nq	2.3	5.5
Bluefin tuna							
1976	7.0	0.06	65	6.9	3.6	8.7	13
1976, "sick"	7.9	0.30	318	78	11	22	34
1978	17.1	0.26	61	14	0.3	2.1	1.2

nq = not quantified
PCB's = quantified as Aroclor 1254 but chlorobiphenyls up to decachlorobiphenyl are present.

Levels of chlordanes and nonachlors. The levels of chlordanes and nonachlors are quite high, particularly in the "sick" tuna (Table 2).

Table 2
Levels of chlordanes and nonachlors (µg/g lipid) in livers of sharks and tunas

Species, year	Chlordane	Nonachlor	
	trans + cis	trans	cis
White shark, 1971	2.60	8.5	1.7
Bluefin tuna			
1976	0.63	1.8	0.53
1976, "sick"	7.8	22	1.6
1978	0.87	2.0	nd

nd = not detectable

Other organochlorine compounds. A number of additional components of chlordane were detected but not quantitated because of lack of standards. For example, $C_{11}H_7Cl_9$, presumably a chlordane component #23 (Sovocool et al. 1977) was detected in the "sick" tuna (Fig. 1), and was present in the liver of the white shark as well. The structure of this chlorinated hydrocarbon is not known. Its composition is different from the "normal" chlordane series $C_{10}H_{12}$ or $C_{10}H_{14}$. It has been suggested that it may be a $CHCl_3$ adduct to chlordene. This compound appears to be another, more persistent component of chlordane, since it was detected in human adipose tissue as well (Wright et al. 1978).

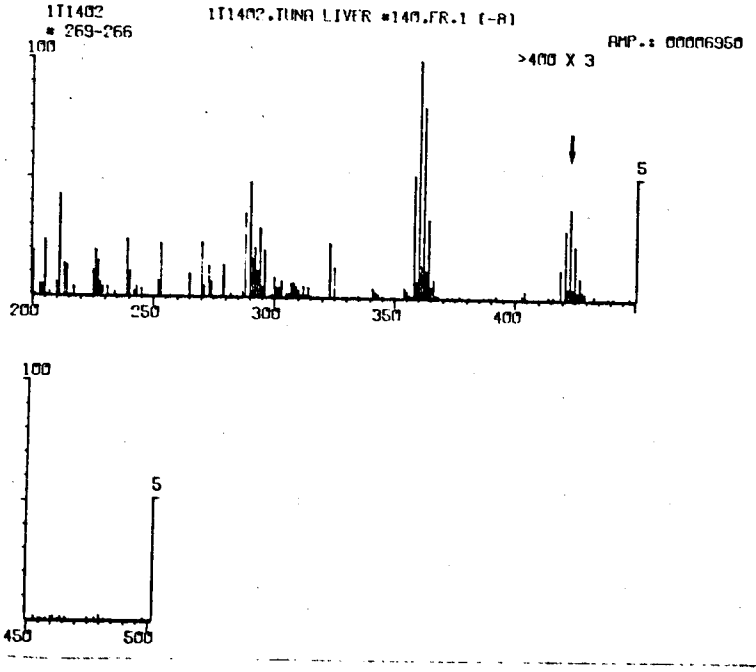

Fig. 1. Mass spectrum of $C_{11}H_7Cl_9$, chlordane component #23 in tuna (8Cl cluster at m/z=419). Co-eluting is a hexachlorobiphenyl (6Cl cluster at m/z=358).

A related, more highly chlorinated hydrocarbon, $C_{11}H_6Cl_{10}$, probably chlordane component #30 (Sovocool et al. 1977), is also present in the "sick" tuna (Fig. 2).

Oxychlordane, a chlordane metabolite, frequently detected in birds and mammals, was found as well (Fig. 3).

Interestingly, the "early" nonachlor (#19, Sovocool et al. 1977) is either not detectable or is not separated from trans-nonachlor (Fig. 4).

The components of toxaphene are derived from hydrocarbons $C_{10}H_{16}$ or $C_{10}H_{18}$ and appear on the gas chromatogram after cis-nonachlor. At least five such hydrocarbons were detected in the "sick" tuna. Spectra indicating the presence of $C_{10}H_8Cl_8$ and $C_{10}H_9Cl_9$ are given in Fig. 5 and 6, respectively.

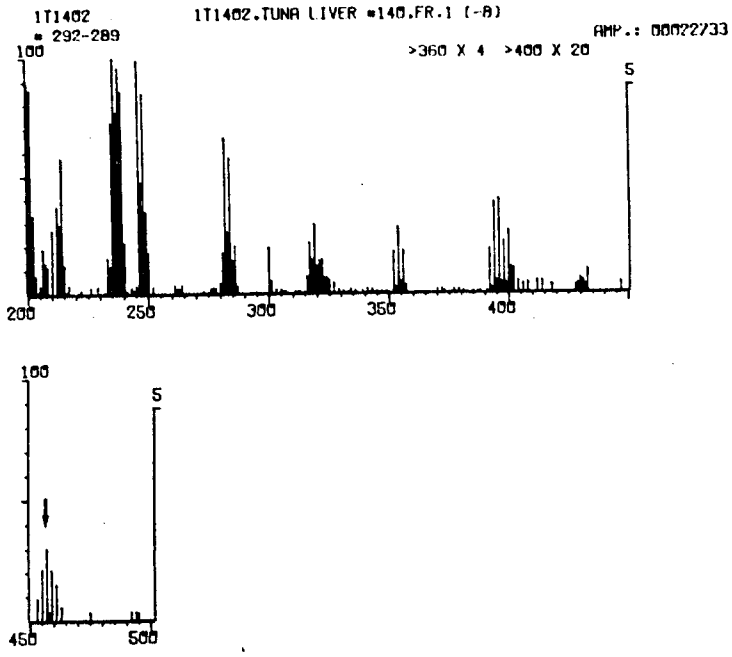

Fig. 2. Mass spectrum of $C_{11}H_6Cl_{10}$, chlordane component #30 in tuna (9Cl cluster at m/z=453). Co-eluting is a heptachlorobiphenyl (7Cl cluster at m/z=392).

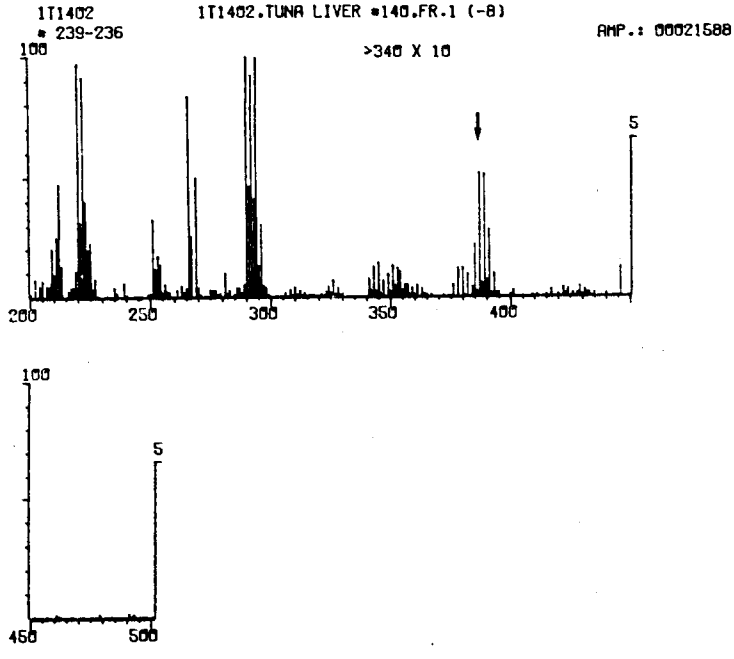

Fig. 3. Mass spectrum of oxychlordane in tuna (7Cl cluster at m/z=385). The co-eluting halogenated compound (Cl cluster at m/z=376) is probably octachlorostyrene.

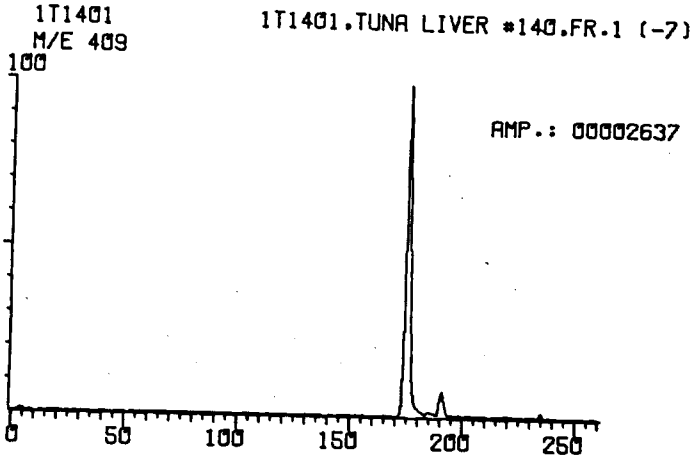

Fig. 4. Reconstructed m/z=409 chromatogram. Peaks in scans 175 and 191 are trans- and cis-nonachlor, respectively. The "early" nonachlor would appear just before trans-nonachlor.

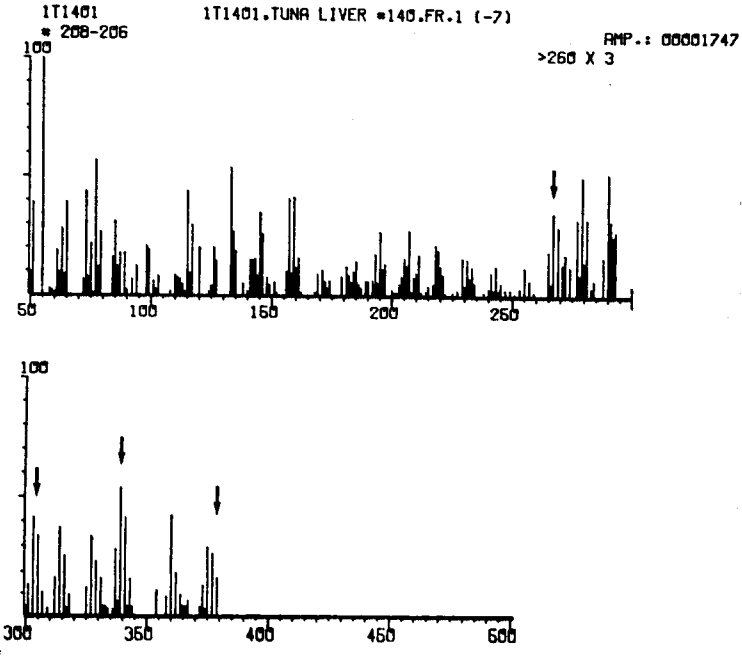

Fig. 5. Mass spectrum of $C_{10}H_8Cl_8$, a component of toxaphene in tuna liver (7Cl cluster at m/z=373).

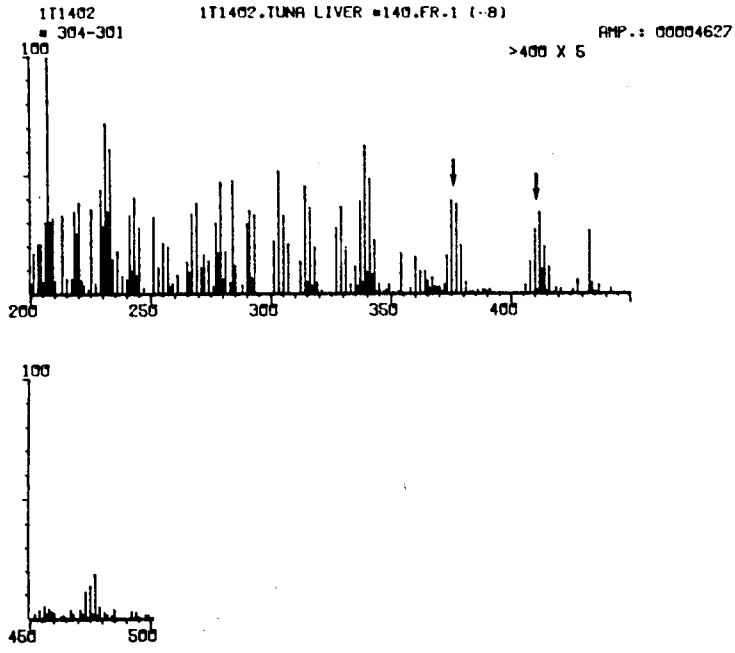

Fig. 6. Mass spectrum of $C_{10}H_9Cl_9$, a component of toxaphene in tuna liver (8Cl cluster at m/z=408).

At least one likely component of toxaphene was present in all fish. Its spectrum is illustrated on the example of the white shark (Fig. 7).

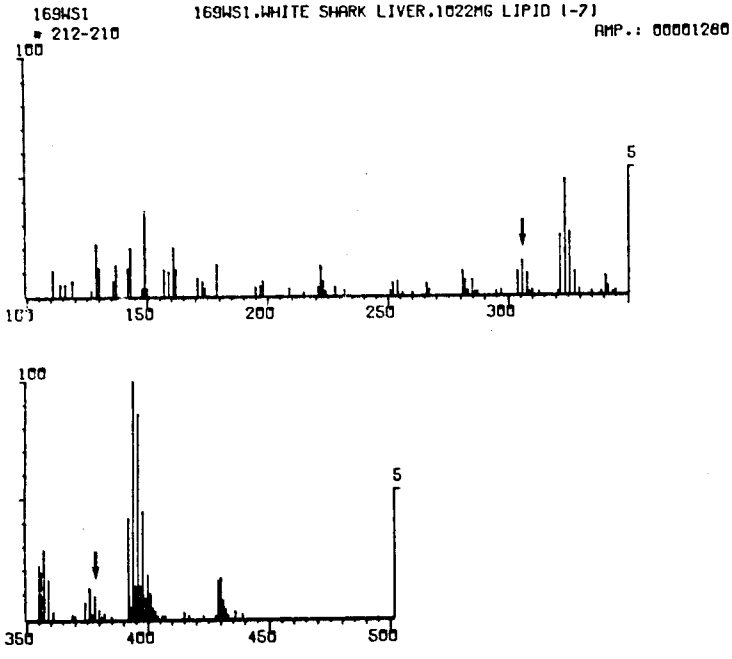

Fig. 7. Mass spectrum of $C_{10}H_9Cl_7$, a component of toxaphene in white shark liver (7Cl cluster at m/z=374).

Additional, generally detectable organochlorine compounds included DDMU (3Cl cluster at m/z=282 and 1Cl cluster at m/z=212) and mirex (6Cl and 5Cl clusters at m/z=270 and 235, respectively). The presence of octachlorostyrene is indicated by the mass spectrum in Fig. 3.

A compound yielding a 4Cl cluster at m/z=366 and fragmenting further by a loss of 2Cl (Fig. 8) could be a tetrachloroterphenyl. Under the given GC conditions, higher chlorinated terphenyls would not be detected.

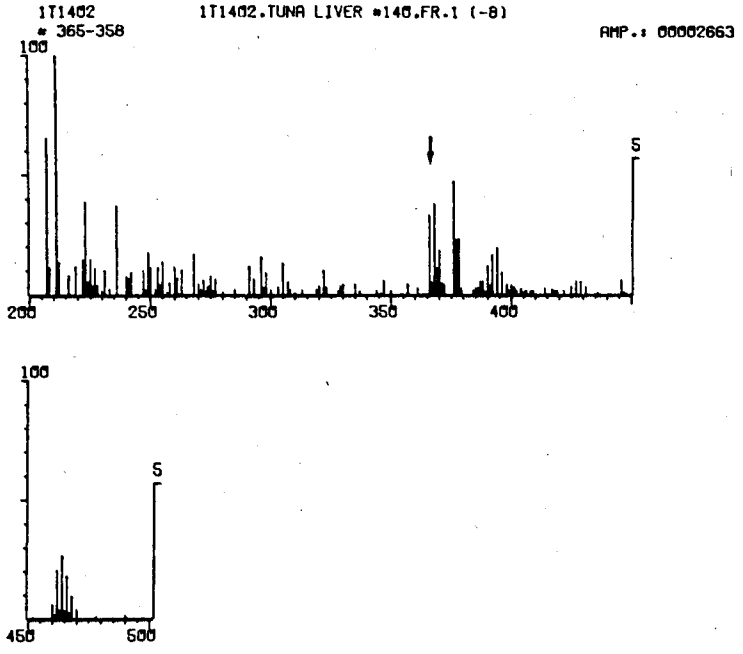

Fig. 8. Mass spectrum of a compound $C_{18}H_{10}Cl_4$ (4Cl cluster at m/z=366), possibly a tetrachloroterphenyl in tuna liver. Co-eluting is a nonachlorobiphenyl (9Cl cluster at m/z=460).

An unidentified compound with a 4Cl cluster at m/z=492 or a 9Cl cluster at m/z=490 was detected in the "sick" tuna (Fig. 9).

Continuing examination of the GCMS data is likely to lead to the detection and, eventually, identification of additional organohalogen compounds.

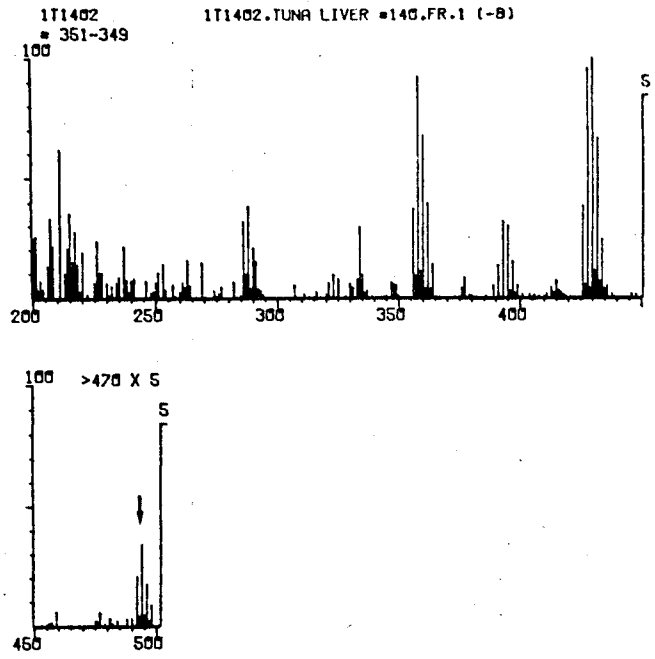

Fig. 9. Mass spectrum of an unidentified compound with a halogen cluster at about m/z=490, detected in tuna liver. Co-eluting is an octachlorobiphenyl (8Cl cluster at m/z=426).

CONCLUSIONS

At the moment there are no criteria to assess the toxicological significance of the levels of organochlorine compounds in the livers of sharks and tunas. The levels certainly appear high enough to warrant further investigation and quantification of not only the "routine" compounds but chlordane and toxaphene components as well.

The bluefin tuna fishery off Nova Scotia involves fish 10-30 yr old. The age of the "sick" tuna was 17 yr (Hurley, pers. comm.). This may indicate migration patterns through particularly contaminated areas. The association of high levels of organochlorine compounds with "sickness" may be a coincidence, but it underlines further the need for combined chemical and biological studies of this species.

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