Congener Specific PCB Analysis of Fish Tissue Samples

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Abstract. The Delaware Estuary is a major focus of scientific and technical studies conducted for the Delaware Estuary Program. This cooperative environmental initiative between the states of Delaware, Pennsylvania, and New Jersey is important for the estuary-protection actions it proposes and the conservation ethic it strives to promote. A fish consumption advisory was issued for striped bass, channel and white catfish, and white perch in the Delaware Estuary in June of 1994 as a result of elevated levels of polychlorinated biphenyls (PCBs). In recent years, there has been a growing awareness of the need to measure the concentrations of toxic chemicals in the flesh of fish taken from Delaware's waters. The procedures established to characterize PCB congener profiles, including non-ortho, mono-ortho and di-ortho congeners as well as organochlorine pesticides, dioxins, and furans in fish tissue are described.

Introduction. Fish samples from Delaware waters were characterized for PCB congener profiles in three categories: selected non-ortho (coplanar) PCBs, other target PCB congeners, and PCB homologs. The target analyte list includes those congeners for which dioxin toxic equivalency factors have been established, congeners specified in the NOAA National Status and Trends Programs,[1] and congeners recommended by researchers at the U.S. Army Corps of Engineers Waterways Experimental Station [2] based on potential toxicity and frequency of occurrence. The list also includes principal components of commercial Aroclor mixtures [3] and congeners most often detected in human tissues.

Experimental Methods. Fish tissue samples were received frozen in amber jars as ground and homogenized specimens. The fish tissue samples were processed for two different instrumental analyses: high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS) for the organochlorine pesticides and mono-ortho and di-ortho PCBs; and high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) for the non-ortho PCBs, PCDDs, and PCDFs.

HRGC/LRMS A 20-g sample size was mixed with sodium sulfate, spiked with a mixture of $^{13}C_{12}$ PCB and pesticide isotopes as surrogates, and placed in a Soxhlet extractor. The extraction solvent was methylene chloride:hexane (1:1). After a 16 hr extraction, the solvent was concentrated, and the extracts were processed through Gel Permeation Chromatography (GPC) and florisil solid-phase extraction cleanup procedures. Each sample extract was concentrated to 1.0 mL final volume and fortified with an internal standard solution containing d_6-3,3',4,4' tetra PCB. Instrument calibration standards containing the 71 target PCB congeners and OCl pesticides were analyzed by HRGC/LRMS. Sample results were calculated relative to response factors for each of the target analytes.

HRGC/HRMS. The extraction procedure used for the LRMS analysis was modified to include more extensive cleanup for the simultaneous determination of three coplanar PCBs (77,126, and 169) with PCDDs and PCDFs. The cleanup procedure relied on a series of chromatography column procedures including acidified silica, neutral alumina and AX-21 carbon. Sample extracts were concentrated to 10 μL for parts-per-trillion detection limits, and the samples were analyzed by HRGC/HRMS utilizing isotope dilution quantitation methodology.

Results and Discussion. Fish samples included in the FY'96 monitoring study were submitted for analysis from specific Delaware stream basins. The fish sampling survey was designed by Delaware's Division of Natural Resources and Environmental Control (DNREC).

Table 1 summarizes the results, by location, for the HRGC/LRMS congener specific PCB analyses of fish samples from locations designated as follow-up sites. The congener distribution is presented as the percentage of total PCBs determined for each of these samples. The detectable quantities of total PCBs, ranging from 45-970 ng/g or parts-per-billion (ppb) are shown at the end of Table 1. These data provide an indication of PCB profiles for various species of fish from multiple locations within two primary basins, shown here as basin codes A and B. Figure 1 illustrates the PCB congener distribution for the mass chromatograms characteristic of the tri, tetra, penta, hexa, hepta, and octa homologs from the HRGC/LRMS analysis of a fish sample collected from location A1.

The total homolog concentrations were studied in addition to the congener profile to determine the overall level of chlorination in the samples. Figure 2 compares the tetra, penta, hexa, and hepta homologs for 17 fish samples. The distribution of coplanar PCBs for tetra 77, penta 126, and hexa 169 is presented in Figure 3. Although the concentrations detected are in the parts-per-trillion range compared to parts-per-billion for total PCBs, these congeners are an important component of the fish contaminant testing program because of their structure and toxicological similarity to 2,3,7,8 TCDD.

The PCB congener profiles reported here continue to be a major focus of the annual toxics in biota monitoring program conducted by DNREC and complement other studies designed to assess levels of these toxic chemicals in water and sediment samples.

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Literature Cited

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2. McFarland, V.A. ; Clarke, J.M. *Environ. Health Perspect.* **1989** *81*:225-239.
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Table 1. PCB Congener Distribution (% of Total PCBs) in Fish Samples Collected From Delaware Waters-FY'96 Monitoring Study

IUPAC Congener No.	White Sucker [a] A-1 [b]	American Eel A-1	White Sucker A-2	Redbreast SunFish A-2	Channnel Catfish B-1	White Perch B-1	Lgmouth Bass B-1	White Catfish B-2	White Perch B-2	Channel Catfish B-3	Lgmouth Bass B-3
28 Tri	4.7	3.0	ND	ND	ND	ND	ND	ND	ND	ND	ND
42 Tetra	2.2	1.5	ND	ND	ND	ND	ND	ND	3.2	ND	ND
44 Tetra	4.6	2.3	3.0	ND	3.4	ND	ND	ND	ND	ND	ND
47 Tetra	4.6	5.1	2.5	2.9	2.8	3.7	2.7	ND	ND	ND	ND
49 Tetra	6.7	2.1	4.0	2.5	4.7	4.5	3.3	ND	ND	ND	ND
52 Tetra	1.1	6.2	ND	5.0	1.8	6.6	3.6	ND	ND	ND	ND
60 Tetra	3.7	1.2	ND	ND	2.0	ND	ND	ND	ND	ND	ND
64 Tetra	5.4	5.2	3.5	ND	3.5	3.7	ND	ND	ND	ND	ND
66 Tetra	ND [c]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
70 Tetra	7.0	0.8	3.9	3.4	4.2	ND	1.9	ND	ND	ND	ND
74 Tetra	5.4	3.8	2.2	3.5	2.7	ND	2.2	ND	ND	ND	ND
80 Tetra	7.8	5.5	3.5	4.7	3.9	ND	3.0	ND	ND	ND	ND
82 Penta	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
84/101 Penta	5.9	5.1	8.6	ND	8.4	18.4	12.5	10.6	18.6	6.7	9.5
87 Penta	4.4	3.4	4.3	4.3	ND	ND	ND	ND	ND	ND	ND
91 Penta	ND	0.6	ND	ND	1.3	ND	ND	ND	ND	ND	ND
92 Penta	ND	1.3	ND	ND	1.5	ND	ND	ND	ND	ND	ND
95 Penta	ND	1.4	3.2	ND	3.7	ND	ND	4.5	ND	ND	ND
97/86 Penta	3.2	ND	3.4	ND	ND	ND	ND	ND	ND	ND	ND
99 Penta	5.1	4.8	4.1	7.3	4.3	ND	8.3	13.8	ND	5.0	5.6
105 Penta	3.5	3.9	3.5	ND	2.1	ND	ND	ND	ND	ND	ND
110 Penta	4.8	6.4	8.5	ND	7.7	9.4	6.6	7.9	9.3	7.0	6.6
114 Penta	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
118Penta	6.2	9.6	6.8	13.8	8.3	8.7	9.0	8.5	11.1	8.4	7.2
119 Penta	ND	0.2	ND	ND	2.2	ND	ND	ND	ND	ND	ND
120 Penta	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
123 Penta	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
137 Hexa	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
138 Hexa	3.3	6.2	7.2	14.1	7.6	12.2	9.9	10.1	12.6	13.0	12.6
141 Hexa	0.9	0.7	1.0	ND	ND	ND	1.9	1.7	ND	ND	2.2
146 Hexa	0.6	1.1	1.5	2.6	1.7	3.5	2.2	ND	4.3	ND	3.1
149 Hexa	1.6	1.9	4.1	4.7	4.5	7.4	5.4	6.4	8.8	7.3	7.5
151 Hexa	ND	ND	1.2	2.1	ND	ND	1.7	2.4	ND	2.2	3.5
153 Hexa	3.2	6.3	7.4	12.9	8.0	15.8	12.5	15.2	17.7	19.0	17.0
156 Hexa	ND	0.4	ND	ND	ND	ND	ND	ND	ND	ND	ND
157 Hexa	ND	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 1. (Continued)

IUPAC Congener No.	White Sucker [a] A-1 [b]	American Eel A-1	White Sucker A-2	Redbreast SunFish A-2	Channnel Catfish B-1	White Perch B-1	Lgmouth Bass B-1	White Catfish B-2	White Perch B-2	Channel Catfish B-3	Lgmouth Bass B-3
158 Hexa	ND	0.6	0.9	ND	0.8	ND	ND	ND	ND	1.3	ND
166 Hexa	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
167/128 Hexa	0.9	1.1	1.5	2.1	1.3	ND	2.2	ND	2.4	2.5	1.8
168 Hexa	ND	0.2	ND	ND	ND	ND	ND	ND	ND	1.8	ND
170,190 Hepta	0.6	0.6	1.2	1.8	ND	ND	2.3	2.2	ND	2.6	2.9
171Hepta	0.7	0.2	ND	ND	ND	ND	ND	1.7	ND	1.2	ND
174 Hepta	ND	0.3	ND	ND	ND	ND	1.6	ND	ND	2.6	2.2
177 Hepta	ND	0.4	ND	ND	ND	ND	ND	ND	ND	ND	ND
179 Hepta	ND	ND	0.4	ND	ND	ND	ND	ND	ND	ND	ND
180 Hepta	1.2	1.7	2.6	4.4	2.5	6.0	5.6	4.5	6.6	9.6	9.0
183 Hepta	0.6	0.5	0.9	ND	ND	ND	ND	1.9	2.9	2.8	2.9
185 Hepta	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
187 Hepta	1.0	1.8	2.2	7.8	2.3	ND	ND	7.3	ND	6.1	6.4
189 Hepta	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
191 Hepta	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
194 Octa	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
195 Octa	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
196,203Octa	ND	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND
198 Octa	ND	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND
200 Octa	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
201 Octa	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
205 Octa	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
206Nona	ND	0.5	1.3	ND	ND	ND	1.7	ND	ND	ND	ND
207 Nona	ND	ND	ND	ND	0.6	ND	ND	ND	ND	ND	ND
208 Nona	ND	0.3	ND	ND	1.0	ND	ND	ND	ND	ND	ND
209 Deca	0.7	0.5	1.6	ND	1.5	ND	ND	1.5	2.5	ND	ND
Total PCBs (ng/g)	243	970	151	88	145	45	90	45	56	77	54

a-Species
b-Unique Basin-Location
C-ND=Congener not detected; not included in distribution percentage

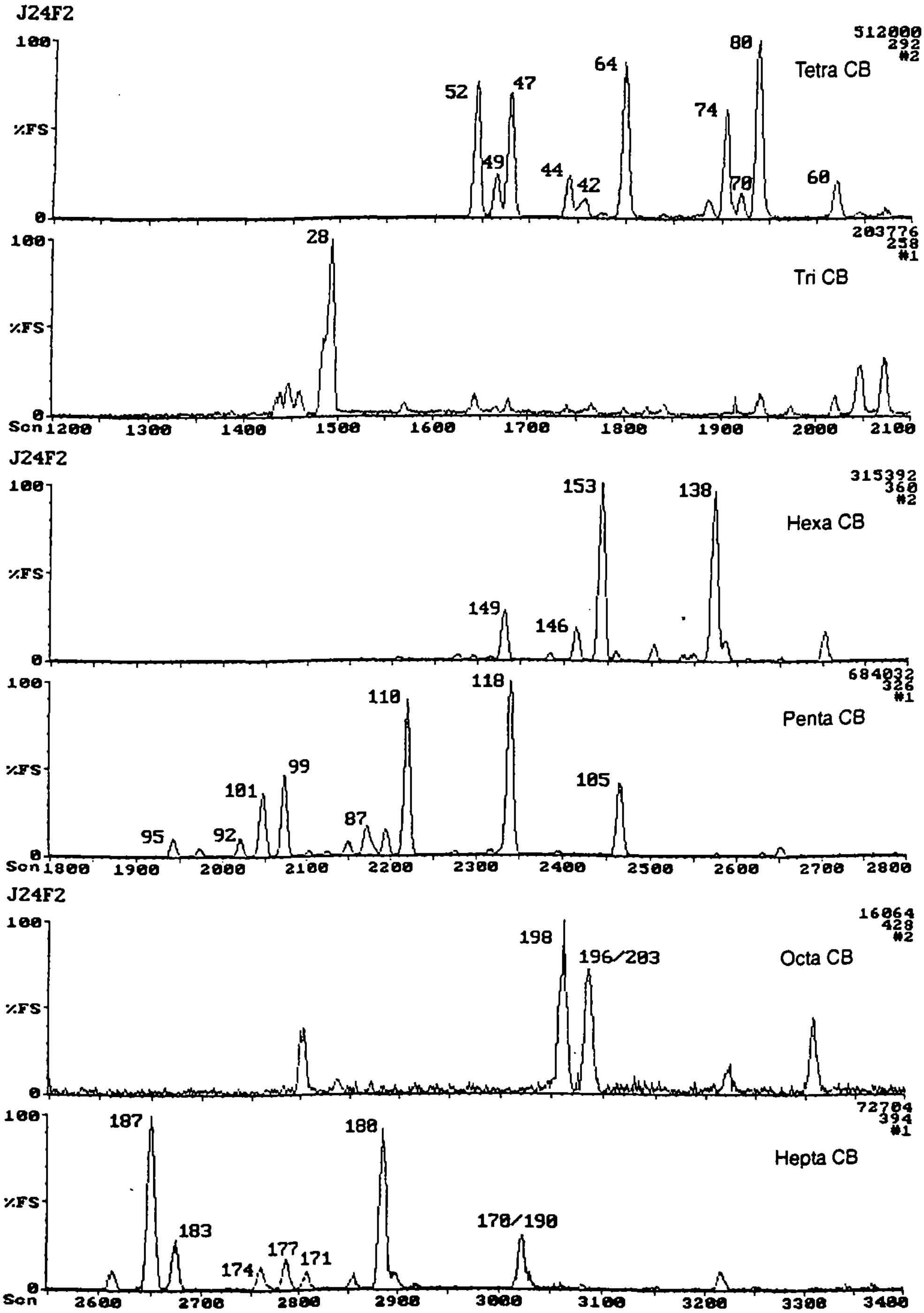

Figure 1. Mass Chromatograms of Tri CB through Octa CB in Fish Sample from Location A1

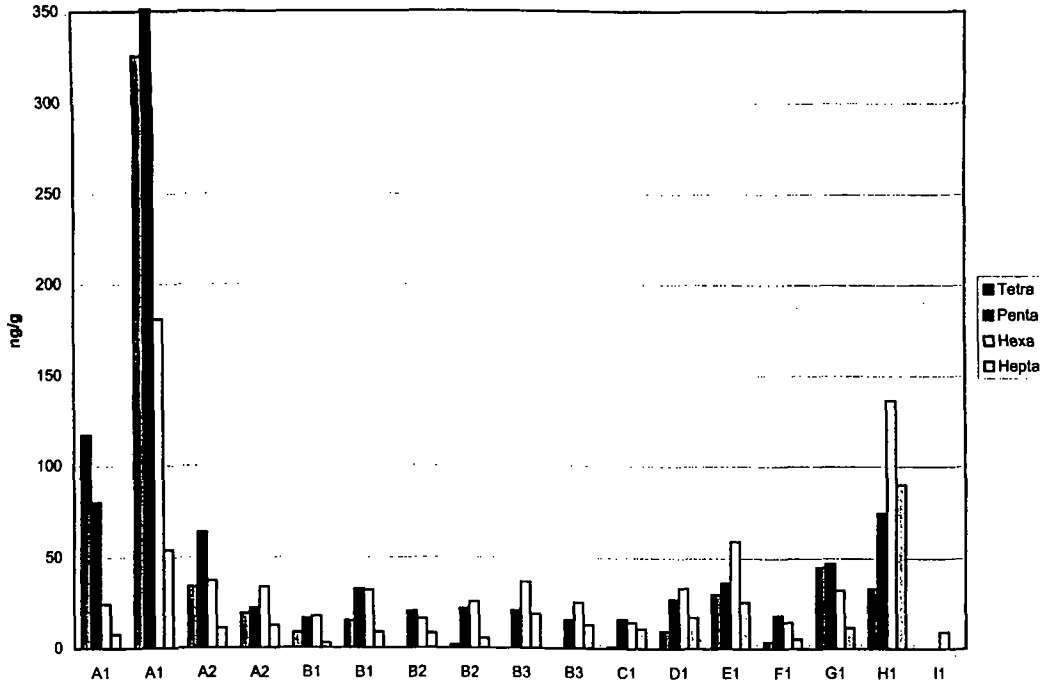

Figure 2. PCB Homolog Distribution in Fish Samples

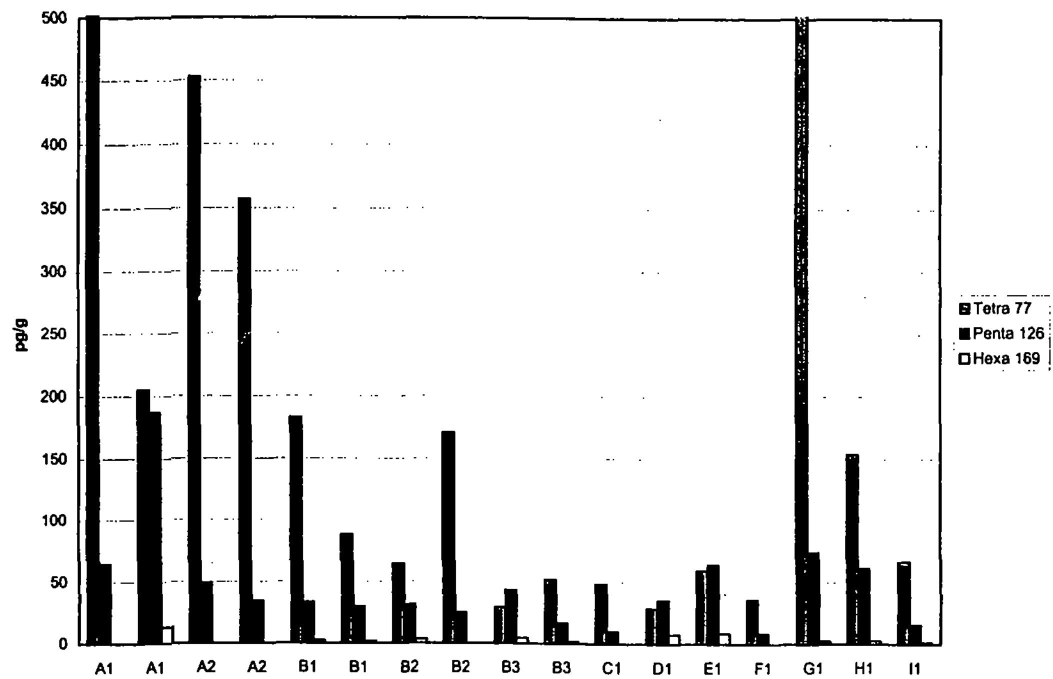

Figure 3. Coplanar (non-ortho) PCB Congener Profile in Fish Samples