DECISION CRITERIA FOR SELECTION AS PCB CONGENER ANALYTE FOR US FOODS.

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Introduction

A more complete assessment of PCB exposure from foods requires a congener-specific analysis of PCBs in foods. Widely varying theories on toxic mechanism and toxicity of congeners, coupled with varying patterns of congener profiles in particular media suggest that a congener-specific analysis may provide the best data for elucidating causal relationships. The available data concerning the occurrence of PCB congeners present a patchwork of media examined, number of congeners examined, detection limits, analysis methods, congener classification schemes, and bias toward particular mechanisms of toxic action. FDA plans to routinely examine PCBs using congener specific methods in the FDA Total Diet Study (TDS). This paper describes a method for choosing congeners for analysis in TDS, based largely on percent contribution to total PCB levels in published analyses of foods.

Laboratories do not provide analytical results for all the PCB congeners identified in Aroclors.[1,2] Studies typically report results for 20 to 40 congeners. The congener sets analyzed by different laboratories usually overlap for about a dozen congeners thought to be most common. Other congeners are reported with varying frequencies between studies. The basis for choosing whether a congener is common (and whether to include it in a particular study) is typically the average concentration in human serum or in fish. Consideration is rarely given to biological half-times or variation in timing of exposures leading to a particular serum or fish tissue result. Congener-specific analyses are most commonly available for fish and human serum, milk, and fat, with a handful of studies of other media.[1] Correlations among congener sets across individuals have been developed for studies of serum [3], but not other media (e.g., the relationship between the presence of CB 153 and CB 126 has not been examined for any food).

Methods and Materials

Screening of published congener data. Studies (and reviews of studies) reporting congener-specific analysis in a variety of media for at least 20 PCB congeners were reviewed (or the non-ortho PCBs were measured in a dioxin/furan/PCB analysis). A list of congeners reported in more than one study was developed (72 total congeners on the list). Four criteria were used to assign a congener to a list of candidate analytes for TDS: 1) the congener was detected in a sample (foods, biota, or human milk, serum, or fat) and contributed more than 5% to total PCB measured, 2) the congener was detected in a sample (foods, biota) and contributed more than 5% to sum dioxin TEQ for the PCBs measured, or 3) the congener was infrequently observed but accounted for more than 2% of the total PCB when measured.

PCB congener specific analysis. To begin confirmation of congeners chosen through literature review, bluefish and rockfish were selected for preliminary PCB screening. Test portions (10 g) were fortified with 2.5 ng $^{13}C_{12}$ PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189. Total PCBs were extracted with 50% cyclohexane/ CH_2Cl_2, de-fatted with sulfuric acid silica gel followed by alumina chromatography. Extracts were screened using quadrupole ion storage tandem mass spectrometry. Test samples with detects for coplanar PCBs were further fractionated with AX21 carbon chromatography before reanalysis with tandem mass spectrometry. PCBs were separated into two fractions. The first fraction contained PCBs eluting with n-hexane. The second fraction contained the remaining PCBs recovered when the column was eluted with toluene. Both fractions were measured for PCBs using the labeled standards for identification and quantification. Mono-ortho and non-ortho PCBs were also distinguished by using differences in daughter ion spectra reported by Lausecvic.[4] Optimized tandem mass spectrometry parameters permitted the easy separation of all PCB response into mono-ortho (and non-ortho) and diortho chlorine substitution. PCBs identified in fish were ranked by their relative area response to the $^{13}C_{12}$ PCB standard.

Results and Discussion

There are 42 congeners on the list of candidate analytes, after applying the three screening criteria (Table 1). Sixteen congeners are considered "marginal" candidates because they met the criteria in only one study. It should be noted that there was limited data for many congeners (e.g., for 20 congeners there were only two studies reporting results, one of which[2] only examined one sample). PCB congeners found in rockfish and bluefish are indicated in Table 2 with relative intensity indicated. The preliminary results from this small group of samples supports the inclusion of some of the candidate analytes. Some marginal candidate PCBs were easily detected as well. Further sampling of foods will be used to refine the list of congeners when CFSAN moves to its new laboratory in 2001.

References

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Table 1. Basis for congeners chosen			
Congener	Reference for analysis data	Congener	Reference for analysis data
3	1	114	13, 7[@]
18	5	118	1, 13, 7, 8, 11, 10, 14, #
28	9 8 10, 12	119	6
33	11*	123	10
37	6, 11*	126	13, 7[@]
44	5, 10	136	1
47	8, 10	137	1, 11*
49	1, 5, 8, 10	138	1, 9 5, 11, 10, 12, 14, #
52	5, 1, 8, 10	146	6
60	11	149	10, #
66	1, 9 10*, #	151	10
70	10	153	1, 9 5, 11, 10, 14, #
74	1, 8, 10, 12, 14	156	6, 9 7 10
77	6, 1, 9, 10	157	6, 7
80	10	163	1
85	1	169	13[@]
95	1, 9, 10	170	6, 10, 12, 14
99	1, 8, 11, 10, 14, #	172	14
101	6, 1, 9 5, 8, 10, #	180	1 9, 11, 10, 12, 14, #
105	13, 1, 7, 11*	182	6
110	9,8,10, #	187	1 10, 14

* Infrequently detected but > 2% of total

[@] Exceeds criteria for TEQ measure only.

Confirmed by analysis of fish samples (Table 2).

Table 2. Candidate PCB analytes and other PCB congeners found in Rockfish and Bluefish; values are the approximate percent of total response measured for PCBs.

PCB Congener	"Rockfish"	Bluefish	PCB Congener	"Rockfish"	Bluefish
18	ND	ND	123	nd	nd
28	2.6%	1.9%	126	0.1%	0.1%
33	0.5%	ND	128	2.6%	ND
37	0.5%	ND	138	15.6%	11.8%
47	3.1%	2.7%	149	2.6%	4.8%
49	1.6%	ND	153	13.0%	7.5%
52	4.2%	3.7%	156	0.4%	0.6%
66/70	2.6%	8.0%	157	0.2%	0.2%
70	2.6	ND	167	0.4%	0.4%
74	2.1%	2.7%	169	nd	nd
77	0.3%	0.1%	170	2.1%	ND
87	0.5%	ND	171	0.5%	ND
95	1.6%	ND	177	2.1%	ND
99	5.2%	14.4%	180	5.2%	0.5%
101	5.2%	15.5%	183	0.3%	ND
105	2.6%	2.7%	187	0.5%	ND
110	5.2%	12.3%	194	0.5%	ND
114	1.0%	0.0%	199	0.3%	ND
118	10.4%	10.2%	201	0.2%	ND
119	1.0%	ND	202	0.5%	ND

nd = not detected, ND = not determined