SELECTIVE ENRICHMENT OF COPLANAR POLYCHLORINATED BIPHENYLS IN LAKE MICHIGAN CHINOOK SALMON: A COMPARISON OF CALCULATION METHODS

Lisa L. Williams* and John P. Giesy

Department of Fisheries and Wildlife, Pesticide Research Center, Center for Environmental Toxicology, Michigan State University, East Lansing, MI 48824

ABSTRACT

Different methods of calculating selective enrichment of toxic PCBs in aquatic biota resulted in different selective enrichment factors for the same samples.

INTRODUCTION

Patterns of concentrations of PCB congeners in environmental samples are not the same as those in the original Aroclor mixtures (1). The toxicity of PCB congeners varies by as much as 100,000 times, thus changes in the relative concentrations of PCB congeners may have a great impact on the toxicity of the PCB mixture. Preliminary research has suggested that the most toxic congeners, which are generally planar and nonortho-substituted, make up a greater proportion of the total concentration of PCBs in some aquatic organisms than they do in the commercial Aroclors. The most toxic congeners are also some of the congeners which are most resistent to degradation and metabolism (2). Each transfer of PCBs from one trophic level to another provides additional opportunities for differential absorption, partitioning, metabolism and depuration among PCB congeners.

Evidence for selective enrichment is not entirely consistent. Some of the discrepancies may be due to the different methods used to calculate selective enrichment. No selective enrichment of toxic PCB congeners appeared to be occurring in Canadian fish-eating birds, seals, whales and polar bears when enrichment was measured as the ratio of congener #126 to #153 or as the ratio of #105 to #153 (3). Selective enrichments of three to seven fold have been calculated for Great Lakes fish and birds using ratios of #126 in samples to #126 in equivalent amounts of Aroclors or using ratios of induction of

ethoxyresorufin-O-deethylase (EROD) activity in samples to induction of EROD activity in equivalent amounts of Aroclors (4).

The purpose of this study is to compare methods of calculating selective enrichment factors (SEFs) within data sets. This study will eventually include measurements of selective enrichment from at least three trophic levels of the Lake Michigan food chain.

METHODS

Sampling. Two groups of samples have been analyzed. Chinook salmon (Oncorhynchus tshawytscha) eggs were collected at a weir in the Little Manistee River, a Lake Michigan tributary, in October, 1986. Fillets from Lake Michigan chinook salmon caught near Ludington, MI, in 1988 were skinned and belly fat, dorsal fat and lateral lines were removed before the fillets were homogenized for analysis.

Analysis. Samples were extracted and clean-up was performed using sodium sulfate/methylene chloride extraction, gel permeation chromatography to remove lipids, and adsorption chromatography with florisil and silica gel (5). Acidic silica gel/silica gel columns were used in place of the two column method for the fillet samples (6). Concentrations of total PCBs and individual ortho-substituted congeners in the samples of eggs were determined by HRGC-ECD using response factors (7) and confirmed for our GC and operating conditions. Relative contributions of Aroclors 1248, 1254 and 1260 were assumed to be 1:3:1.2 for all of the egg samples. Concentrations of total PCBs and estimated Aroclor compositions of the fillet samples were calculated from HRGC-ECD results with the multiple regression package COMSTAR (8).

Concentrations of PCB congeners #77, 105 and 126 (IUPAC numbering system) were determined on HRGC-ECD following separation of coplanar congeners from interfering PCB congeners. This separation was performed on particulate carbon (PX-21, Amoco, Chicago, IL) and glass fiber column. Most PCB congeners were removed with elutions of 10% methylene chloride in hexane and 30% methylene chloride in hexane. Coplanar congeners were eluted with toluene in the reverse direction.

Calculation of SEFs. SEFs are dimensionless ratio between the concentrations of coplanar congeners and in the total PCBs in the sample and the concentrations of coplanar congeners in an equivalent amount of Aroclor mixture representative of the sample PCB burden. Put more simply, SEFs are the ratio of the observed to the expected concentrations of toxic congeners. Concentrations of #77 and 126 in Aroclors were determined by Kannan et al.(9).

SEF1: Ratio of the concentration of an individual congener in the samples to that expected based on the total concentration of PCBs in the sample consisting of Aroclor 1248.

SEF2: Same as SEF1 except that total concentration of PCBs is assumed to consist of Aroclor 1254.

SEF3: Same as SEF1 except that total concentration of PCBs is assumed to consist of Aroclor 1260.

SEF4: Same as SEF1 except that the total concentration of PCBs is assumed to consist of the linear combination of Aroclors 1248, 1254 and 1260 that provides the best fit for the pattern observed in that sample or group of samples.
SEF5: Ratio of the concentration of the coplanar congener relative to the concentration of #138 in the sample to the concentration of the toxic congener relative to the concentration of #138 in Aroclor 1254.

RESULTS

Measurements of selective enrichment of congener #77 varied depending on the method used for calculating SEFs (Table 1). Concentrations of congener #77 in egg samples appeared to be enriched relative concentrations of #77 in Aroclors when enrichment was calculated with SEF2 and SEF3. No values of SEF1 or SEF4 were greater than 1.0 in the egg samples and values of SEF5 varied from 0.52 to 8.21 for the samples of eggs. SEF5 was not correlated with SEF2 (R^2=0.029), which is the other SEF which assumes that all PCBs are present as Aroclor 1254. Correlations among SEF1, SEF2, SEF3 and SEF4 were much greater (R^2>0.9). All measurements of enrichment of #126 (Table 2) were greater than 1, although relationships among the SEFs were similar to those calculated for congener #77.

DISCUSSION

Different methods of calculating selective enrichment give different results. It is not known if selective enrichment is actually occurring and, if so, to what extent. Thus, the measurements of selective enrichment by the SEFs described in this paper cannot be compared to known, true values. The magnitude of selective enrichment of #126 expressed as SEF1, SEF2, SEF4 and SEF5 are similar to those calculated from studies of induction of EROD activity (4). SEFs based on ratios between individual congeners and congener #138 (SEF5) are easier to obtain than measures based on the pattern of total PCBs observed but may not integrate information on changing patterns of congener concentrations as well. Unfortunately, a comparison to the work of Norstrom et al. (3) was not possible because #153 and #132 were not resolved in the chinook salmon eggs and fillets.

ACKNOWLEDGEMENTS

Ted Schwartz and Kevin Feltz generously shared carbon column chromatography technology with us. We would also like to thank Tim Kubiak, Dave Verbrugge and Nicole DeGalan for their help. This study was supported by the USDA Water Science Fellowship program, the MSU Agricultural Experiment Station and the MSU Pesticide Research Center.

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Table 1. Selective enrichment factors (SEFs, see text for explanation) for 3,3',4,4'-tetrachlorobiphenyl (#77) in chinook salmon eggs and fillets.

Sample	SEF1	SEF2	SEF3	SEF4	SEF5
Eggs 6	0.15	1.56	3.65	0.59	0.77
Eggs 8	0.17	1.73	4.06	0.66	0.81
Eggs 9	0.14	1.44	3.38	0.55	2.46
Eggs 10	0.10	1.03	2.41	0.39	0.52
Eggs 11	0.15	1.56	3.66	0.60	3.54
Eggs 14	0.15	1.49	3.49	0.57	0.76
Eggs 15	0.13	1.29	3.04	0.50	2.87
Eggs 19	0.15	1.50	3.52	0.57	8.21
Eggs 20	0.13	1.30	3.06	0.50	0.60
Fillet 1	0.56	5.69	13.36	3.30	-
Fillet 2	0.42	4.28	10.05	0.96	-
Fillet 3	0.15	1.54	3.61	0.85	-
MEAN for eggs	0.14	1.43	3.36	0.55	2.28
MEAN for fillets	0.38	3.84	9.01	1.70	-

Table 2. Selective enrichment factors (SEFs, see text for explanation) for 3,3',4,4',5-tetrachlorobiphenyl (#126) in chinook salmon eggs and fillets.

Sample	SEF1	SEF2	SEF3	SEF4	SEF5
Eggs 6	2.49	3.37	18.63	3.84	1.66
Eggs 8	2.55	3.45	19.04	3.92	1.62
Eggs 9	1.82	2.47	13.65	2.81	4.23
Eggs 10	2.29	3.11	17.16	3.54	1.58
Eggs 11	2.57	3.48	19.24	3.96	7.91
Eggs 14	3.14	4.25	23.46	4.83	2.16
Eggs 15	3.61	4.89	27.02	5.57	10.83
Eggs 19	4.06	5.50	30.39	6.26	30.16
Eggs 20	2.26	3.06	16.88	3.48	1.39
Fillet 1	12.67	17.16	94.77	22.36	-
Fillet 2	6.58	8.91	49.20	8.75	-
Fillet 3	5.96	8.07	44.59	10.10	-
MEAN of eggs	2.76	3.73	20.61	4.24	6.84
MEAN of fillets	8.40	11.38	62.85	13.73	-