LEVELS OF PCDD/Fs, PCBs, AND PBDEs IN EDIBLE FISH FROM CALIFORNIA COASTAL WATERS

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Introduction

Persistent organic pollutants (POPs) such as PCDDs, PCDFs, PCBs, and polybrominated diphenyl ethers (PBDEs, a widely used class of brominated flame retardants), enter the environment through numerous pathways. Once in the environment, they can then enter the food web, where they can bioaccumulate in upper trophic level species, including humans. While the toxicity of PCDD/Fs and PCBs is clearly documented [1], relatively little is known about the toxicity of PBDEs. However, there is increasing concern that PBDE exposures can cause thyroid hormone disruption, neurodevelopmental deficit, and cancer, with pregnant women, their fetuses, and newborn infants being especially sensitive populations [2,3]. Our group is working with other state agencies to measure the levels of PCDDs, PCDFs, coplanar PCBs, and PBDEs in edible fish taken from the San Francisco Bay and from California coastal waters. These results may be used in exposure assessment studies and to determine the need for fish advisories, community education, or other public health interventions.

Methods and Materials

Fish were collected in 2000 from the San Francisco Bay and in 2001 from Pacific coastal waters. Fish were selected using human consumption patterns, and only edible parts (filets with or without skin) were analyzed. Each sample was a composite of several individual fish of the same species within a certain size, collected from distinct geographic areas. Species analyzed included both bottom feeders and surface fish, including white croaker, California halibut, diamond turbot, surf perch, shiner perch, and striped bass [4].

Edible portions of fish (with or without skin) were homogenized and stored frozen at -20 ºC until analysis. Frozen samples were lyophilized, fortified with $^{13}C_{12}$-labeled internal standards (PCDD/Fs, coplanar PCBs), homogenized and extracted in 1:1 hexane/methylene chloride with anhydrous sodium sulfate, and filtered. Lipids were determined gravimetrically using a small portion of this extract. Another portion was set aside for PBDE analysis, and the remainder of the extract was used for PCDD/F analysis.

The PBDE portion was fortified with internal standard ($^{13}C_{12}$-labeled 3,3',4,4'-tetrabromo-diphenyl ether, BDE-77) and lipids removed by gel permeation chromatography (GPC) followed by a sulfuric acid-impregnated silica gel column. Recovery standards were added and the volume reduced to 10 μL in tetradecane. Samples were analyzed on a Finnigan 4510 low resolution GC/MS on a DB5 column (60 m, 0.25 μL film, 0.25 mm id, helium carrier gas) using negative ion chemical ionization and research grade methane as the reagent gas. Typical operating conditions include an ion source temperature of 150 ºC, an ionization energy of 70 eV, an electron current of

0.3 mA, and a methane pressure of 0.6 torr. Multiple ion detection was used to monitor m/z 79/81 (bromine) and the molecular ions of the recovery standards.

The PCDD/F portion was passed through a silica gel/potassium silicate column and a carbon column, with PCDD/Fs being retained on the carbon column. The carbon column was eluted with hot toluene, the eluate evaporated to residue, reconstituted in hexane, and passed through a potassium silicate/acid silica/neutral silica column. After concentration and addition of recovery standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD), it was brought to a final volume of 10 μL in tetradecane. The sample was analyzed on a ThermoFinnigan MAT90 high resolution GC/MS using a DB5 column (60 m, 0.25 μL film, 0.25 mm id, helium carrier gas). The mass spec was operated in multiple ion detection mode using electron impact ionization. The source temperature was 250 ºC, the ionization voltage was 42 V, and the current was 0.6 mA. PFK was used as the mass reference.

Results and Discussion

Analysis of fish samples is currently in progress. To date, 63 samples have been analyzed for PCDD/Fs and coplanar PCBs. Four congeners (2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PeCDF, account for approximately 94% of the total I-TEQ, and we will focus on these PCDD/F congeners only, in addition to the three PCBs. Summary statistics for these seven analytes, the I-TEQ, and PCB-TEQ, are shown in Table 1. To date, 25 samples have been analyzed for PBDEs, and these summary statistics are also shown in Table 1. For both sets of analyses, the data include fish from several different species, samples with or without skin, and from different locations within a general area (e.g., several locations within San Francisco Bay). When all samples were combined and expressed on a lipid basis, PCDD/F and PCB congeners, as expected, were highly and significantly correlated with each other and with I-TEQ and PCB-TEQ (Spearman rho > 0.75, $p < 0.001$). Similarly, all individual PBDE congeners were strongly and significantly correlated with Σ PBDEs (Spearman rho > 0.75, $p < 0.001$). Only BDE-100, however, correlated with all other analytes (Spearman rho > 0.58, $p < 0.01$). With very few exceptions, BDE-47 was the dominant congener, followed by BDE-100. Further analyses are underway to explore profiles and pathways. Congener profiles for PBDEs are shown in Figure 1.

In addition to these fish which were collected in 2000, our laboratory has also analyzed fish from previous sampling efforts in 1994 and 1997. Based on the preliminary results presented here, the levels of PCDD/Fs and PCBs in general are comparable to the levels from the previous sampling efforts. This is the first time that PBDEs have been measured as a part of this sampling program. Thus, there are no data from past sampling efforts to compare with the PBDE data presented here. Overall, it appears that while the levels of PCBs in San Francisco Bay are higher than other California coastal waters, the levels of PCDD/Fs and PBDEs are comparable.

References

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Figure 1. Profiles of primary PBDE congeners in composite fish samples. Concentrations in ng/g lipid weight.

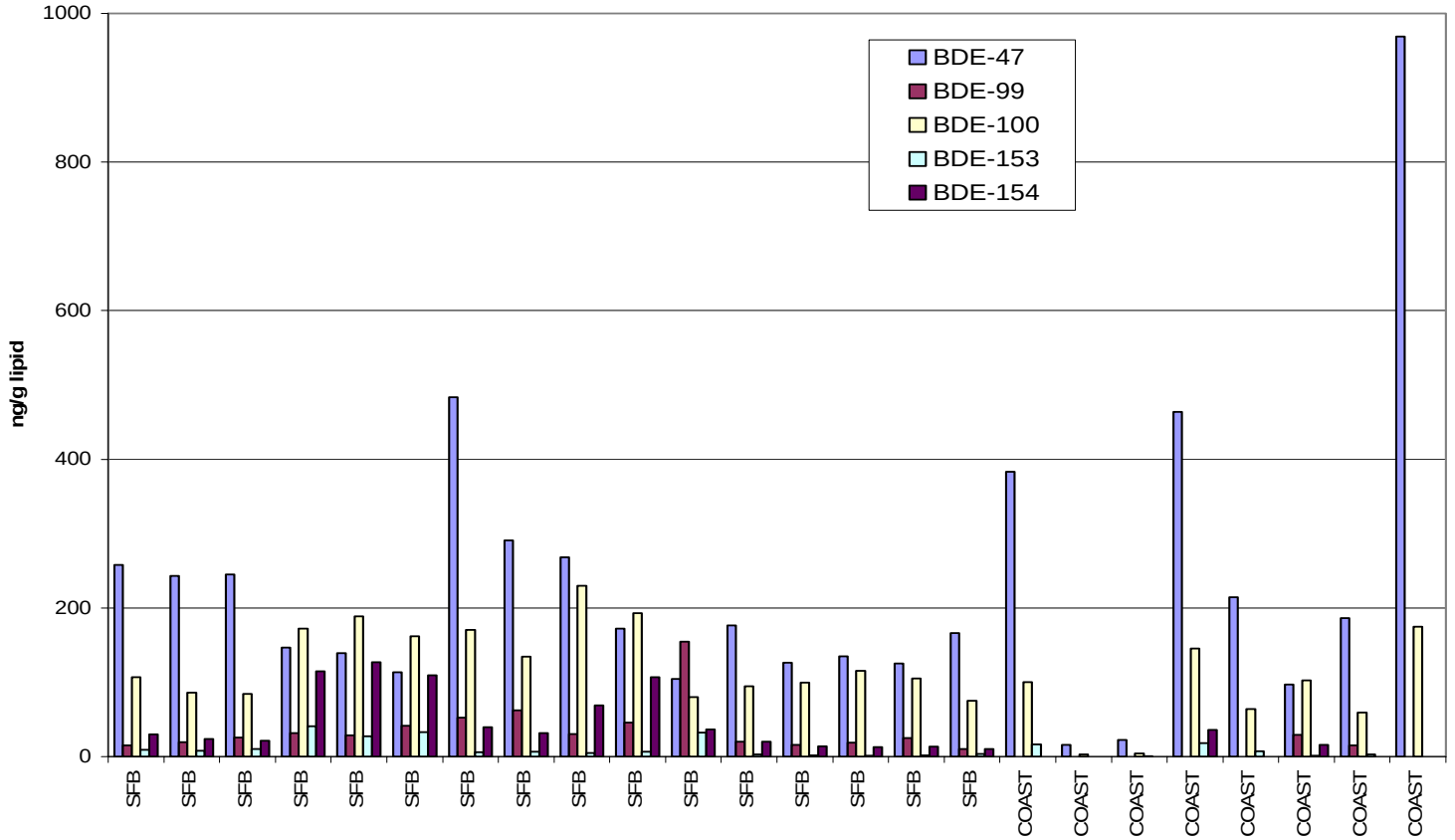

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Table 1. Summary statistics for PCDD/Fs, PCBs (pg/g lipid weight), and PBDEs (ng/g lipid weight) in fish composite samples from San Francisco Bay and other California coastal waters. Statistically significant differences are indicated by p-values.

		San Francisco Bay						Other California Coastal Waters					
	n	Mean	Std Dev	Min	Max	Median	n	Mean	Std Dev	Min	Max	Median	p
% Lipid	34	2.66	1.56	0.71	6.26	2.36	34	0.97	1.02	0.04	3.57	0.49	0.00
TCDD	32	5.62	7.66	0.18	37.4	4.01	25	4.55	3.27	0.35	12.5	3.68	
PeCDD	32	13.1	17.6	0.34	87.9	10.1	28	7.44	8.46	0.35	27.1	3.48	
TCDF	32	108	117	1.26	441	61.0	20	163	209	9.47	644	78.8	
PeCDF	32	30.4	22.8	1.26	105	25.7	28	18.9	15.1	1.75	55.7	17.0	0.03
I-TEQ	32	38.2	36.7	2.65	176	30.9	29	27.9	29.1	2.90	117	19.0	
PCB-77	33	4914	9460	1.26	46412	2140	28	6139	16077	249	85857	1221	
PCB-126	33	1308	1580	5.04	7427	879	28	963	1200	62.3	4800	312	0.03
PCB-169	32	89.2	86.3	9.97	442	64.7	27	69.2	102	4.55	431	27.6	0.01
PCB-TEQ	33	134	163	0.61	769	90.0	29	96.6	126	0.27	525	29.9	0.03
PBDE-47	16	200	97	105	483	169	8	294	316	16	969	200	
PBDE-99	16	37	34	10	155	27	2	22	10	15	29	22	
PBDE-100	16	131	48	75	230	111	8	82	62	3.1	175	82	
PBDE-153	16	12	13	1.1	41	6.9	6	7.8	7.8	0.65	18	5.2	
PBDE-154	16	49	42	10	127	31	2	26	14	16	36	26	
Sum PBDEs	16	429	138	257	752	414	8	394	372	19	1144	275	

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