Levels of PBDEs and Other Persistent Organic Pollutants in Edible Fish From California Coastal Waters

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Introduction

Persistent organic pollutants (POPs) such as PCDD/Fs, PCBs, and PBDEs, enter the environment through a variety of pathways. Once in the environments, they can enter the food web, where they can accumulate in upper trophic level species, including humans. While the toxicity of POPs such as PCDD/Fs and PCBs have been clearly documented[1], relatively little is known about the toxicity of PBDEs. However, in the last 10 -15 years, PBDEs have come under increased scrutiny, and many of these studies are suggesting that PBDEs can cause a variety of adverse health effects, including thyroid hormone disruption, neurodevelopmental deficits, and cancer; with pregnant women and their fetuses, newborns, and children who are nursing being especially sensitive populations.[2,3]

One possible route of exposure to POPs in general, and to PBDEs specifically, is through the consumption of contaminated fish. Our group has been working with other state agencies to measure levels of PCDD/Fs, PCBs, and PBDEs in edible fish taken from the California coast, including open coastline as well as bays and harbors. 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 followed by a sulfuric acid-impregnated silica gel column. Recovery standards ($^{13}C_{12}$ labeled PCB128/178) 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 congeners measured were BDEs-47, 99, 100, 153, and 154. Details of the PCDD/F and coplanar PCB cleanup may be found elsewhere.[5]

Results and Discussion

A total of 43 composite samples were analyzed for PBDEs, collected from along the entire California coast, ranging from Crescent City in the north, to San Diego Harbor in the south. For all fish of all species from all sampling locations, the most prevalent congener was BDE-47, with concentrations of the other BDEs in the order of: BDE-47 > BDE-100 > BDE-99 ~ BDE-154 > BDE-153. Summary statistics for the concentrations of the PBDEs are shown in Table 1. These samples were also analyzed for PCDD/Fs and coplanar PCBs, and the summary statistics for the four PCDD/F congeners that contribute the most to the I-TEQ and the coplanar PCBs are also shown in Table 1. In addition, the data on all of these analytes were evaluated for statistical correlation. The PCDD/Fs and coplanar PCBs were highly correlated, but there was no statistical correlation between PCDD/Fs and PBDEs, or between coplanar PCBs and PBDEs. This would suggest that PCDD/Fs and PCBs share a common source, while PBDEs have a different source.

Sixteen of the 43 samples were collected from various locations within San Francisco Bay, with the remaining 27 samples being collected from along the coast. A statistical comparison between all fish from San Francisco Bay and all fish collected from the coast shows that the concentrations of all five PBDE congeners of interest as well as total PBDEs are statistically greater in San Francisco Bay than the concentrations along the coast. This is shown in Figure 1.

However, additional data indicates that the levels in San Francisco Bay may be even higher now. In a separate study from San Francisco Bay, our laboratory has analyzed a few individual fish of six species collected in 2002.[6] Two of these six species in this separate study, jack smelt and striped bass, were species also measured in our study. The levels of total PBDEs in jack smelt were higher in our study by about 30%, whereas the

levels in striped bass were higher in the other study by a factor of almost 5. The levels of total PBDEs in the other fish in the other study were also very high.

A qualitative examination of our data by looking at total PBDE concentrations as a function of sampling location suggests that PBDE levels are highest in enclosed bays and harbors, and, not surprisingly, in areas of high population density. There are, however, results that cannot be explained solely on the basis of geography, proximity to population density, or species alone. We observed that samples of two different species from the same sampling location had very different PBDE levels, while two samples of the same species from two separate but similar locations (enclosed location near high population density) also had very different PBDE levels. We are continuing our evaluation of these data.

References

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Tables and Figures

Table 1. Summary statistics for concentrations of PBDEs in all fish collected from California coast and harbors. Summary statistics of major PCDD/Fs and coplanar PCBs are included for comparison purposes.

	All Fish (pg/g lipid) (PBDEs ng/g)						
	Mean	Median	Min	Max	Stnd Dev	Stnd Error	Count
PBDE 47	163	140	0.22	688	134	20.5	43
PBDE 99	27.3	15.6	0.28	202	40.7	6.21	43
PBDE 100	78.5	75.2	3.08	256	68.4	10.4	43
PBDE 153	8.25	4.67	0.28	49.1	11.1	1.70	43
PBDE 154	25.4	13.5	0.34	127	32.8	5.00	43
Total PBDE	302	271	13.3	1020	238	36.2	43
2,3,7,8-Cl4DD	4.58	3.17	0.18	37.4	5.93	0.76	61
1,2,3,7,8-Cl5DD	9.52	4.72	0.34	87.9	14.2	1.79	63
2,3,7,8-Cl4DF	104	55.9	1.26	644	133	17.8	56
2,3,4,7,8-Cl5DF	22.4	18.2	0.78	105	20.5	2.58	63
PCB-77	5080	1840	1.26	85600	12700	1590	64
PCB-126	1073	758	5.04	7430	1420	177	64
PCB-169	74.1	47.8	3.77	442	93.2	11.8	62
I-TEQ	33.1	27.1	3.43	193	34.9	4.36	64
PCB-TEQ	109	74.4	1.26	771	147	18.3	65
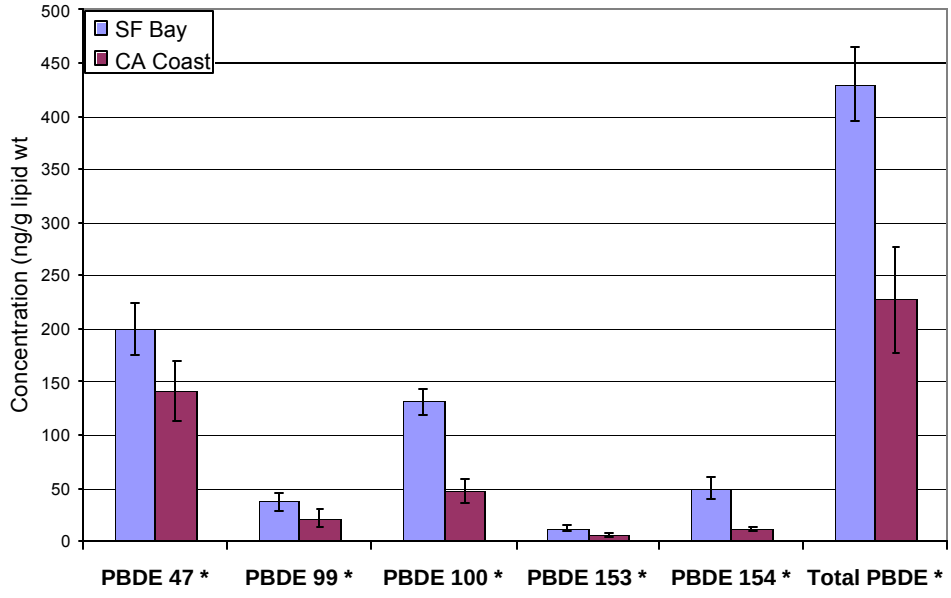
Figure 1. Comparison of concentrations of PBDEs of all fish collected from San Francisco Bay with all fish colleted from the California coast. The "*" indicates a statistically significant difference between Bay and Coast concentrations.