

PBDEs IN THE SAN FRANCISCO BAY AREA: MEASUREMENTS IN FISH

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Introduction

High levels of polybrominated diphenylethers (PBDEs) have been found in humans and wildlife from the San Francisco Bay Area^{1,2}, with levels in women among the highest in the world, and levels in harbor seals doubling every 2-3 years². To further investigate the extent of contamination of the Bay Area with PBDEs, we analyzed 22 commonly-eaten game fish collected in 2002 as well as 6 archived fish from 1997.

Materials and Methods

22 individual fish (4 halibut, 3 jack smelt, 4 striped bass, 4 kingfish, 4 walleye perch, 1 black perch, 1 rubber-lipped surfperch, and 1 leopard shark) from various locations on San Francisco Bay were collected, cleaned, frozen and delivered to our laboratory by the Environmental Working Group (EWG). An additional 6 samples, cleaned, composited by species, ground and frozen were supplied by the Regional Monitoring Program from their archives of the SFEI's 1997 pilot study of Contaminant Concentration in San Francisco Bay³. The fish were stored at -20° C until analysis. When required, the individual fish were divided into suitable sized pieces with a hand saw while still frozen and were then lyophilized. The moisture content was determined gravimetrically. The dried fish sample was ground and homogenized in a Waring blender. An appropriate aliquot (equal to 0.2 to 0.4 g fat based on reported lipid content for that species) was transferred to a wide-mouth Teflon jar equipped with a screw cap. 100 mL of 1:1 hexane:methylene chloride was added to the dried sample. The suspension was spiked with nine ¹³C-PCBs and ¹³C-PBDE 77, sonicated for a ½ hour and allowed to stand overnight. Following decantation, the extraction was repeated twice more with 70 mL of solvent. A fraction of the combined extracts was centrifuged and a measured volume of the supernatant liquid was transferred to a tared dish and allowed to evaporate to dryness providing a "fat content". The remaining extract was passed over a mixed silica gel column and the eluate and washing solvent was combined and reduced to 5 to 7 mL. This concentrated extract was placed on an ABC GPC column (60 g of Bio Beads SX-3 supplied by BIORAD) and eluted with 387 mL of 1:1 hexane:methylene chloride, the final 170 mL of which was collected. This fraction was reduced to dryness with tetradecane keeper and after addition of a recovery standard was analyzed for PCBs and PBDEs by HRGC-HRMS (Finnigan Mat 95). HRGC/MS was operated in EI multiple ion monitoring mode with 9000 resolution. A 1 µL sample was injected onto a 60 meter DB 5 ms column with 0.25 µm film thickness in pulsed splitless mode.

Results and Discussion

Average Σ PBDEs (of tetra to hepta-PBDEs) for various fish species from the San Francisco Bay are listed in Table 1. PBDE 28, 33, 47, 99, 100, 154, 153 were detected in all fish. Among the congeners detected, PBDE 47 predominated, followed by PBDE 100, PBDE 154, PBDE 99 and PBDE 153. PBDE 183 was not found in the samples.

Comparison of the levels of PBDE congeners by species indicates that halibut and bass had the highest Σ PBDEs (2ppm, lipid based), with shark and smelt having the lowest Σ PBDEs (480 and 310 ppb lipid based, respectively).

Table 1: Average PBDE and PCB 153 levels in fish from 2002

Fish type	Perch	Halibut	Smelt	King Fish	Bass	Shark
No. of sample	6	4	5	4	4	1
Moisture%	72.7	75.6	71.9	71.7	76.8	78.5
Fat% dry weight	10.4	2.1	10.7	22.3	4.68	1.35
ng/g, dry based						
PBDE-28	1.64	0.617	0.637	3.02	1.23	0.350
PBDE-33	8.73	6.09	1.46	13.3	6.82	0.184
PBDE-47	53.7	34.4	8.06	97.7	43.9	4.18
PBDE-100	12.4	11.1	3.60	34.5	18.7	1.19
PBDE-99	0.732	1.92	4.82	1.60	0.80	0.299
PBDE-154	0.932	2.45	0.809	4.74	5.13	0.241
PBDE-153	0.440	1.01	0.943	1.39	1.16	0.133
Σ PBDE	78.6	57.8	20.3	156	77.8	6.61
ng/g, lipid based						
PBDE-28	15.5	24.2	10.7	13.5	30.3	25.9
PBDE-33	73.8	219	23.3	63.1	169	13.6
PBDE-47	482	1286	122	444	1021	310
PBDE-100	106	463	53.5	159	511	88.1
PBDE-99	7.16	84.7	67.1	7.62	14.8	22.1
PBDE-154	8.13	108	14.6	21.9	149	17.9
PBDE-153	3.80	43.8	14.2	6.48	30.2	9.85
Σ PBDE	696	2235	306	716	1925	489
PCB 153	1500	2490	514	1020	2060	978

Comparison of levels and profiles of PBDEs in humans, shorebird eggs, seals, and fish from the San Francisco Bay Area

The same major congeners were found in humans, shorebird eggs, seals and fish: PBDE 47, 99, 100, 153 and 154. PBDE 47 was the dominant congener in all matrices. Σ PBDE concentrations were orders of magnitude higher in eggs (6 ppm) and seals (2 ppm) and fish (1 ppm) than in humans (86 ppb)^{1,2}.

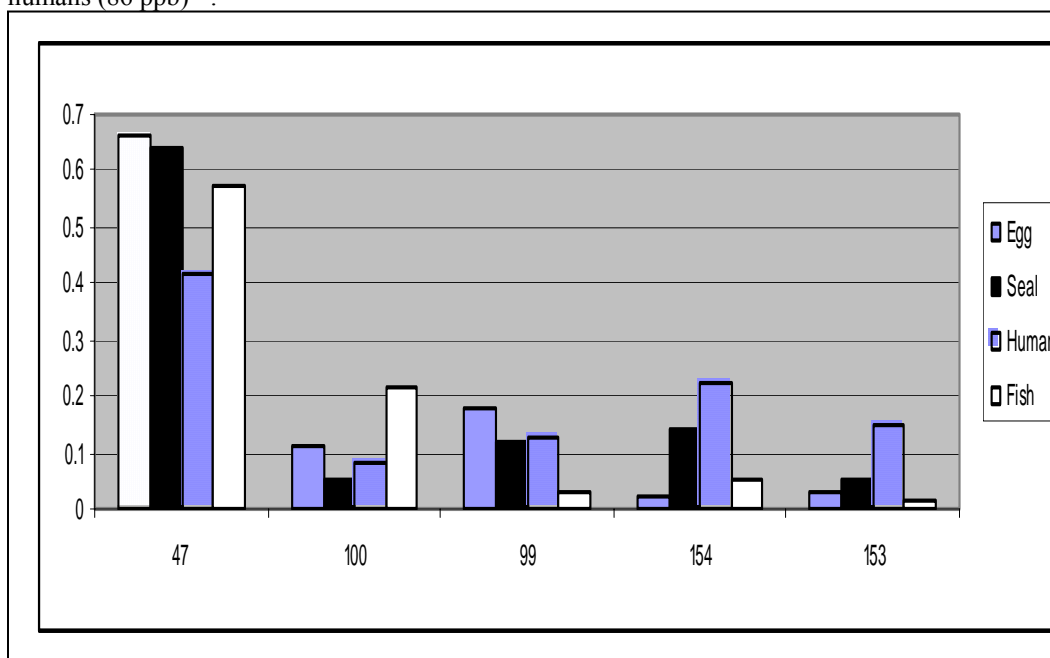


Fig 1. Comparison of the relative congener profile of PBDEs in egg, seal, human and fish from the San Francisco Bay Area

PBDE 47 averaged about 60% of Σ PBDEs in egg, fish and seal samples, but only 42% in human adipose tissue samples, as can be seen in Figure 1. Hexa congeners (PBDE 153 and 154) appear proportionally lower in eggs and fish than in humans.

Comparison of levels of PBDEs and PCBs

The measured levels of PCBs in the fish samples were higher than the measured levels of PBDEs. PCB 153 is the congener with the highest level in the current fish samples. The summary data of PCB 153 is listed in Table 1. The level of PCB 153 is about 2 to 4 times the level of PBDE 47 in the same species. Interestingly, we found that in egg samples from various terns, (collected in 2001) from San Francisco Bay, levels of PCB 153 and PBDE 47 were the same. Regression analysis of the PCB 153 and PBDE 47 for all 2002 fish samples indicated that there is a correlation between PCB 153 and PBDE 47. The correlation relationship is shown in Fig. 2.

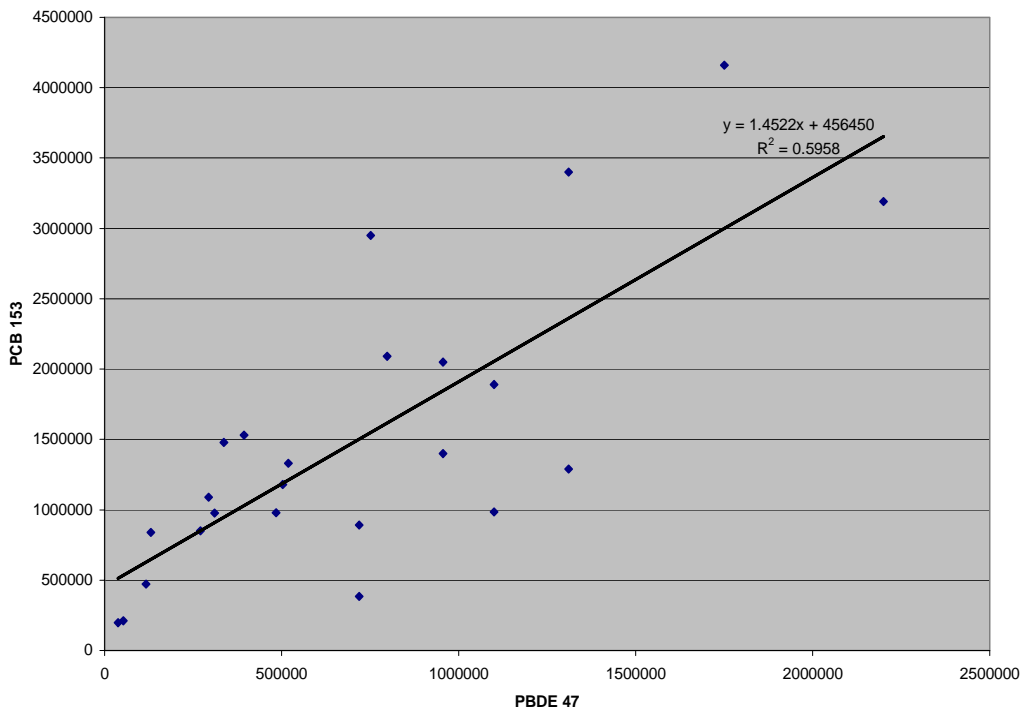


Figure 2. Correlation between PCB 153 and PBDE 47 in 2002 fish from SF Bay (in pg/g, lipid)

Comparison of PBDE level of 1997 and 2002 in fish from San Francisco Bay

Preliminary results from two species (halibut and striped bass) from San Pablo Bay suggested there is a doubling of the level of Σ PBDE occurring from 1997 to 2002. Time trend data is not available for other species.

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References

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