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HIGH PBDE LEVELS IN PISCIVOROUS SEABIRD EGGS FROM THE SAN FRANCISCO BAY AND WASHINGTON STATE

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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 years[2]. To further investigate the extent of contamination of the Bay Area with PBDEs and their associated co-pollutants, 73 eggs of three species of fish-eating seabirds and one benthic omnivore species were analyzed for PBDEs, PCBs, PCDD/Fs, and PBDD/Fs. Seabirds are useful for monitoring and assessing ecosystem health at various times and places because they occupy a high trophic level within the marine foodweb, are long-lived, and site fidelity for breeding and non-breeding sites is relatively high. For comparison, measurements were made on Caspian tern eggs from the State of Washington.

Materials and Methods

73 individual eggs of four species and multiple nesting sites were provided by USFWS. Table 1 summarizes the species studied, the location of their nesting sites and the egg selection criteria.

Table 1: Species studied and the location of nesting sites

Common Name	Scientific Name	Nesting sites	Selection	N
Caspian Tern	*Sterna caspia*	Napa Marsh, Hayward, Alviso, CA; Grays Bay, WA	Random	34
Forster's Tern	*Sterna forsteri*	Napa Marsh, Hayward, Alviso, Mountain View, CA	Random	29
CA Least Tern	*Sterna antillarum brownie*	Alameda NAS	Fail-to-hatch eggs	6
CA Clapper Rail	*Rallus longorostrus obsoletus*	Corte Madera, Palo Alto, CA	Fail-to-hatch eggs	4

The eggs were received shell-less and frozen. They were stored at -20º C until analyzed. The eggs were lyophilized, and moisture content was determined gravimetrically. Dried samples were homogenized with a glass rod, and an aliquot representing 0.2 to 0.4 g of fat was spiked with nine ^{13}C-PCBs, fifteen ^{13}C-PCDDs/Fs, and ^{13}C- PBDE77 and then extracted by sonication and standing (3x) with 1:1 hexane: methylene chloride. A fraction of the extract was centrifuged, and "fat content" was determined by evaporating a known volume of supernatant extract to dryness. The remaining extract was passed over a mixed silica gel column and a carbon column (AX-21) in series. The eluate was labeled fraction 1, containing PCBs and PBDEs. The carbon column was eluted in the reverse direction with warm toluene, and this fraction, containing PCDD/Fs and coplanar PCBs, was labeled fraction 2. Both fractions were reduced to 5-7 mL and passed over an ABC Gel Permeation chromatographic column containing 60 g of BioBeads SX-3 with 357 ml of 1:1 hexane:methylene chloride, the final 170 mL of which was collected. These fractions were reduced to dryness with tetradecane keeper. After addition of recovery standard, the samples were analyzed by HRGC/HRMS (Finnigan Mat 95). HRGC/MS was operated in EI multiple ion monitoring mode with 9000 resolution. A 1µL sample was injected onto a 60 meter, 0.25 µm film thickness DB 5 ms column in pulsed splitless mode.

Results and Discussion

∑PBDE (tetra to hepta-PBDEs) in the California egg samples averaged 6.2 ppm (lipid weight), with a range of 0.30 to 62 ppm. Five PBDE congeners (PBDE 47, PBDE 99, PBDE 100, PBDE 153, and PBDE 154), were found in all egg samples from SF Bay and the State of Washington. However, the hepta PBDE (PBDE 183) was not detected in any of the egg samples. In SF Bay samples, PBDE 47 was the predominant congener, averaging 4.1 ppm (66% of the total), followed by PBDE 99 (18%), PBDE 100 (11%), PBDE 153 (3%) and PBDE 154 (2 %). Analytical results are summarized in Table 2.

Table 2. PBDE levels (ng/g fat) in tern and rail eggs from San Francisco Bay, CA (n=53)

	Min	Max	Average	Median	STDEV	%PBDE congener
Moisture%	74.0	79.1	77.1	77.4	1.19	
Fat% dry wt.	30.7	41.5	38.2	38.4	2.21	
PBDE 47	129	52600	4120	2420	7260	66
PBDE 100	52.7	2920	658	452	630	11
PBDE 99	68.2	5650	1120	798	1110	18
PBDE 154	3.86	579	150	116	127	2
PBDE 153	1.67	895	163	115	172	3
∑PBDE	291	62400	6200	4410	8830	

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

The major congeners found in humans, bird eggs, seals and fish were the same: PBDE 47, 99, 100, 153 and 154. PBDE 47 predominated in all matrices. ΣPBDE concentrations were orders of magnitude higher in eggs (6 ppm), seals (2 ppm) and fish (1ppm) than in humans (86 ppb)[1,2].

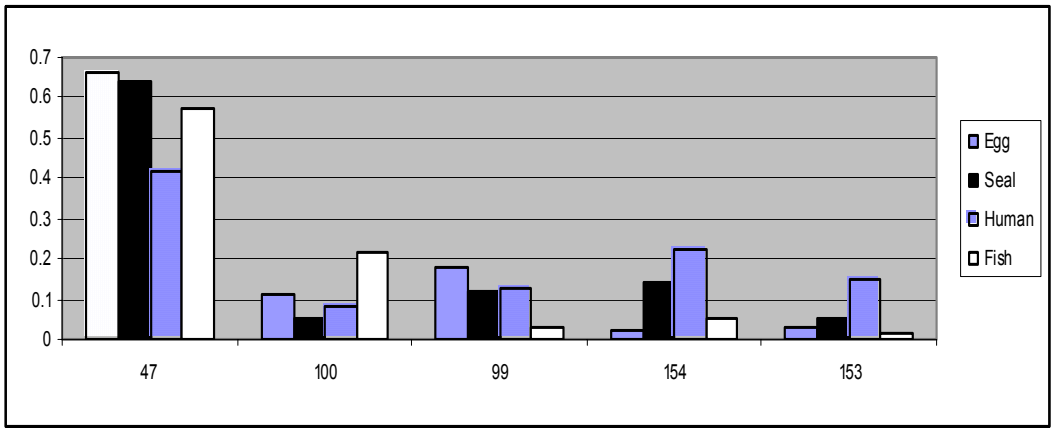

Fig. 1. Relative congener patterns of PBDE in bird eggs, seals, and samples of human breast adipose, and fish from the San Francisco Bay Area

PBDE 47 averaged about 60% of ΣPBDEs in egg, seal and fish 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 and seals. The ratio of PBDE 100/PBDE 99 is higher in fish than in the other matrices.

A subset of egg samples was tested for PBDDs, PBDFs and methoxy-PBDEs. No PBDDs, PBDFs and/or methoxy-PBDEs were found in the egg samples analyzed.

Comparison of levels and profiles of PBDEs in eggs from different species

Among eggs from San Francisco Bay there are 14 Caspian tern, 29 Forster's tern, 6 CA Least tern, and 4 CA Clapper Rail. The comparison of the levels and patterns of PBDE congeners from four species is shown in Fig. 2. Of the four species, Forster's terns had the highest ∑PBDE, whereas the CA Clapper rail had the lowest ∑PBDE.

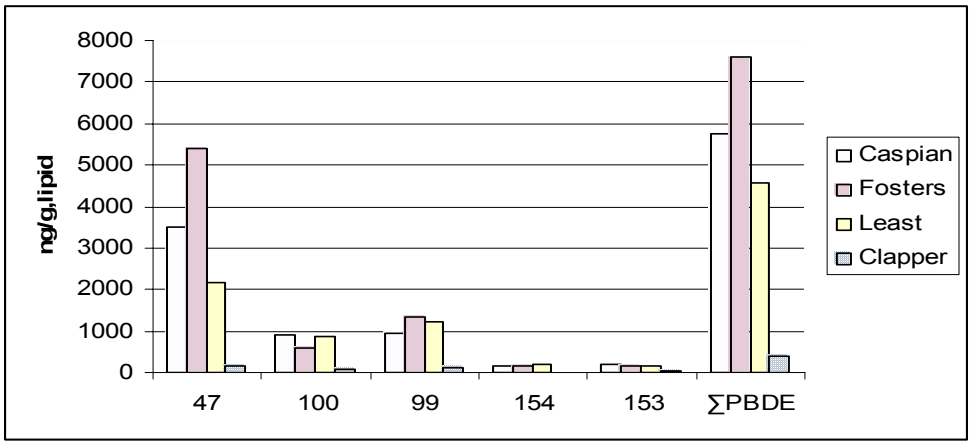

Fig. 2. Comparison of PBDE levels in eggs from different species (SF Bay only)

Comparison of levels and profiles of PBDEs in eggs from different locations

In addition to eggs from San Francisco Bay, 20 Caspian tern eggs from Washington State were also analyzed for PBDEs. ΣPBDEs in eggs from Washington State were lower than ΣPBDEs in eggs from San Francisco Bay. Table 3 compares the levels of PBDEs in eggs of Caspian terns from San Francisco Bay and the State of Washington.

Table 3: Comparison of PBDE Levels (ng/g, lipid)in Caspian Tern Eggs from SF Bay and Washington State

Washington State Eggs (n=20)						
	Min	**Max**	**Average**	**Median**	**Std Dev**	**Ratio**
Moisture %	75.8	79.1	77.5	77.5	0.79	
Fat % dry wt.	30.7	41.5	38.5	39.0	2.31	
PBDE 47	1050	8840	2660	2070	1710	0.57
PBDE 100	266	1760	564	474	318	0.12
PBDE 99	542	3200	1210	1100	640	0.26
PBDE 154	44.2	349	96.8	80.4	65.3	0.02
PBDE 153	43.7	843	145	102	169	0.03
Total PBDE	**1970**	**15000**	**4670**	**3920**	**2820**	**1.00**

San Francisco Bay Area Eggs (n =14)						
	Min	**Max**	**Average**	**Median**	**Std Dev**	**Ratio**
Moisture %	71.2	78.2	75.9	76.0	1.64	
Fat % dry wt.	22.3	45.1	37.7	38.7	5.76	
PBDE 47	744	10500	3490	3100	2740	0.61
PBDE 100	185	2770	919	660	796	0.16
PBDE 99	238	2910	956	730	798	0.17
PBDE 154	39.2	499	168	124	137	0.03
PBDE 153	61.0	733	200	140	205	0.03
Total PBDE	**1340**	**17300**	**5730**	**4680**	**4620**	**1.00**

Comparison of levels of PBDEs and PCBs

Among the PCB congeners analyzed, levels of PCB 153 were the highest, averaging 4.4 ppm (fat based). As noted above, PBDE 47 averaged 4.1 ppm. These results suggest that the PBDE brominated flame retardants are fast becoming a newer version of the 'PCB problem'.

References

1. Jianwen She, Jennifer Winkler, Pat Visita, Michael McKinney, Myrto Petreas (2000), Analysis of PBDEs in Seal Blubber and Human Breast Adipose Tissue Samples, Organohalogen Compounds, 47, 53, 2000

2. Jianwen She, Myrto Petreas, Jennifer Winkler, Patria Visita, Michael McKinney, Dianne Kopec (2002), PBDES in the San Francisco Bay Area: measurements in the harbor seal blubber and human breast adipose tissue, 46, 697, 2002