Highest PBDE Levels (max 63 ppm) Yet Found in Biota Measured in Seabird Eggs from San Francisco Bay

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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 piscivorous seabird eggs at the ppm level. Seabirds are useful for monitoring and assessing ecosystem health at various times and places because they occupy a high trophic level in the marine food web, are long-lived, and are generally localized near their breeding and non-breeding sites.

In collaboration with the US Fish and Wildlife Services (USFWS), we are carrying out a three-year investigation of dioxin, PCB and PBDE levels in eggs from fish-eating seabirds. Year 1 (2002) PBDE measurements from 73 bird eggs were reported at Dioxin2003. Year 2 (2003) PBDE measurements from 45 samples are presented in this report. The highest PBDE level measured in eggs was 63 ppm, lipid, which is the highest PBDE level, yet reported in biota.

Materials and Methods

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

Table 1: Species studied and location of nesting sites

Common Name	**Scientific Name**	**Nesting sites**	**Selection**	**N**
Caspian Tern	Sterna caspia	Napa Marsh, Hayward Alviso	Random	20
Forster's Tern	Sterna forsteri	Napa Marsh, Hayward Alviso, Mountain View	Random	20
CA Least Tern	Sterna antillarum brownie	Almeda Nas	Fail-to-hatch	5

Eggs were received shell-less and frozen, and were stored at -20^{o}C until analyzed. 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-PCB, fifteen ^{13}C-PCDD/Fs, and ^{13}C-PBDD 77, 153 and 209, and extracted 3 times with 1:1 hexane: methylene chloride and sonication. A fraction of the extract was centrifuged, and the 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 carbon column (AX-21) in series. Details of further cleanup were described in (3). The target analytes were identified and measured using a Finnigan Mat-95 high-resolution GC/MS equipped with a splitless injector and a 15-meter DB 5 ms column operating in electron impact ionization-selective ion monitoring mode with 10,000 resolution. Molecular ions were monitored to identify tri- to hexa-BDEs, and M-2Br ions identified hepta-, and deca-BDEs.

Results and Discussion

The analytical results for three species of the tern eggs were shown in Table 2.

Table 2: Comparison of PBDE levels in eggs collected in 2003 from three species of terns inhabiting SF Bay (ng/g, lipid).

	Min	Max	Mean	Median	SD	% mean	% median
Caspian Tern (n=20)							
PBDE28/33	0.971	374	129	111	103	1.9	3.0
PBDE-47	675	11700	2760	1790	2780	41	48
PBDE-66	3.53	142	24.3	14.1	32.7	0.4	0.4
PBDE-100	190	7490	1150	592	1750	17	16
PBDE-99	233	9790	1590	724	2300	24	19
PBDE-154	39.4	2100	342	136	576	5.1	3.6
PBDE-153	73.8	4470	717	235	1240	11	6.3
Total PBDEs	**1270**	**36100**	**6760**	**3720**	**8640**	**100**	**100**
Forster tern (n=20)							
PBDE28/33	15.5	433	81.9	54.8	89.0	0.9	1.0
PBDE-47	1140	18200	3920	3020	3760	42	55
PBDE-66	9.87	137	48.0	39.0	33.5	0.5	0.7
PBDE-100	295	8240	1220	675	1740	13	12
PBDE-99	426	17400	2550	1310	3710	27	24
PBDE-154	60.7	6360	578	163.5	1410	6.1	3.0
PBDE-153	54.3	12400	1000	170	2760	11	3.1
Total PBDEs	**2590**	**63300**	**9420**	**5460**	**13400**	**100**	**100**
Least tern (n=5)							
PBDE28/33	43.6	72.7	56.0	54.5	11.8	1.0	1.1
PBDE-47	1760	3360	2520	2510	732	43	49
PBDE-66	21.9	51.8	36.5	33.9	13.4	0.6	0.7
PBDE-100	690	1430	967	744	374	16	14
PBDE-99	1350	2780	1900	1500	677	32	29
PBDE-154	109	214	165	153	44.4	2.8	3.0
PBDE-153	123	287	224	252	68.9	3.8	4.9
Total PBDEs	**4210**	**7820**	**5870**	**5170**	**1800**	**100**	**100**

Forster tern eggs had the highest levels of PBDEs. Total PBDEs (∑PBDEs) in Forster tern eggs averaged 9.4 ppm (median 5.5), Caspian tern eggs averaged 6.8 ppm (median 3.7 ppm), and least tern eggs averaged 5.8 ppm (median 5.2 ppm). The highest PBDE levels (63 ppm for 2003 and 62 ppm for 2002) were found in Forster tern eggs.

We saw slight decreases in ∑PBDE levels from 2002-2003 in eggs from Caspian and Forster terns. The decreases of ∑PBDEs in 2003 eggs were attributed mainly by

decreases in levels of PBDE 47. Levels of PBDE 47 averaged more than 60% of ∑PBDE in fish, seals and 2002 eggs[3], PBDE 47 percentages were lower (around 50%) in 2003 eggs. A similar pattern shift for PBDE 47 was seen in breast milk and serum samples from the US and Europe[4,5]. Because of the small number of Least tern eggs received, we were not able to include their results in the comparison. Levels of other congener were comparable over the two-year time period (Figures 1 and 2).

Average and median congener patterns for eggs from the three species in 2002 and 2003 are similar, with PBDE 47 dominating, followed by PBDE 99 > 100 >153 > 154. In Caspian tern eggs, PBDE 100 = PBDE 99, whereas in Forster tern eggs, PBDE 100 = ½ PBDE 99. PBDE 183 was found in one Caspian tern egg (121 ng/g lipid) and five Forster tern eggs.

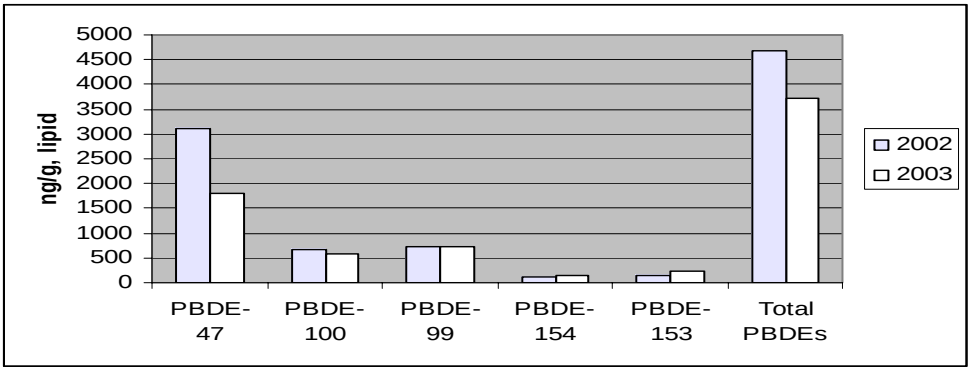

Figure 1: Comparison of PBDE levels in Caspian tern eggs from 2002 and 2003 (n = 20)

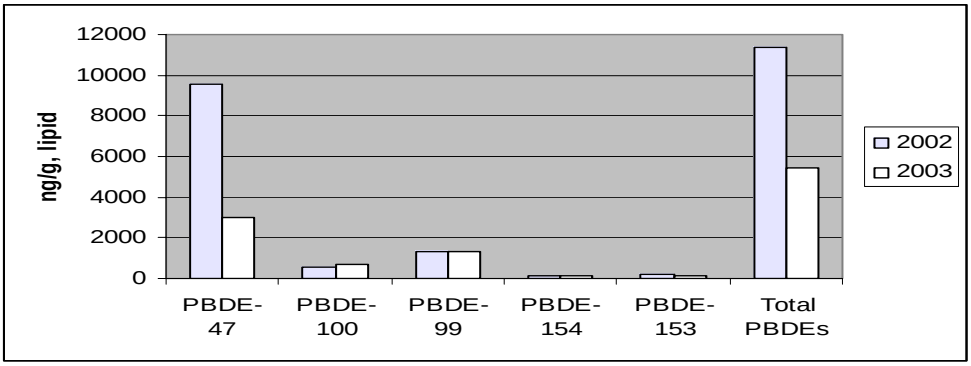

Figure 2: Comparison of PBDE levels in Forster tern eggs from 2002 and 2003 (n = 20)

Comparison of PCB and PBDE levels in eggs. ΣPCBs (ppm, lipid) for eggs from the three species of terns are as follows: Forster tern (n=20) mean 48 ppm (median 18 ppm); Caspian tern (n =20) mean 16 ppm (median 13 ppm); and least tern (n = 5) mean 35 ppm (median 36 ppm). Highest PCBs were found in one of the Forster tern eggs with a value of 385 ppm. This sample also had the highest PBDE level (63 ppm).

∑PBDEs (ppm, lipid) in eggs from Forster terns averaged 9.4 ppm (median 5.5) and from Caspian terns averaged 6.8 ppm (median 3.7 ppm). Eggs from Least terns averaged 5.8 ppm (median 5.2 ppm).

Levels of ΣPCBs and ∑PBDEs were correlated as shown in Figure 3. ∑PCBs was 3 to 7 times higher than ∑PBDEs.

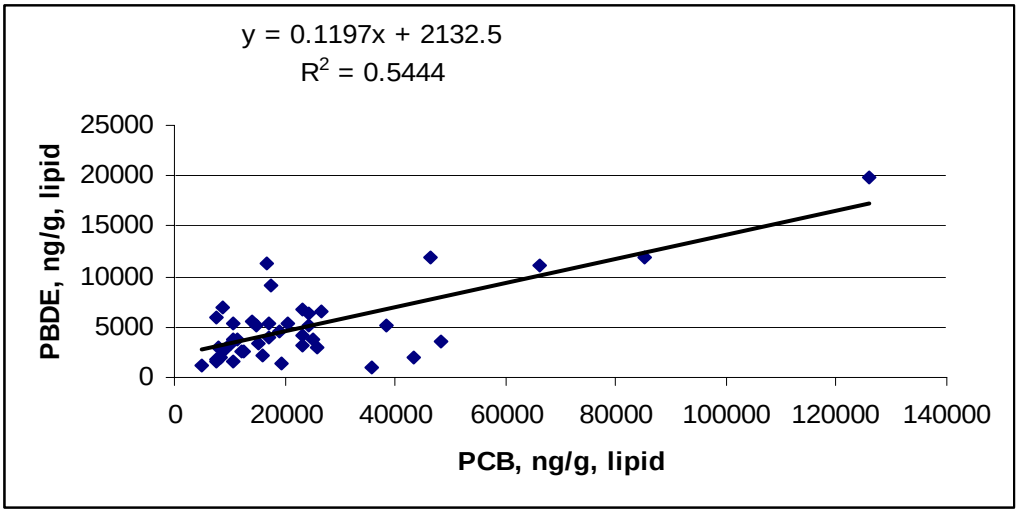

Figure 3: Correlation between ∑PCBs and ∑PBDEs in the tern eggs (three outliners were removed: the highest value and 2 samples with higher ∑PBDEs than ∑PCBs)

The 63 ppm (lipid-based) of ∑PBDEs in one of the Forster tern eggs is the highest level reported for wildlife or humans. Other high PBDE levels have been reported in carp (47 ppm)[6] and in eggs of peregrine falcons (39 ppm)[7].

The finding of unusually high levels of PBDEs and PCBs in tern eggs, especially in eggs from Forster terns, suggests that tern eggs may provide a useful matrix for monitoring persistent organic pollutants (POPs). Tern eggs may also serve as an important metric for assessing ecosystem health: Extensive biomagnification of POPs in tern eggs may make it possible for us to identify POPs of concern earlier than is possible using other biota.

*The opinions given by the authors are not necessarily those of the DTSC or the California Environmental Protection Agency (Cal-EPA). Mention of any products or organization does not constitute an endorsement by DTSC or Cal-EPA.

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