Time-Trends of PBDEs in Shorebird 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 shorebird eggs at the ppm level. Shorebids 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 (2001) PBDE measurements from 73 bird eggs were reported at Dioxin2003. Year 2 (2002) PBDE measurements from 45 samples were reported in Dioxin2004. Year 3 (2003) PBDE measure measurements from 30 samples are reported in this study. Time-trends of PBDE in tern eggs from San Francisco Bay over three year period will be discussed.

Materials and Methods

30 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	14
Forster's Tern	Sterna forsteri	Napa Marsh, Hayward Alviso, Mountain View	Random	16

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 two species of the tern eggs were shown in Table 2.

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

	Min	Max	Mean	Median	SD
Caspian Tern (n=14)					
Moisture	58.8	81.1	73.3	74.1	5.06
Fat%	29.2	46.6	35.3	34.6	4.48
PBDE-47	647	17200	3360	1820	4280
PBDE-100	161	4150	863	462	1031
PBDE-99	164	3770	1030	528	1170
PBDE-154	38.6	388	114	90.5	100
PBDE-153	63.7	627	184	142	162
Total PBDEs	**1200**	**26300**	**5860**	**3190**	**6670**
Forster Tern (n=16)					
Moisture	59.0	77.1	71.3	72.2	5.01
Fat%	16.8	39.3	31.7	34.5	6.99
PBDE-47	362	6980	2460	1820	1980
PBDE-100	56.4	1410	361	304	320
PBDE-99	151	4390	1110	671	1120
PBDE-154	27.1	388	162	120	106
PBDE-153	40.3	845	225	155	198
Total PBDEs	**666**	**11900**	**4450**	**3300**	**3390**

High level of PBDE in tern eggs. Similar to the results from first two years (2001 and 2002) studies, the level of PBDEs (2003) in tern eggs is still very high in the two species tested. Total PBDEs (∑PBDEs) in Forster tern eggs averaged 4.4 ppm lw (median 3.3), Caspian tern eggs averaged 5.8 ppm lw (median 3.2 ppm lw). The highest PBDE levels (26 ppm lw) were found in Caspian tern eggs. In previous two years, we have found about 60 ppm lw in Forster's tern eggs.

Time-trends of PBDEs during three year period. Table 2 compares PBDE data of year 2001, 2002 and 2003. We saw slight decreases (or no changes) in ∑PBDE levels from 2001-2003 in eggs from Caspian and Forster terns. Congener patterns for eggs from the three species in 2001, 2002 and 2003 are similar, with PBDE 47 dominating, followed by PBDE 99 > 100 >153 > 154. It is very interesting that the level of 153 and 154 in tern eggs are almost same, however the level of 153 is much higher than that of 154 in human milk samples.

Table 2. Comparison of median PBDE levels (ng/g lw) in tern eggs from year 2001 to 2003

PBDES	Caspian Tern Median		
	2001 (n=14)	2002 (n=20)	2003 (n=14)
PBDE47	3103	1790	1815
PBDE100	660	592	384
PBDE99	730	724	638
PBDE154	124	136	98
PBDE153	140	235	142
Total PBDEs	**4683**	**3720**	**3275**
	Forster's Tern Median		
	2001 (n =29)	2002 (n=20)	2003 (n=16)
PBDE47	2694	3020	1815
PBDE100	364	675	304
PBDE99	825	1310	671
PBDE154	116	164	120
PBDE153	115	170	155
Total PBDEs	**4380**	**5460**	**3295**

Figure 1 compares the media level of 5 major PBDE congeners from Caspian Tern eggs. Again, we did not see any significant changes of level of PBDEs over the three year period. This is also true for the levels of PBDE congeners from Forster's tern eggs. It seems that the level of PBDEs in tern eggs from San Francisco Bay stabilize itself at the current level for last few years.

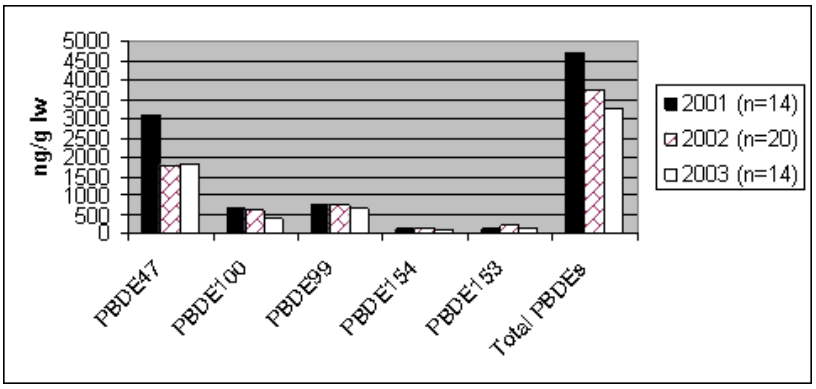

Figure 1: Comparison of PBDE levels (median) in Caspian tern eggs from 2001 to 2003

*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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