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Concentrations and time trends of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in aquatic bird eggs from San Francisco Bay, CA 2000–2003

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ABSTRACT

Concentrations of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) were measured in 169 avian eggs. We analyzed randomly collected eggs of two species of piscivorous birds: Caspian tern (*Sterna caspia)* ($n = 78$) and Forster's tern *(Sterna forsteri*) ($n = 76$). We also analyzed fail-to-hatch eggs from two species protected under the Federal Endangered Species Act of 1973, that breed in the San Francisco Bay region: the piscivorous California Least tern (*Sterna antillarum brownii*) ($n = 11$) and the omnivorous California Clapper rail (*Rallus longirostris obsoletus*) ($n = 4$). San Francisco Bay eggs were collected annually for four years (2000–2003), and additional 20 eggs were collected and analyzed from Gray's Harbor, Washington in 2001. Geometric mean PBDE concentrations did not significantly differ in the three tern species, but concentrations in eggs from the fail to hatch California Clapper rail eggs were significantly lower than those found in the randomly collected tern eggs. Median concentrations of ∑PBDEs in Caspian tern eggs for 2000–2003 were 2410, 4730, 3720 and 2880 ng/g lipid weight (lw), respectively, in Forster's terns 1820, 4380, 5460 and 3600 ng/g lw, respectively, and in California Least terns for 2001 and 2002 were 5060 and 5170 ng/g lw, respectively. In contrast, median ∑PBDEs concentration in California Clapper rail eggs for 2001 was 379 ng/g lw. Five PBDEs were the major congeners found and decreased in the order BDE-47, -99, -100, -153, and -154. BDE-32, -28, -71, -66, -85, -183 were less prevalent, minor congeners, as was BDE-209, which was measured in a subset of samples. PBDE concentrations in bird eggs from San Francisco Bay were site related. There was no significant difference in PBDE concentrations in Caspian tern eggs from San Francisco Bay and Gray's Harbor, WA. Average PBDE concentrations in eggs did not significantly increase over the period 2000–2003.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are used as non-covalently bound flame retardant additives to many synthetic plastic and textiles to reduce their flammability. PBDEs have been found to be increasing in environmental and biological matrices. Structurally related to the polychlorinated biphenyls (PCBs), PBDEs show neurodevelopmental toxicity in the same animal test systems as did the PCBs, perhaps by interfering with normal thyroid hormone homeostasis and binding to thyroid transport proteins (Hooper and McDonald, 2000). PBDE's toxic effects to the birds monitored in this study are largely unknown. High PBDE concentrations have been found in humans and wildlife from the San Francisco Bay area (She et al., 2000; She et al., 2002; Holden et al., 2003; Petreas et al., 2003; Oros et al., 2005), with concentrations in women among the highest in the world, and concentrations in harbor seals doubling every 2–3 years (She et al., 2002). To further investigate the extent of contamination of the Bay region with PBDEs and selected co-pollutants, we analyzed randomly collected eggs of two species of piscivorous birds: Caspian tern (*Sterna caspia)* and Forster's tern *(Sterna forsteri*). We also analyzed fail-to-hatch eggs from two species protected under the Federal Endangered Species Act that breed in the San Francisco Bay region: the piscivorous California Least tern (*Sterna antillarum brownii*) and the California Clapper rail (*Rallus longirostris obsoletus*), a littoral omnivore. Eggs were analyzed for PBDEs, PCBs, and polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs).

California Least terns, Forster's terns, and Caspian terns are small, medium and large bodied terns, respectively, whose diet

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consists almost entirely of fish captured at the water's surface. They forage at relatively high trophic levels within aquatic food webs. Each of these species is migratory, spending the winter months in Central and South America, and breeding from Baja California to British Columbia. The California Least and Forster's terns have moderate life spans (10–12 years; McNicholl et al., 2001), while Caspian terns live longer (up to 20 years) (Cuthbert and Wires, 1999). The California Clapper rail diet consists of crustaceans, fish, mollusks, insects, and some plant seeds (Harvey, 1987) and average lifespan in San Francisco Bay is likely much shorter than terns based on telemetry determinations of mortality rates in rails (Albertson, 1995).

PCBs (measured as Aroclors) and organochlorine pesticides have been previously monitored in terns and the California Clapper rail (Ohlendorf et al., 1988; Schwarzbach et al., 2001). No analysis for either PBDEs or congener-specific PCBs has previously been conducted in eggs of terns or Clapper rails in the San Francisco Bay estuary. We present here analytical results of a four-year monitoring program carried out to measure congener-specific concentrations in eggs of PBDEs, PCBs and PCDD/Fs, and to assess the potential risks to these birds. Caspian tern eggs from Gray's Harbor, WA were analyzed for the same target compounds to compare concentrations within another west coast estuary along the Pacific Flyway.

2. Methods and materials

2.1. Sample collection

Eggs were obtained from various locations in the San Francisco Bay estuary (Fig. 1) and Gray's Harbor, WA. Sampling sites in the San Francisco Bay estuary are given in Fig. 1 and Table 1. For the San Francisco Bay estuary, they included: (1) North Bay – Pond 3 of the California Department of Fish and Game's (CDFG) Napa–Sonoma Marshes Wildlife Area (Napa Marsh), and the Corte Madera Ecological Preserve (Corte Madera); (2) Central Bay – the former Alameda Naval Air Station (NAS), and the East Bay Regional Parks District's (EBRPD) Brooks Island Regional Park; (3) Upper South Bay – EBRPD's Hayward Regional Shoreline, and Ponds B10 and B8A of the CDFG's Eden Landing Ecological Preserve (Baumberg); (4) Lower South Bay East – Ponds A16, A7, and A1 of the Don Edwards National Wildlife Refuge, and (5) Lower South Bay West – the City of Mountain View's Charleston Slough Regional Park, Belmont Slough, and Faber Marsh within the Palo Alto Baylands. In 2000 and 2001, eggs were collected at random without regard for developmental stage. In 2002 and 2003 eggs were collected at 16–20 days of incubation, a developmental stage targeted for a reproductive monitoring program that allowed assessment of embryo development. Egg stage was assessed in the field via floatation in water. Eggs were deemed failed-to-hatch by directly monitoring nest success. For non-listed species, eggs were called failed-to-hatch if they had not hatched 1–2 days after sibling eggs. For listed species, the criterion used was fail-to-hatch after 35 days or more of incubation. After egg dimensions were recorded, eggs were de-shelled and egg status was assessed (i.e., fertile, infertile, early development, late stage development, etc.). Late-stage embryos were examined for abnormalities. Egg contents were transferred to labeled, chemically clean, clear glass jars. Eggs were frozen at −20 °C, and shipped to the laboratory where they remained frozen at −20 °C until analysis.

2.2. Analytical methods

The eggs were lyophilized, and the moisture content was determined gravimetrically. Dried samples were homogenized using a glass rod. An aliquot representing 0.2–0.4 g of fat was spiked with nine $^{13}C_{12}$-PCBs, fifteen $^{13}C_{12}$-PCDDs/Fs, $^{13}C_{12}$-BDE-77, and $^{13}C_{12}$-BDE-153, and extracted by three cycles of sonication followed by standing and decantation of the supernatant liquid with 1:1 hexane: dichloromethane. A fraction of the extract was centrifuged, and the fat content was determined by evaporating a measured volume of supernatant extract to dryness (3% of total extract). No correction of internal standard recoveries was made. The remaining extract was passed over a column containing beds of (from bottom up) sodium sulfate, silica gel, potassium silicate, silica gel, 20 g of 44% sulfuric acid supported on silica gel, and sodium sulfate, with a carbon column (AX-21) added in series. The first eluate (1:1 hexane: dichloromethane), labeled Fraction 1 (170 ml), contained non-coplanar PCBs and PBDEs. After elution of Fraction 1, the carbon column was eluted in the reverse direction with 75 ml warm toluene to give Fraction 2, containing PCDD/Fs and coplanar PCBs. Each fraction was reduced in volume on a RapidVap Evaporation System (LabConco, Kansas City, MO, USA) to 5–7 ml and applied to an ABC Gel Permeation chromatographic column containing 60 g of BioBeads SX-3 (BioRad, Hercules, CA, USA) with 360 ml of 1:1 hexane: dichloromethane; the final 170 ml of which was collected. The eluate was reduced in volume to less than 1 ml with heat, vortexing and a gentle stream of pure nitrogen. It was then transferred to a 1 ml vial containing tetradecane, and any remaining 1:1 hexane: dichloromethane solvent was removed under a gentle stream of nitrogen. For Fraction 1 the final volume was 10 μl after addition of the recovery standards ($^{13}C_{12}$-PCB-128 and $^{13}C_{12}$-PCB-178 or $^{13}C_{12}$-BDE-99). The samples were analyzed by HRGC/HRMS (Finnigan Mat 95, Bremen, Germany) coupled to an Agilent 6890 gas chromatograph equipped with a 60-meter DB5 MS column (Agilent Technology, San Jose, CA, USA) with a 0.25 μm film thickness, operated in the pulsed splitless mode. HRGC/HRMS was operated in EI multiple ion monitoring mode with 9000 resolution. A 1 μl or 0.5 μl sample was injected into the Gas Chromatograph. Tri- to Penta-BDEs and PCBs were identified using molecular ions, hexa-, hepta- and deca-BDE were identified using the M-2Br ions. Concentrations of BDE-209 (deca-BDE) were measured in a subset ($n = 42$) of the eggs, using a 15-meter DB 5MS column with a 0.25 μm film thickness (Agilent Technology, San Jose, CA, USA).

2.3. Quality assurance and quality control

The eggs were analyzed in batches of six. For every thirteen eggs analyzed, one duplicate sample, one reference sample, and three blanks were also analyzed. For $\sum$PBDEs, the average of 39 blanks, lipid normalized, was less than 1/10 of the lowest concentration found of all the eggs (Clapper rail minimum, Table 2). For $\sum$PCBs, the average blank was less than 1/8 of the lowest concentration of all the eggs found (Clapper rail minimum, Table 3). The mean relative percent difference (mean RPD) for 12 duplicates was less than 20% for BDEs-47, -99, -100, -153, and -154. The mean RPD for 12 duplicates was less than 20% for PCBs-28, -101, -153, and -180. For a variety of standard and in-house reference materials, the biases for all reported congeners were less than 20%. Recovery of internal standard (spiked after lyophilization) for BDE-153 was 57.7 ± 3.4, for BDE-77, 65.4 ± 8.8%, and for BDE-209, 30.4 ± 3.9% (in the subset of eggs for which it was measured). Recoveries of internal standards for PCBs ranged from 84.8 ± 3.9 for PCB-138 to 41.1 ± 2.13 for PCB-189. Matrix spike recoveries from corn oil for all measured BDE congeners ranged from 91% for BDE-100 to 108% for BDE-99 and 94.7% for PCB-153.

2.4. Statistical analyses

Tern eggs collected in the San Francisco Bay were classified into five general regions: (1) North Bay (CDFG Pond 3), (2) Central Bay

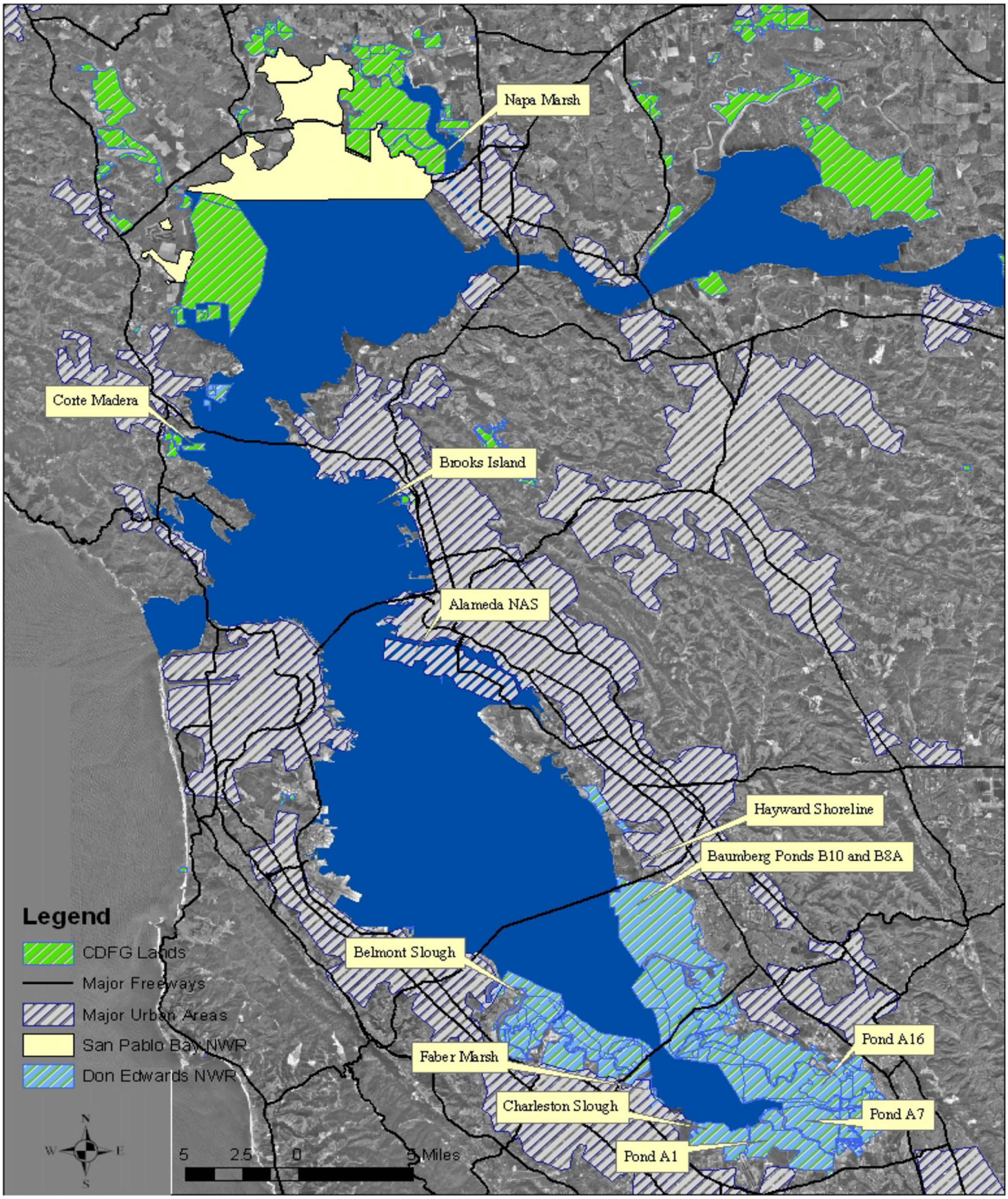

Fig. 1. Sampling sites for tern and rail eggs in the San Francisco Bay Area.

(Alameda NAS, and Brooks Island), (3) Upper South Bay (Hayward, Baumberg B10 and B8A), (4) Lower South Bay East (Pond A7, and A16), and (5) Lower South Bay West (Pond A1 and Charleston Slough). We used ANOVA to model and test for differences in $\sum$PBDEs and $\sum$PCBs in samples from the San Francisco Bay area among tern species, years, and regions. If any effects were found significant at the 0.10 level, we conducted pair-wise tests to determine where differences occurred. We also used linear contrasts to test the hypothesis of a time trend from 2000 to 2003. If regional effects were found, we used a linear contrast to test the differences between Clapper rail and tern species from Lower South Bay West and Central Bay, the only regions where both rails and terns were sampled. If a San Francisco Bay region was found to be significantly different, then we used a nested region effect to model and test differences in $\sum$PBDEs and $\sum$PCBs between Gray's Harbor, WA and San Francisco Bay for Caspian terns, the only species for which samples were collected in Gray's Harbor, WA. Finally, we examined the correlation between $\sum$PBDEs and $\sum$PCBs. We log-transformed $\sum$PBDEs and $\sum$PCBs in all analyses to correct skewness in the data. We confirmed that after transformation, all residuals went from visually skewed to symmetric.

We used the least squares method in ANOVA to estimate mean log-transformed $\sum$PBDEs and $\sum$PCBs. The least squares method adjusts the means for unbalanced sampling across species, years,

Table 1
Study species, with location of nesting sites, collection status, sample size by year and cumulative sample size

Common name	Scientific name	Nesting sites	Selection	Collection by year	N
Caspian tern	*Sterna caspia*	Napa Marsh, Brooks Is, Baumberg Ponds B10 and B8A, Pond A7, CA; Grays Harbor, WA	Random	2000 (5) 2001 (33) 2002 (20) 2003 (20)	78
Forster's tern	*Sterna forsterii*	Napa Marsh, Hayward Shoreline, Baumberg Pond B10, Belmont, Charleston Slough, Pond A16, Pond A1	Random	2000 (5) 2001 (29) 2002 (20) 2003 (22)	76
CA Least tern	*Sterna antillarum brownii*	Alameda NAS	Fail-to-hatch	2001 (6) 2002 (5)	11
Clapper rail	*Rallus longirostris obsoletus*	Corte Madera, CA; and Faber Marsh, Palo Alto	Fail-to-hatch	2001 (4)	4

and regions. Whenever species, year, or location effects were found, we back-transformed the estimates and applied the delta method to determine mean contamination and standard errors (Christensen, 1990). The back-transformation of least squares means of log-transformed data produces estimates analogous to geometric means adjusted for unbalanced sampling. All analyses were conducted in SAS (SAS Institute, 2004; Littell et al., 1996).

3. Results and discussion

3.1. Time trend of PBDEs and PCBs

Among the four species analyzed for PBDEs and PCBs, we have four years of data for two species, Caspian and Forster's terns. Table 2 lists PBDE concentrations in eggs from these two species for 2000–2003. There were no differences found in PBDEs ($F_{3,134}$ = 1.81, p = 0.1484; Table 4) and in PCBs ($F_{3,133}$ = 0.81, p = 0.4889; Tables 3 and 5) among the four years. Similarly, there were no linear trends over time (PBDEs: $F_{1,134}$ = 0.65, p = 0.4230; PCB: $F_{1,133}$ = 0.60, p = 0.4398). Congener patterns in the two species from year to year are similar, with BDE-47 dominating, followed by BDE-99 > 100 > 153 > 154. Concentrations of BDEs-153 and -154 in tern eggs were similar, while BDE-153 concentrations in human milk samples have been found to be much higher than BDE-154 (She et al., 2007). The ∑PBDEs concentration in tern eggs from 2000–2003 contrasts with previously reported results demonstrating an exponential increase in ∑PBDEs concentrations in seal blubber from San Francisco Bay from 1988–1999 (She et al., 2002). This suggests PBDE concentrations have not been changing, at least in the dietary pathway of birds, as rapidly as in the earlier period in the aquatic food web represented by seals of San Francisco Bay. Such changes are not unprecedented. Environmental concentrations of PBDE in Sweden showed a rapid increase in the mid-1980s, after which environmental concentrations decreased or remained unchanged in various matrices (Kierkegaard et al., 1999; Sellstroem, 1999). A similar trend has been seen in human milk samples from Sweden where PBDE concentrations showed a significant increase from the early 1970s to 1997 (Meironyté et al., 1999) and then a decrease from 1997 to 2000 (Norén and Meironyté, 2000), due mainly to reduced concentrations of BDE-47 (Meironyté and Norén, 2001).

3.2. Comparison of PBDEs and PCBs in different bird species within San Francisco Bay

There were no significant differences in ∑PBDEs among tern species ($F_{2,134}$ = 0.82, p = 0.4416). All terns had geometric mean ∑PBDEs ranging from 3744 to 4790, ten times higher than the mean for Clapper rails (geometric mean 386; Table 4). This is in contrast to ∑PCB concentrations which varied significantly among terns ($F_{2,133}$ = 9.16, p = 0.0002), with Least terns from Alameda exhibiting concentrations nearly three times higher than Caspian terns and twice as high as Forster's terns (Table 5). This is likely a local site effect due to PCB contamination of the Least tern diet at the former Alameda NAS. Forster's terns were significantly different, nearly twice the average concentration of PCBs in eggs than Caspian terns (Table 5). The Clapper rail had significantly lower ∑PBDEs ($F_{1,40}$ = 32.09, p < 0.0001) and ∑PCB ($F_{1,40}$ = 32.86, p < 0.0001) when compared to tern species.

The two highest ∑PBDE Concentrations, 62,000 and 63,000 ng/g lw (62 and 63 ppm lw) were found in two Forster's tern eggs from the Eden Landing region in 2001 and 2002. The median ∑PBDE concentrations in Caspian tern eggs collected from 2000 to 2003 were 2410, 4730, 3720 and 2880 ng/g lw, respectively. The median ∑PBDEs concentrations in Forster's tern eggs collected from 2000 to 2003 were 1820, 4380, 5460 and 3600 ng/g lw, respectively. The median ∑PBDE concentrations in Least tern eggs collected from 2001 to 2002 were 5060 and 5170 ng/g lw, respectively. Median ∑PBDEs concentration in Clapper rail eggs collected in 2001 was 379 ng/g lw. Concentrations and patterns of PBDE congeners from these species are compared in Fig. 2.

Average PCB concentration in fail to hatch California Least tern eggs was 2–3 times higher than their non-listed counterparts. These concentrations were near known effects thresholds for impacts on reproduction (Giesy et al., 1994; Hoffman et al., 1996) and suggest that California Least terns nesting at the former Alameda Naval Air Station may be currently impacted by PCBs and related compounds. If contaminants are affecting the hatchability of eggs then it is to be expected that failed eggs will have higher concentrations than randomly collected eggs. As other tern species had eggs collected randomly statistical comparisons between species are necessarily limited.

Much higher ∑PBDEs concentrations in eggs from the piscivorous terns compared with the omnivorous Clapper rail, despite the fact that only failed eggs of rails were collected, suggest that fish consumption is the primary exposure pathway for PBDEs in the San Francisco Bay aquatic food web. Clapper rails primarily consume a variety of invertebrate species that occupy tidal marshes. PBDE concentrations have been found to exhibit trophic level biomagnifications. PBDE in muscle tissue have been shown to be lower in herbivorous mammals (reindeer and moose) than in Peregrine falcons, which are carnivorous, preying on other birds (Sellstroem, 1999).

3.3. Comparison of ∑PBDE and ∑PCB concentrations in eggs from different locations

The highest average ∑PBDEs in our project were observed in the Eden Landing region of the upper South San Francisco Bay.

Table 2
PBDE Concentrations (ng/g lw) in tern eggs from the San Francisco Bay, year 2000–2003

Year 2000	**Min.**	**Max.**	**Mean**	**Median**	**SD**
Caspian tern (n = 5)					
Moisture%	63.8	71.6	68.9	70.6	3.25
Fat%	35.7	42.6	39.7	40.0	2.54
PBDE-47	1080	1990	1350	1180	377
PBDE-100	275	605	399	371	124
PBDE-99	344	664	521	474	137
PBDE-154	30.3	121	60.1	49.7	36.2
PBDE-153	75.2	166	108	103	34.9
Total PBDEs	2010	3540	2590	2410	701
Forster's tern (n = 5)					
Moisture%	55.4	65.1	61.6	62.6	3.65
Fat%	37.0	41.4	39.5	39.6	1.87
PBDE-47	586	1500	1036	1100	356
PBDE-100	116	185	157	157	29.0
PBDE-99	265	1610	672	313	583
PBDE-154	20.2	111	57.0	51.9	34.5
PBDE-153	44.8	518	167	92.3	199
Total PBDEs	1080	3560	2160	1820	1010
Year 2001					
Caspian tern (n = 13)					
Moisture%	71.2	78.2	75.8	75.9	1.69
Fat%	22.3	45.1	37.6	38.5	5.99
PBDE47	744	10500	3630	3380	2800
PBDE100	185	2780	950	682	820
PBDE99	238	2910	977	771	827
PBDE154	39.0	499	171	117	142
PBDE153	61.0	733	204	140	213
Total PBDEs	1340	17300	5930	4730	4750
Forster's tern (n = 29)					
Moisture%	72.2	77.6	75.3	75.0	1.29
Fat%	30.8	42.0	37.0	37.4	2.59
PBDE47	914	52600	5400	2690	9550
PBDE100	182	2920	573	364	560
PBDE99	280	5650	1320	825	1320
PBDE154	3.86	579	156	116	128
PBDE153	1.67	895	167	115	178
Total PBDEs	1460	62400	7610	4380	11400
Least tern (n = 5)[a]					
Moisture%	47.0	71.5	61.1	62.2	8.89
Fat%	32.7	40.4	36.7	36.9	3.02
PBDE47	2030	3410	2550	2180	634
PBDE100	733	1620	1030	943	341
PBDE99	907	1980	1440	1540	414
PBDE154	125	294	220	238	74.5
PBDE153	124	249	186	163	56.0
Total PBDEs	4070	7540	5420	5060	1390
Clapper rail (n = 4)					
Moisture%	48.1	75.0	67.2	72.9	12.8
Fat%	38.8	44.7	41.5	41.3	2.96
PBDE47	129	223	162	148	41.7
PBDE100	52.7	111	77.5	72.8	26.8
PBDE99	68.2	145	103	98.7	36.3
PBDE154	10.9	25.1	16.8	15.6	6.80
PBDE153	29.5	50.4	38.1	36.2	9.73
Total PBDEs	291	540	397	379	113

Year 2002	**Min.**	**Max.**	**Mean**	**Median**	**SD**
Caspian tern (n = 20)					
Moisture%	68.9	77.0	74.1	74.8	2.20
Fat%	20.5	40.8	33.0	33.7	5.36
PBDE-47	675	11700	2760	1790	2780
PBDE-100	190	7490	1150	592	1750
PBDE-99	233	9790	1590	724	2300
PBDE-154	39.4	2100	342	136	576
PBDE-153	73.8	4470	717	235	1240
Total PBDEs	1270	36100	6760	3720	8640
Forster's tern (n = 20)					
Moisture%	8.4	77.5	67.7	71.7	14.8
Fat%	21.1	41.3	32.7	33.8	5.62
PBDE-47	1140	18200	3920	3020	3760
PBDE-100	295	8240	1220	675	1740
PBDE-99	426	17400	2550	1310	3710
PBDE-154	60.7	6360	578	164	1410
PBDE-153	54.3	12400	1000	170	2760
Total PBDEs	2590	63300	9420	5460	13400
Least tern (n = 5)					
Moisture%	69.9	81.1	75.4	76.5	4.51
Fat%	29.6	41.9	34.9	34.5	5.07
PBDE-47	1760	3360	2520	2510	732
PBDE-100	690	1430	967	744	347
PBDE-99	1350	2780	1900	1500	677
PBDE-154	109	214	165	153	44.4
PBDE-153	123	287	224	252	68.9
Total PBDEs	4210	7820	5870	5170	1800
Year 2003					
Caspian tern (n = 20)					
Moisture%	58.8	81.1	73.5	74.0	4.34
Fat%	29.2	46.6	35.2	34.8	4.26
PBDE-47	644	17200	2900	1650	3680
PBDE-100	161	4150	744	436	888
PBDE-99	164	3770	925	558	1010
PBDE-154	38.6	388	127	95.5	100
PBDE-153	60.9	627	184	142	146
Total PBDEs	1200	26300	5160	2880	2760
Forster's tern (n = 22)					
Moisture%	59.00	77.5	71.6	72.3	4.86
Fat%	16.8	39.3	31.4	32.6	6.29
PBDE-47	362	17500	3280	1970	3680
PBDE-100	56.4	1530	429	334	379
PBDE-99	151	4390	1260	859	1180
PBDE-154	27.1	900	205	176	185
PBDE-153	40.3	1270	281	189	289
Total PBDEs	666	26000	5610	3600	5540
Year 2001, *Gray's Harbor, WA, Caspian tern (n = 20)*					
Moisture%	75.8	79.1	77.5	77.5	0.79
Fat%	30.7	41.5	38.5	39.0	2.31
PBDE47	1050	8840	2660	2070	1710
PBDE100	266	1760	564	474	318
PBDE99	542	3200	1210	1100	640
PBDE154	44.2	349	96.8	80.4	65.3
PBDE153	43.7	843	145	102	169
Total PBDEs	1970	15000	4670	3920	2820

[a] QC did not pass for one sample for PBDE analysis.

The comparison among site locations was marginally significant for ∑PBDEs ($F_{4,134} = 2.25$, $p = 0.0666$; Table 4). However, the sites were significantly different for ∑PCBs ($F_{4,133} = 6.48$, $p < 0.0001$; Table 5). A recent study of PBDE Concentrations in sediments from the San Francisco Bay indicated that the highest PBDE Concentrations occurred in sediment from the South Bay (Oros et al., 2005).

Twenty Caspian tern eggs from Gray's Harbor, WA in 2001 were compared to 14 eggs from the same species and same year in San Francisco Bay. Table 3 lists the Concentrations of PCB-153 and ∑PCBs in eggs of Caspian terns from Gray's Harbor, WA and San Francisco Bay, California. We found no significant differences between the two regions in concentrations of ∑PBDEs (Table 2, $F_{1,70} < 0.01$, $p = 0.9806$) or ∑PCBs ($F_{1,69} = 1.79$, $p = 0.1857$).

PBDE concentrations in wildlife have recently been reviewed (Law et al., 2003). In general, few data are available on PBDE concentrations in wildfowl eggs from North America. PBDEs (tetra- to hexa-BDEs) were detected in Herring gull eggs from 15 locations throughout the Great Lakes region (Nordstrom et al., 2002), with concentrations ranging from a high of 16,500 ng/g lw for Big Sister Island in Lake Michigan, to a low of 1830 ng/g lw at Port Colbourne in Lake Erie.

Table 3
PCB concentrations (ng/g lw) of different species from San Francisco Bay and Gray's Harbor, WA

Year 2000	Min.	Max.	Mean	Median	SD	Year 2002	Min.	Max.	Mean	Median	SD
Caspian tern (n = 5)						*Caspian tern (n = 20)*					
Moisture%	63.8	71.6	68.9	70.6	3.25	Moisture%	68.9	77.0	74.1	74.8	2.20
Fat%	35.7	42.6	39.7	40.0	2.54	Fat%	20.5	40.8	33.0	33.7	5.36
PBDE-153	173	5350	3005	3120	2010	PCB-153	922	7640	3230	2550	1840
Total PCBs	9180	197000	54700	16500	80140	Total PCBs	4890	38500	15800	13400	8710
Forster's tern (n = 5)						*Forster's tern (n = 20)*					
Moisture%	55.4	65.1	61.6	62.6	3.65	Moisture%	8.4	77.5	67.7	71.7	14.8
Fat%	37.0	41.4	39.5	39.6	1.87	Fat%	21.1	41.3	32.7	33.8	5.62
PCB-153	981	5280	2040	1270	1820	PCB-153	1160	79700	9950	3900	17500
Total PCBs	7200	37100	15200	11100	12400	Total PCBs	75600	385000	47600	18100	84900
Year 2001						*Least tern (n = 5)*					
Caspian tern (n = 12)[a]						Moisture%	69.9	81.1	75.4	76.5	4.51
Moisture%	71.2	78.2	75.8	75.8	1.76	Fat%	29.6	41.9	34.9	34.5	5.07
Fat%	22.3	45.1	37.1	38.3	6.01	PCB-153	4250	10200	7460	7630	2480
PCB-153	1360	8020	3280	2800	2020	Total PCBs	19500	48300	34500	35600	11900
Total PCBs	6840	36100	16500	14400	9450	**Year 2003**					
Forster's tern (n = 29)						*Caspian tern (n = 20)*					
Moisture%	72.2	77.6	75.3	75.0	1.29	Moisture%	58.8	81.1	73.5	74.0	4.34
Fat%	30.8	42.0	37.0	37.4	2.59	Fat%	29.2	46.6	35.2	34.8	4.26
PCB-153	867	17600	5340	3980	4210	PCB-153	1290	14700	3740	2840	3110
Total PCBs	5710	80000	26500	21200	18200	Total PCBs	5920	59200	16800	13400	13100
Least tern (n = 5)[a]						*Forster's tern (n = 22)*					
Moisture%	47.0	71.5	61.1	62.2	8.89	Moisture%	59.0	77.5	71.6	72.3	4.86
Fat%	32.7	40.4	36.7	36.9	3.02	Fat%	16.8	39.3	31.4	32.6	6.29
PCB-153	5410	8500	7030	6960	1200	PCB-153	3820	13300	6870	5060	3840
Total PCBs	27900	42400	34800	35700	5750	Total PCBs	17200	56700	31400	26600	15400
Clapper rail (n = 4)						**Year 2001**, *Gray's Harbor, WA, Caspian tern (n = 20)*					
Moisture%	48.1	75.0	67.2	72.9	12.8	Moisture%	75.8	79.1	77.5	77.5	0.79
Fat%	38.8	44.7	41.5	41.3	2.96	Fat%	30.7	41.5	38.5	39.0	2.31
PCB153	644	1720	1080	977	455	PCB-153	1660	3630	2340	1700	925
Total PCBs	3360	7830	5120	4640	1910	Total PCBs	7250	17500	11000	7370	5070

[a] QC did not pass for two samples for PCB analysis.

Table 4
Geometric mean ∑PBDE ± standard error by year, tern species, and region, estimated using the least squares method to adjust for unbalanced sampling

Year		Tern species		Location	
2000	3266 ± 933	Caspian tern	3744 ± 447	North Bay[b]	4821 ± 948
2001	4788 ± 635	Forster's tern	4407 ± 524	Central Bay[ab]	4109 ± 823
2002	5468 ± 780	Least tern	4790 ± 1607	Upper South Bay[b]	5387 ± 1041
2003	3967 ± 631			Lower South Bay West[ab]	4413 ± 1035
				Lower South Bay East[a]	3091 ± 526

Locations with the same superscript letter did not have significantly different means ($p > 0.10$). No differences were found among years or tern species. As a comparison for terns, four samples of Clapper rail eggs yielded a geometric mean of 386 ± 54. Concentrations are reported as ng/g lipid weight.

Table 5
Geometric mean ∑PCB ± standard error by year, tern species, and region, estimated using the least squares method to adjust for unbalanced sampling

Year		Tern species		Location	
2000	31465 ± 7862	Caspian tern[a]	15922 ± 1676	North Bay[a]	19490 ± 3351
2001	21501 ± 2516	Forster's tern[b]	23055 ± 2397	Central Bay[a]	21855 ± 3831
2002	24021 ± 2999	Least tern[c]	43566 ± 12791	Upper South Bay[b]	40714 ± 6933
2003	24794 ± 3452			Lower South Bay West[ab]	29804 ± 6118
				Lower South Bay East[a]	19640 ± 2924

Categories with the same superscript letter did not have significantly different means ($p > 0.10$). No differences were found among years. For comparison, four samples of Clapper rail eggs yielded a geometric mean of 4876 ± 854. Concentrations are reported as ng/g lipid weight.

The PBDE congener pattern found in Herring gull eggs by Nordstrom et al. (2002) was similar to that seen in terns and other aquatic biota, and resembles that of the Penta-BDE commercial mixture. PBDE concentrations in San Francisco Bay terns are comparable to those found in the Great Lakes for Herring gulls.

3.4. Congener patterns of PBDEs in humans, bird eggs, fish and commercial Penta-BDE mixture from the San Francisco Bay Area

The PBDE congener pattern in various environmental matrices is of interest because it may provide clues to sources, pathways and metabolic and environmental transformation potential of PBDEs. The pattern of the five major PBDE congeners (BDE-47, -99, -100, -153, and -154) found in bird eggs appears consistent with that found in breast milk, and fish (She et al., 2000; She et al., 2002; Holden et al., 2003). BDE-47 was the predominant congener in all matrices. ∑PBDEs were orders of magnitude higher in bird eggs (6200 ng/g lw), and fish (1000 ng/g lw) than in human breast milk (86 ppb) (She et al., 2000; She et al., 2002; She et al., 2007).

BDE-47 averaged about 60% of ∑PBDEs in egg, and fish samples, and 52% in human breast milk samples (Fig. 3). It appears that the PBDE congener patterns in samples from the marine species of

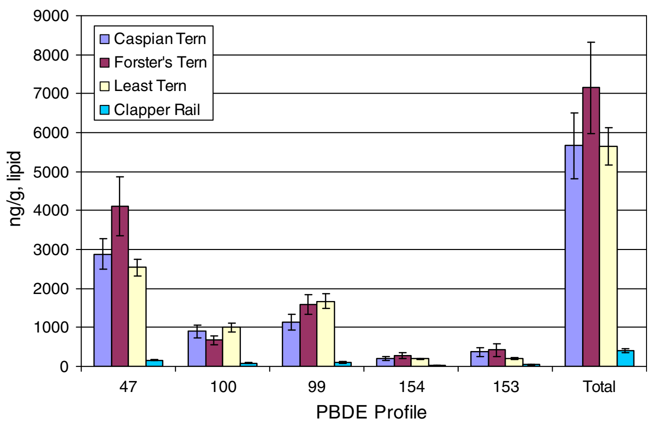

Fig. 2. Comparison of PBDE geometric mean concentrations in eggs from different species (San Francisco Bay area only).

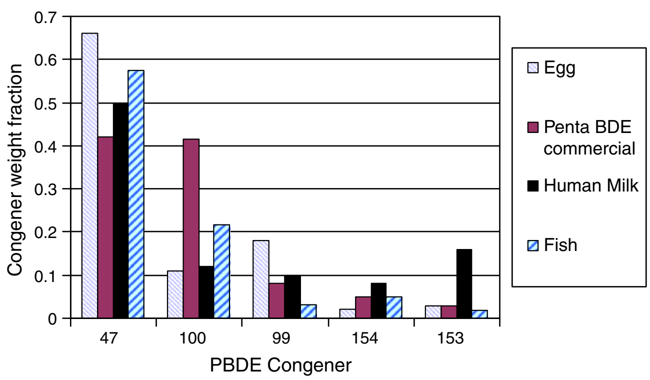

Fig. 3. Relative congener patterns of PBDE in samples of bird eggs, Penta-BDE commercial, human breast milk, and fish from the San Francisco Bay Area.

birds, and fish from the San Francisco Bay more closely resemble the congener pattern of the Penta-BDE commercial mixture than does the pattern previously reported in breast milk from the Pacific Northwest (see Fig. 3). In addition, 7% of the 100 human breast milk samples analyzed from the US show BDE-153 as the dominant congener, with BDE-153 > BDE-47, whereas the ratio of BDE-153: ∑PBDEs was lower in eggs than breast milk. This change in ratio has not been seen in any of the samples of bird eggs, and fish we have analyzed. The difference suggests that humans may have additional sources of PBDE exposures than those experienced by species in the marine food web.

3.5. Comparison of concentrations of PBDEs and PCBs

Table 3 lists PCB concentrations of different tern species from San Francisco Bay and Gray's Harbor, WA. Among eggs collected in the San Francisco Bay, Least terns have the highest ∑PCBs and PCB-153 concentrations, followed by Forster's terns, and Caspian terns and Clapper rails. The 5:1 ratio between mean ∑PCB concentrations in terns and rails is 1/2 the ratio (10:1) of mean ∑PBDEs Concentrations for the same two species, again suggesting that there are some differences in the exposure pathways for PBDEs and PCBs. Trophic biomagnification in open water food chains of terns is currently creating a much higher bioaccumulation potential for PBDEs to the exclusively piscivorous species than the wetland omnivores.

Concentrations of ∑PCBs and ∑PBDEs in tern eggs generally correlated (Figs. 4–6), and concentrations of ∑PCBs were 3–7

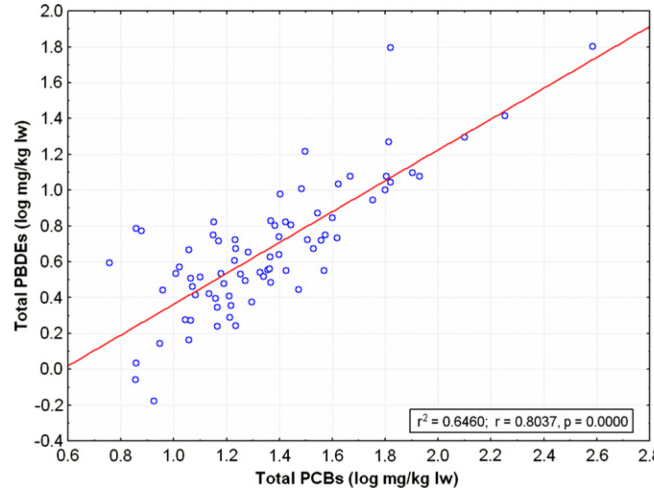

Fig. 4. Correlation between ∑PBDEs and ∑PCBs in individual eggs from Forster's terns.

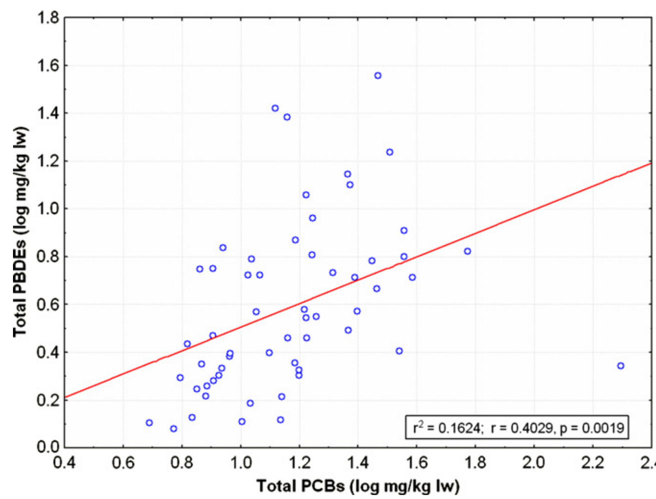

Fig. 5. Correlation between ∑PBDEs and ∑PCBs in individual eggs from Caspian terns.

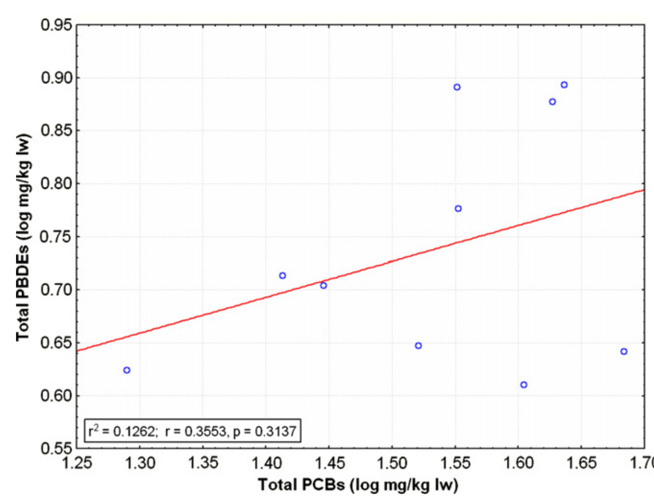

Fig. 6. Correlation between ∑PBDEs and ∑PCBs in individual eggs from California Least terns.

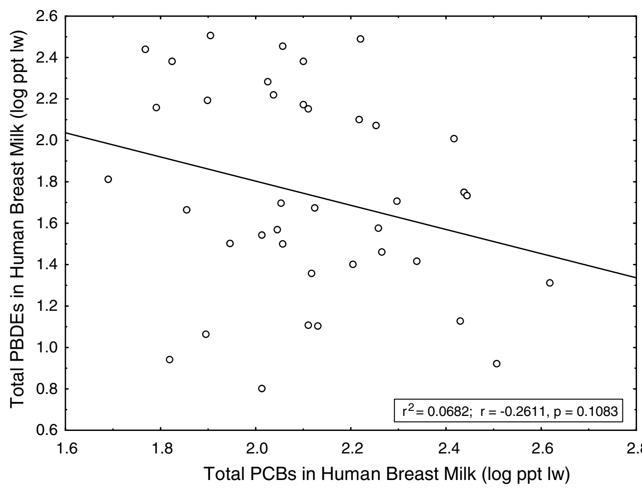

Fig. 7. Correlation between ∑PBDEs and ∑PCBs in individual human milk from the Pacific Northwest.

times higher than ∑PBDEs. In contrast, concentrations of ∑PCBs and ∑PBDEs in human milk from Pacific Northwest, USA seem negatively correlated as shown in Fig. 7 (She et al., 2007). Concentrations of BDE-47, the major PBDE in tern eggs, were close to those of PCB-153, the major PCB in tern eggs. In two samples, ∑PBDEs concentration was higher than ∑PCBs concentration.

3.6. No significant amounts of BDE-183 and BDE-209 were found in any samples

BDE-183, the major congener of Octa-BDE commercial mixtures, and BDE-209 were present at low concentrations in the egg samples. Thus, components of the octa-BDE mixture and deca formulation are either not present in the San Francisco Bay food web, or they have been substantially debrominated to lower congeners. High concentrations of both octa and deca formulations have been reported in the eggs of Peregrine falcons from northern and southern Sweden (Sellstroem et al., 2001) so these congeners have been shown to bioaccumulate. Patterns of PBDE congeners observed in Peregrine falcon eggs from Sweden were different from those seen in the samples from marine species from California and Pacific Northwest that we analyzed, with the falcon eggs containing several of the more highly brominated congeners including BDE-209. Dominant congeners in falcon eggs were BDE-153, and BDE-99, compared to the dominant BDE-47 congener in marine biota. This may indicate that terrestrial species have different sources/pathways of PBDE exposures or that they metabolize PBDEs differently than do marine species.

The 62,000 and 63,000 ng/g lw of ∑PBDEs in two of the Forster's tern eggs is the highest ∑PBDEs concentration yet reported for wildlife or humans. Other high PBDE Concentrations have been reported in carp (47,000 ng/g lw) (Hale et al., 2001) and in eggs of Peregrine falcons (39,000 ng/g lw) (Lindberg et al., 2003).

The finding of unusually high concentrations of PBDEs and PCBs in tern eggs suggests that tern eggs may prove a useful matrix for monitoring these compounds. Whether the elevated concentrations of PBDEs seen in the eggs of terns have effects on the status of these birds in San Francisco Bay remains to be investigated, but tern eggs are likely to remain an important environmental assessment matrix.

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