GEOGRAPHICAL DISTRIBUTION OF PBDEs AND PCBs IN SAN FRANCISCO BAY

She Jianwen[1], Adelsbach Terrence L[2], Yee Julie L[3], Zhu Kunning[1], Lunder Sonya[4], Sharp Renee[4] and Schwarzbach Steven E.[3]

[1]Environmental Health Laboratory, California Department of Public Health, 850 Marina Bay Parkway, Suite G365, Richmond, CA 94804, USA
[2]Environmental Contaminants Division, Sacramento Fish and Wildlife Office, US Fish and Wildlife Service, 2800 Cottage Way, Suite W-2605, Sacramento, CA 95825, USA
[3]US Geological Survey – Western Ecological Research Center, Modoc Hall, USGS, 3020 State University Drive East, Sacramento, CA 95819, USA
[4]Environmental Work Group, 1904 Franklin St. Suite 703, Oakland, CA 94612

Introduction

San Francisco Bay (Bay) is considered an impaired water body under section 303(d) of the Clean Water Act due to polychlorinated biphenyls (PCB) and related compounds. Recent monitoring data shows that Bay is also contaminated with PBDEs in sediment, fish and tern eggs. Davis et al[1] reviewed polychlorinated biphenyls (PCBs) in San Francisco Bay and concluded that in-Bay contaminated sites are likely also a major contributor of PCBs to the Bay food web. Since late 1990, we conducted a series of studies of PBDE in seal[2], fish[3, 4] and bird eggs[5] in San Francisco Bay and today it will be possible to examine the geographical distribution of PBDE in the Bay. By examining the PBDE data of sediment from Oros et al[6], PBDE in fish and PBDE in tern eggs, we found that Upper South Bay was heavily contaminated with PBDEs. The PBDE data examined in this study includes sediments samples from year 2002 from Oros et al[6], 24 fish samples from year 2002[3,4] and 149 aquatic bird eggs from year 2000 – 2003[5].

Experimental Methods

Bird egg sample collection and analysis. Eggs were obtained from various locations in the Bay estuary (Fig. 1). Sampling sites in the Bay estuary 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 contents were transferred to labeled, chemically clean, clear glass jars. Eggs were frozen at -20ºC, and shipped to the laboratory where they remained frozen at -20ºC until analysis. Details of the analytical method and QA/QC are presented elsewhere[5].

Fish sample collection and analysis. We collected 22 fish from six of the 10 most commonly caught and eaten species in the Bay: halibut, striped bass, white croker (also called kingfish), walleye surfperch, jacksmelt and leopard shark. Halibu, bass and shark samples were collected from anglers on private or charter boats around South San Francisco or in San Pablo Bay. All other samples were donated by fishmen at public piers in San Francisco, South San Francisco, Alameda, Berkeley, Richmond and Point Pinole. Samples were prepared as the species are typically eaten – skinning the shark, halibut and bass but leaving the skin on the croker, surfperch and smelt. The fish were stored at -20º 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. And 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. Detailed sample prepare procedures can be found elsewhere[3]. For PBDE analysis, a HRGC-HRMS (Finnigan Mat 95) was operated in EI multiple ion monitoring mode with 9000 resolution. A 1μL sample was injected onto a 60 meter DB 5 ms column with 0.25μm film thickness in pulsed mode. ^{13}C –PBDE 77 was used as an internal standard.

Sediments data source. Sediment data are from a publication of Oros et al.[6] regarding the analysis of 48 sediments from San Francisco Bay collected in year 2002.

Statistical Analysis. There was an adequate number of egg samples for statistical analysis. We log-transformed ∑PBDEs and ∑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 ANOVA to model and test for differences in ∑PBDEs and ∑PCBs in samples from the Bay area among regions. We used the least squares method in ANOVA to estimate mean log-transformed ∑PBDEs and ∑PCBs. The least squares method adjusts the means for unbalanced sampling across species, years, and regions. Whenever location effects were found, we back-transformed the estimates and applied the delta method to determine mean contamination and standard errors. 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. Non-statistical analyses were conducted for fish and sediment data. For fish, we mapped individual PBDE values in the San Francisco Bay since there were not enough samples for each species at each location for a valid statistical analysis. For sediment we used the mapping from Ores et al.[6]. No statistical analysis was done for the PBDE data in sediment either, since there are quite a few PBDE congeners below detection values.

Results and discussion

Among four species of the eggs, only Caspian and Forster's eggs were sampled in more than two locations. The discussion here will focus on these two terns only. Table 1 lists the PBDE data and Table 2 lists PCB data for Caspian and Forster's tern and their locations. Highest PBDE samples (62 and 63 ppm) are from Upper South Bay and highest PCB sample (385 ppm) is also from the same area. However, without statistical analysis of the data in Table 1 and 2, it is hard to picture the geographical distribution of the PBDE and PCB contamination in the Bay due to large standard deviation with the data from each location. We regrouped the sample locations into five sample regions and use ANOVA to model and test for region difference for ∑PBDE and ∑PCB. Table 3 lists the geometric mean ∑PBDE ± standard error and ∑PCB ± standard error by region, estimated using the least squares method to adjust for unbalanced sampling. Regions in column 1 of Table 3 with the same letter did not have significantly different means for ∑PBDE ($p > 0.1$). Region in column 3 of Table 3 with the same letter did not have significantly different means for ∑PCB ($p > 0.1$). The highest average ∑PBDE and ∑PCB were both observed in the Eden Landing region of the Upper South San Francisco Bay. The comparison among regions was marginally significant for ∑PBDEs ($F_{4, 134} = 2.25$, $p = 0.0666$; Table 1). However, the sites were significantly different for ∑PCBs ($F_{4, 133}$) $= 6.48$, $p < 0.0001$; Table 2). Fig. 1 shows the sample sites, regrouped 5 sample regions and geometric mean of ∑PBDE and ∑PCB. PCB spatial distribution in eggs is consistent with the conclusion from Davis et al.[1] obtained from the study of the sediments from the Bay (Fig. 4).

The highest ∑PBDE concentrations in tern egg samples (62 and 63 ppm) were found in Upper South Bay. Six species of fish were collected from three locations: North Bay, Central Bay and Upper South Bay. However, only three species (Smelt, Halibut and Walleye Surfperch) were collected on more than one location. In Upper South Bay, ∑PBDE concentrations in these species of fish were the highest among the three locations (Fig 3). In addition, sediment samples from Upper South Bay had the highest ∑PBDE concentration (212 ppm)[6], which was 1-3 orders of magnitude higher than the samples collected from other locations, as shown in Fig. 2. The co-occurrence of the highest ∑PBDE concentration in sediment, fish and tern eggs could be explained by the food web through which the PBDES in contaminated sediment accumulated in the fish-eating birds and marine fish in Upper South Bay.

References

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Table 1. PBDE concentration (ng/g lw) in tern eggs from the different location from the Bay

Location	Species	N Obs	Minimum	Maximum	Mean	Median	Std Dev
Napa Marsh	Caspian	10	1759	26300	6523	5437	7241
Napa Sonoma Marsh	Caspian	5	1650	36100	15278	9160	14459
Brook Island	Caspian	10	1200	12600	5014	3300	3973
Baumberg Pond B10	Caspian	10	1310	6650	3917	4445	2079
Baumberg Pond B8A	Caspian	5	4633	17260	9335	6065	5882
Pond A7	Caspian	18	1270	8130	2816	2305	1751
Napa Marsh	Forster's	9	666	12461	5148	4639	3544
Napa Sonoma Marsh	Forster's	5	3730	5940	4906	5200	979
Hayward Shoreline	Forster's	10	1872	63300	12743	5161	18680
Baumberg Pond B10	Forster's	5	3050	11900	6844	5630	3926
Baumberg Pond B8A	Forster's	3	2561	62433	23422	5273	33811
Pond A16	Forster's	21	871	26000	4747	3223	5472
Pond A1	Forster's	15	1750	18551	5562	4720	4079
Charleston Slough	Forster's	5	2477	16478	8661	10140	5790
Belmont Slough	Forster's	3	1456	7426	4766	5417	3038

Table 2. PCB concentration (ng/g lw) in tern eggs from the different location from the Bay

Location	Species	N Obs	Minimum	Maximum	Mean	Median	Std Dev
Napa Marsh	Caspian	10	6580	17500	10219	8060	3919
Napa Sonoma Marsh	Caspian	5	7610	29300	15902	14400	8389
Brooks Island	Caspian	10	5920	23600	14597	15600	6048
Baumberg Pond B10	Caspian	10	10800	59200	25750	22550	15048
Baumberg Pond B8A	Caspian	5	13500	36100	25200	24200	8311
Pond A7	Caspian	18	4890	197000	23801	10500	44116
Napa Marsh	Forster's	9	8400	80000	26722	16300	22301
Napa Sonoma Marsh	Forster's	5	7560	17000	12792	14100	3744
Hayward Shoreline	Forster's	10	7770	385000	74517	26400	115492
Baumberg Pond B10	Forster's	5	23000	63600	42060	37400	20245
Baumberg Pond B8A	Forster's	3	16200	66100	38133	32100	25491
Pond A16	Forster's	21	5710	179000	26018	15100	37683
Pond A1	Forster's	15	12100	67600	27293	23300	15292
Charleston Slough	Forster's	5	14400	42100	27240	30400	11183
Belmont Slough	Forster's	3	11400	41500	29300	35000	15839

Table 3. Geometric mean ∑PBDE ± standard error and ∑PCB ± standard error by region, estimated using the least squares method to adjust for unbalanced sampling.

Region	PBDE	Region	PCB
North Bay [b]	4821 ± 948	North Bay [a]	19490 ± 3351
Central Bay [ab]	4109 ± 823	Central Bay [a]	21855 ± 3831
Upper South Bay [b]	5387 ± 1041	Upper South Bay [b]	40714 ± 6933
Lower South Bay West [ab]	4413 ± 1035	Lower South Bay West [ab]	29804 ± 6118
Lower South Bay East [a]	3091 ± 526	Lower South Bay East [a]	19640 ± 2924

Region in column 1 of Table 3 with the same letter did not have significantly different means for ∑PBDE ($p > 0.1$). Region in column 3 of Table 3 with the same letter did not have significantly different means for ∑PCB ($p > 0.1$).

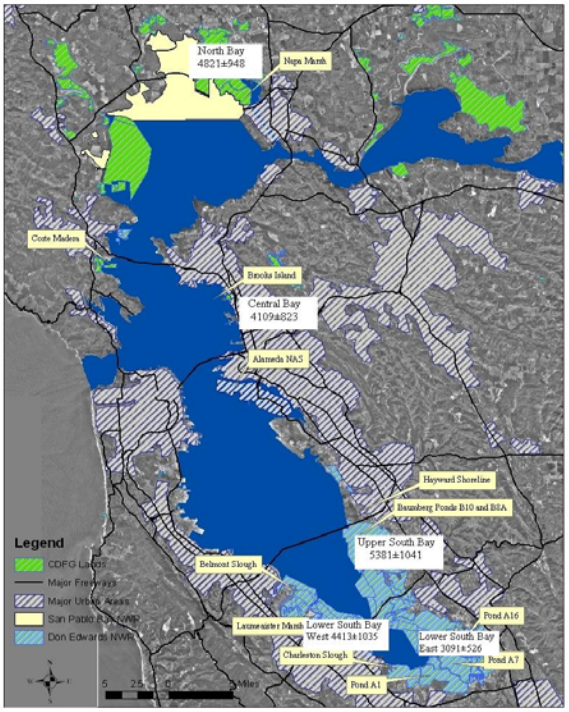

Fig 1. Sampling sites for tern eggs in the San Francisco Bay Area

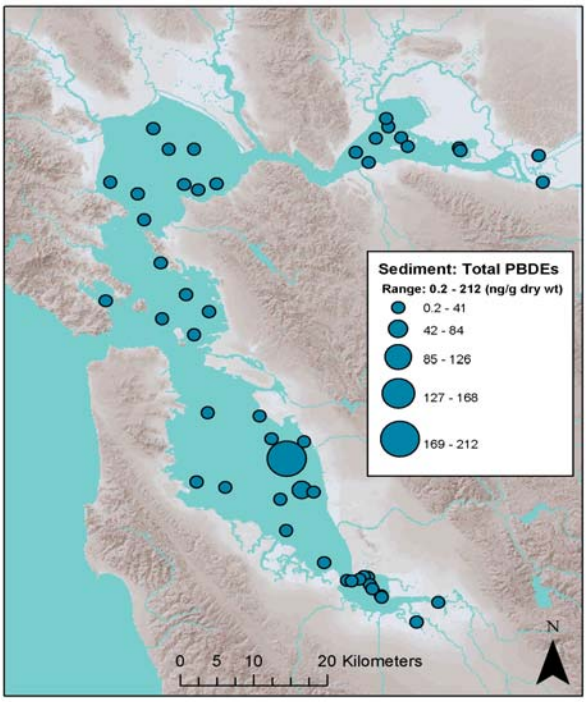

Fig 2. PBDE concentrations in Bay Area sediment (Oros et al., 2005)

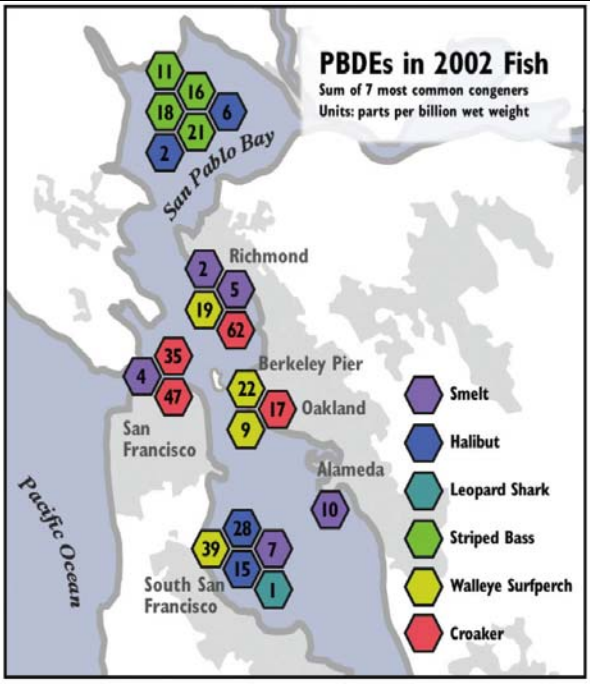

Fig 3. PBDE in fish from SF Bay (Sonya et al., 2002)

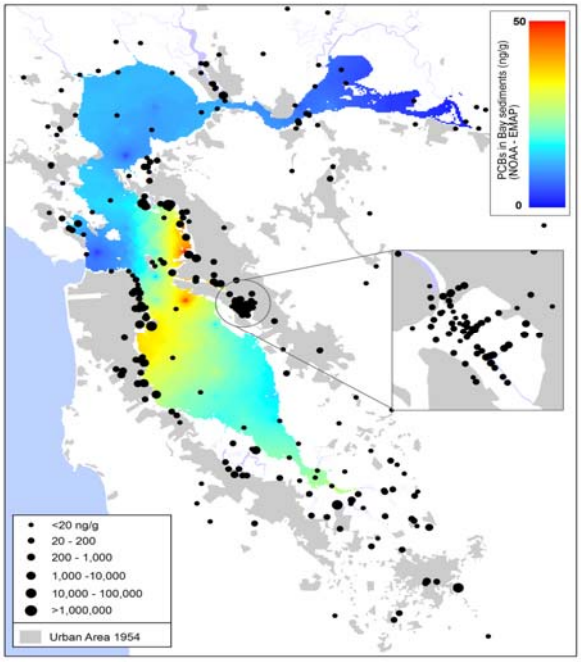

Fig 4. Average PCB concentrations in Bay Area sediment (Davis et al., 2007)