

## **APPENDIX C: PBDE Sources and Distribution in the SCB**

# Distribution and sources of polybrominated diphenyl ethers in the southern California Bight

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## ABSTRACT

Polybrominated diphenyl ethers (PBDEs) were measured in surface sediments from 121 locations within the southern California Bight. Site selection was based on a probabilistic approach to determine the spatial extent and magnitude of PBDE concentrations with known confidence intervals. Coastal embayments (including estuaries, marinas, ports, and bays) and the continental shelf out to the lower slope were sampled. Thirteen PBDEs were detected at 92 of the sites, with a geometric mean and maximum of 4.7 and 560 ng/g dry weight (sum of 13 congeners), respectively. PBDE concentrations were higher in coastal embayments as opposed to offshore locations. Embayments had an area weighted geometric mean total PBDE concentration of 12 (95% confidence interval 8.0 - 17) ng/g dry weight and total PBDE mass of 110 (77 - 160) kg. The offshore stratum, which is 99% of the total area, had an area weighted geometric mean total PBDE concentration of 2.0 (1.6 - 2.5) ng/g dry weight and total PBDE mass of 860 (700 - 1100) kg. The five highest PBDE concentrations were associated with the mouths of urban rivers, indicating that urban runoff is a major input of PBDEs in to coastal marine waters. The outfalls of wastewater treatment plants were not observed to be major sources.

## INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants for a variety of materials including plastics, foams, and textiles (Yogui *et al.* 2009). The three PBDE technical formulations are commonly referred to as penta-BDE, octa-BDE, deca-BDE. Each formulation contains a range of congeners (La Guardia *et al.* 2006), and the formulation name specifies the approximate average number of substituted bromines. PBDEs are a potential risk to the environment due to their ability to migrate from treated products, biomagnification in food webs (Johnson-Restrepo *et al.* 2005), long range transport (Hoh *et al.* 2005), detection in humans (Petreas *et al.* 2011), generally increasing environmental concentrations since the 1970s (Zhu *et al.* 2005), and concern regarding their toxicity (Birnbaum, *et al.* 2004). In the United States, production of the penta-BDE and octa-BDE technical mixtures by the primary manufacturer ceased in 2004 (Vonderheide *et al.* 2008). This was followed by bans on the manufacture, distribution, and processing in California in 2006 (CEPA 2006). These two formulations were added to the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2009, subjecting them to international controls (SC 2011). In contrast, the deca-BDE technical formulation is not currently restricted, but is scheduled to be phased out of production and sale within the U.S. market by 2013 (USEPA 2011).

Due to their use in a variety of household and industrial products, urban areas are sources of PBDEs to the environment (Newsome *et al.* 2010). The southern California Bight (SCB) is the second most populated coastal region in the United States, where approximately 17 million people live in the metropolitan regions of Los Angeles, Orange County, and San Diego (USCB 2009). The shoreline of the SCB extends from Point Conception (200 km northwest of Los Angeles), where the coast turns sharply to the east, to Cabo Colnett in Baja California (70 km south of the U.S.-Mexico border). There are 4 major publically owned treatment works (POTWs) that discharge treated wastewater through outfall pipes that extend kilometers offshore at depths of 60 to 100 m. In 2009, these POTWs discharged a combined 380 million L/day of effluent (Stein *et al.* 2009). Historically, the POTWs discharged partially treated sewage and had a significant negative impact on the coastal ecosystem in this region (Schiff *et al.* 2000, Stein *et al.* 2009). Mass emissions of many constituents from the POTWs peaked in the 1970s and has since been reduced by a combination of improved wastewater treatment systems and restrictions on chemical contaminants, in particular DDT. However, over the same time period, population growth and increased conversion of natural landscapes to impervious surfaces (concrete and other construction materials) has led to an increase in non-point source surface runoff into the SCB (Schiff *et al.* 2000, Lyon *et al.* 2009).

Previous work indicated relatively high concentrations of PBDEs may be pervasive in this region. For example, concentrations of 60 to 236,000 ng/g lipid weight (sum of 14 congeners) was observed in the blubber of sea lions that frequent the urbanized southern California coast (Meng *et al.* 2009). These animals were stranded between 1994 and 2006. The PBDE concentrations were described as the highest in marine mammals reported in the literature. A survey of bivalves (mussels and oysters) and surface sediments sampled between 2004 to 2007 at >100 sites covering much of the U.S. coastline found the single highest concentrations for both matrices in southern California (Kimbrough *et al.* 2008). A tissue concentration of 40,823 ng/g lipid weight was measured in Anaheim Bay, CA, and a sediment concentration of 88 ng/g dry weight (dw) was measured in Marina del Rey, CA (both sum of 38 congeners).

Motivated by these previous studies, we conducted a survey of marine sediments to determine unbiased estimates of the extent and magnitude of PBDE concentrations within a 14,500 km<sup>2</sup> region of the SCB, and the location of impacted habitats in this highly urbanized coastal zone. Although extensively monitored for legacy contaminants, data on the occurrence of PBDEs in a variety of inshore and offshore habitats within the SCB and at this spatial scale was missing. In addition, suspected major sources PBDEs, urban runoff and wastewater from POTWs, were investigated based on geographic proximity to the sampling sites.

## **METHODS**

### **Study Design**

A stratified-random probability-based approach was used to select 121 sediment sampling sites within the SCB (Stevens *et al.* 2003, 2004). Two strata were selected: (1) 61 embayment sites with estuary, port, bay, and marina sub-strata; and (2) 60 offshore sites including the inner continental shelf (5-30 m water depth), mid-shelf (30-120 m), outer shelf (120-200 m), upper slope (200-500 m), and lower slope (500-1000 m) sub-strata. Grab samples of the top 5 cm of sediment at embayment sites and the top 2 cm at offshore sites were collected between July 1, 2008 and September 30, 2008. Samples were placed in pre-

cleaned glass containers and kept at 4 °C during transport from the field, then stored at -20 °C. Analysis of the p,p'-DDE concentration was performed as described previously (Maruya *et al.* 2009).

## Sample Preparation

Known masses, ranging from 8 to 15 g, of freeze dried sediments were loaded into pressurized liquid extraction (PLE) cells and spiked with the surrogate standards listed in Supplemental Information (SI) Table SI-1. Samples were extracted over 2 cycles; each cycle used 100% dichloromethane at 1500 psi and 100°C with a static pressure time of 2 minutes. The sample extract was concentrated using evaporative solvent reduction. Samples were passed through 5% deactivated silica, 1% deactivated alumina, and acidified copper granules with 1:1 pentane/dichloromethane. Prior to instrumental analysis, all samples were spiked with the internal standards listed in Table SI-1.

## Instrumental Analysis

Quantification was performed by gas chromatography/mass spectrometry (GC/MS) in selected ion monitoring mode (SIM). The injection system was operated in splitless mode at 290°C. Separation was performed using an Agilent Technologies DB-XLB (30 m long × 0.25 mm ID and 0.10 µm film thickness) capillary column with helium as the carrier gas. The GC temperature program was: hold at 110°C for 1 minute, ramp at 8°C/minute to 320°C, and hold for 18 minutes (total run time 45.2 minutes). The transfer line to the MS was 290°C. Ionization was performed in electron capture negative chemical ionization (ECNI) mode with methane as the reagent gas and the source at 225°C. The quantification and confirmation ions for the analytes, surrogate standards, and internal standards are in Table SI-1.

The target congeners were classified as either PBDE<sub>13</sub> or PBDE<sub>minor</sub>. PBDE<sub>13</sub> is defined as the 13 congeners present in the calibration solutions, and are listed in Table SI-1. The calibration solutions were prepared at five concentrations, and contained uniform concentrations of the surrogate and internal standards. For each analyte, a relative response factor (RRF) was determined for each calibration level using the internal standard. The 5 response factors were then averaged to produce a mean RRF for each congener. PBDE<sub>minor</sub> is defined as the 38 congeners in Table SI-2 not present in the calibration solutions. The RRFs for PBDE<sub>minor</sub> were assumed equal to that of a similar congener in PBDE<sub>13</sub>. Standards of the PBDE<sub>minor</sub> congeners were used to verify the retention times in the analytical runs. Reported analyte concentrations are corrected for surrogate recoveries. The reporting limit was 0.1 ng/g dw for all congeners except for BDE-209, which was 1 ng/g dw.

## Quality Control

The extracted profiles of the primary and the confirmation ions for each analyte met the following criteria. (1) The characteristic *m/z* values of each analyte were at a maximum in the same scan or within one scan of each other. (2) The retention time fell within ±5 seconds of the retention time of the authentic compound in the daily calibration check. (3) The relative peak heights of the primary ion compared to the confirmation ion fell within ±30 percent of the relative intensities of the ions in a reference mass spectrum. A matrix spike consisting of the PBDE<sub>13</sub> congeners was analyzed with each extraction batch. The average recovery for all compounds fell between 80% and 120%. A method blank was extracted and

analyzed with every extraction batch. Within a batch, if the blank concentration was greater than 50% of the sample concentration, the sample concentration was set to non-detect. If the blank concentration was less than 50% of the sample concentration, then the blank concentration was subtracted from the sample concentration.

There was less certainty in the identity and quantitative results for PBDE<sub>minor</sub> than PBDE<sub>13</sub>, because PBDE<sub>minor</sub> congeners were infrequently detected at low concentrations near the reporting limit, other brominated compounds may interfere in their analysis when monitoring bromine ions at  $m/z$  79 ( $[^{79}\text{Br}]^-$ ) and 81 ( $[^{81}\text{Br}]^-$ ) in ECNI mode (La Guardia *et al.* 2010), and the relative response factors for quantification were assumed. Therefore, the discussion and conclusions are focused on the PBDE<sub>13</sub> congeners, and the PBDE<sub>minor</sub> congeners are reported in the Supporting Information.

## Data Analysis

Summary statistics and estimates of spatial extent were calculated by setting non-detects to  $\frac{1}{2}$  the reporting limits. The measured concentration data showed a right skew; i.e., the median is lower than the mean (Table 1). Therefore, geometric means are reported. Quantitative spatial analysis was performed using R (RDCT 2011) and the *cont.analysis* function within the *spsurvey* package (Kincaid *et al.* 2011). This function estimated the spatial extent and corresponding confidence intervals of the PBDEs in the two strata (embayments and offshore sites) based on the randomized survey approach. The area weighted geometric mean concentration ( $m$ ) for a stratum is defined as:

$$m = \exp \left[ \frac{\sum_{i=1}^n (\ln(p_i) \times w_i)}{\sum_{i=1}^n w_i} \right]$$

where  $p_i$  is the concentration at site  $i$ ,  $w_i$  is the area weight for the site  $i$ , and  $n$  is the number of sites in the stratum. A sensitivity analysis on the treatment of non-detects was performed by, instead of setting non-detects to  $\frac{1}{2}$  the reporting limits, the non-detects were set to values determined by regression order statistics using the *ros* function in the NADA R package (Helsel 2006). This did not significantly change the summary statistics.

The mass of PBDE in the sampled sediment layers was estimated as:

$$M = m \times \rho \times a \times d$$

where  $M$  is the mass in the stratum,  $m$  is the area weighted geometric mean concentration of the stratum,  $\rho$  is the dry density of the sediment (assumed  $1.5 \text{ g/cm}^3$ ),  $a$  is the stratum area, and  $d$  is the sampling depth. Sources of error in the mass estimations and comparison between strata include variations in the sediment dry density and sedimentation rates. The sampling depths, 5 cm in embayments and 2 cm offshore, may account for an assumed greater sedimentation rate in embayments.

## RESULTS AND DISCUSSION

PBDEs were detected at 92 of the 121 sampling sites and are thus widely distributed in SCB sediments. A summary of the PBDE<sub>13</sub> concentrations is shown in Table 1; the concentrations of all 52 measured congeners are shown in Table SI-2. The total PBDE<sub>13</sub> concentration was dominated by BDE-209 at 80%, followed by BDE-47 at 7.5% and BDE-99 at 4.9%. The dominance of BDE-209 is frequently observed in sediment samples (Hale *et al.* 2003, Shaw *et al.* 2009, Yogui *et al.* 2009) and results from the congener distribution and relative production levels of the PBDE technical mixtures (La Guardia *et al.* 2006).

The range of PBDE<sub>13</sub> concentrations measured in the SCB (non-detect to 560 ng/g dw, mean 20 ng/g dw) is on the high end of marine and estuary concentrations reported in other North American regions. Marine sediment concentrations of non-detect to 212 ng/g dw were reported in San Francisco Bay, CA (Oros *et al.* 2005), a comparably highly urbanized system; and 0.087 to 12.7 ng/g dw in the Strait of Georgia, British Columbia, Canada (Grant *et al.* 2011), a less populated region than described in this study. The sediment concentrations reported at 16 sites along the entire coast of California was reported as non-detect to 88 ng/g dw, and at 12 sites along the New York coast as 2.9 to 41.3 ng/g dw; the shorelines of these two states had the highest PBDE concentrations among those sampled (Kimbrough *et al.* 2008). The relatively high concentrations observed in the SCB are not unexpected given the level of urbanization. In contrast, the concentrations observed in the SCB are lower than in surveys that targeted rivers and embayments adjacent to industrial sources of PBDEs. Maximum BDE-209 concentrations reported for Dongjiang River, China, near electronics manufacturing plants (Mai *et al.* 2005), and industrialized bays in Korea (Moon *et al.* 2007) were one order of magnitude higher than in the SCB. Concentrations up to 16,088 ng/g dw (sum of 14 congeners) were observed in the Nanyang River, China, which receives e-waste discharge (Luo *et al.* 2007). This indicates that the concentrations measured in the SCB were not due to adjacent industrial point sources, and that other sources are responsible for PBDE input.

The spatial distribution of PBDEs in marine sediments indicates sources to the SCB, and which habitats are the most impacted. Figure 1 shows the distribution of four congeners representative of the three technical mixtures. BDE-47 and BDE-99 are the two most abundant congeners in penta-BDE, BDE-183 is the most abundant congener in octa-BDE, and BDE-209 is the most abundant congener in deca-BDE. The spatial distributions of all 52 measured congeners are shown in Figure SI-1. Higher concentrations of PBDEs occur predominantly in embayments near urban areas and decrease at offshore locations. Embayments distant from heavily urbanized areas, those north of the Los Angeles metropolitan area and between the Los Angeles and San Diego metropolitan areas, have relatively low concentrations.

The spatial distribution can be described quantitatively using area weighted estimates, in which concentrations at sites representing a greater area are given more weight. Table 2 shows the estimates and confidence intervals for a set of representative congeners and total PBDE in the embayment and offshore strata. The embayment strata had significantly higher concentrations than the offshore strata for congeners originating from the technical mixtures: BDE-47, BDE-99, BDE-183, and BDE-209. The concentration of BDE-47 at each site was moderately correlated with BDE-183 (Spearman's rank correlation coefficient  $\rho = 0.395$ , p-value  $<0.01$ ) and BDE-209 ( $\rho = 0.374$ , p-value  $<0.01$ ), indicating that

the terrestrial sources either emit the three technical mixtures in a spatially uniform manner; or, more likely, there is mixing of the technical mixtures prior to discharge to the marine waters.

The five highest PBDE sediment concentrations occurred at or near urban river mouths. Ballona Creek (33.97125° N, -118.43955° W), 240 ng/g dw, the Dominguez Channel (33.76666° N, -118.24890° W), 140 ng/g dw, and the Los Angeles River (33.78074° N, -118.20596° W), 560 ng/g dw, drain basins within Los Angeles County. Within the metropolitan area these rivers flow through concrete channels. Los Cerritos Channel (33.76580° N, -118.10354° W), 230 ng/g dw, receives urban runoff from the city of Long Beach. A site within San Diego Bay (32.65989° N, -117.12241° W), 150 ng/g dw, may be influenced by both the Sweetwater River, which flows through the city of San Diego, and a naval station. BDE-209 was the most abundant congener at these sites, except at Ballona Creek where BDE-47 was most abundant and BDE-209 was not detected. This indicates a relatively high input of the penta-BDE technical mixture at that site, which may be influenced by local manufacturing. The high abundance of PBDEs at urban river mouths indicates runoff is the primary source of PBDEs to the Bight. PBDEs can enter the environment from the manufacturing and disposal of products containing PBDEs, or from office and household sources when they migrate out of the products in which they are used. They then bind to dust (Leung *et al.* 2011) and exist in the atmosphere in the gas and particle phases (Strandberg *et al.* 2001). During seasonal storm events they can be transported to urban rivers and flushed out of the watersheds. They may also be transported to urban rivers as dry weather runoff.

Estimates of the mass of PBDE in SCB sediments describe the total amount of contaminant to which the ecosystem is exposed through inputs over a period of time from all sources (excluding water phase PBDEs). The time period is dependent on the sediment deposition rate, which is unknown for the SCB, but we assume the sampling depths of 5 cm in embayments and 2 cm offshore represent relatively recent inputs as of 2008. The estimated masses for selected congeners are shown in Table 2. The embayment stratum has a combined area of 128 km<sup>2</sup> and the offshore stratum has an area of 14,400 km<sup>2</sup>; therefore, the estimated PBDE masses in the offshore stratum are greater despite smaller concentrations. For comparison, the 1100 km<sup>2</sup> San Francisco Bay was estimated to have sediment inventories of BDE-47 and BDE-209 of 33 (95% CI 30 - 36) kg and 153 (107 - 198) kg, respectively (Oram *et al.* 2008). In the 2016 km<sup>2</sup> Pearl River Estuary, which is highly industrialized and populated, estimated inputs of ΣPBDE<sub>10</sub> (10 congeners excluding BDE-209) and BDE-209 from rivers were 132 and 1350 kg/year, respectively. The annual outflows of ΣPBDE<sub>10</sub> and BDE-209 from the Pearl River Estuary to the coastal ocean were estimated at 126 and 940 kg/year, respectively (Guan *et al.* 2009).

We measured 12 of 13 congeners that were not detected in the technical mixtures by La Guardia *et al.* and possibly result from debromination (2006). BDE-32, -37, -77, -181, and -190 were detected at between 12 to 41 sites each (Table S-1), with BDE-77 and BDE-190 the most abundant. In addition, BDE-209 was 68% of the total PBDE<sub>13</sub> mass in embayments and 45% of the mass offshore, indicating it is either debrominating or degrading while being transported away from the coast, or it is more slowly transported relative to the other congeners. Debromination of highly brominated congeners is a cause for concern because bioavailability increases with decreasing bromination to congeners with 4 or 5 bromines (Debruyne *et al.* 2009).

POTWs are potential sources of contaminants to the SCB, and water currents will distribute emitted contaminants in characteristic spatial patterns. From 1965 to 1980 the primary source of DDT to the SCB was the POTW outfall located 2.8 km off the Palos Verdes Peninsula (Schiff *et al.* 2000). The predominant inshore oceanic current in this region flows to the northwest and distributed DDT and breakdown products in that direction from the outfall. Figure 2 compares the spatial distributions, both measured in 2008, of the breakdown product p,p'-DDE with total PBDE<sub>13</sub>. The spatial variation of p,p'-DDE does not match that of PBDEs due to their different sources, nor does the spatial pattern indicate the other three POTW outfalls are major sources of PBDEs to the SCB.

The risk of the widespread extent of PBDEs in the SCB to coastal and marine ecosystem health is unknown. The terrestrial reservoir of PBDEs in existing products will likely continue to be released to the environment despite current and future restrictions on their use (Harrad *et al.* 2006, Shaw *et al.* 2010). Correlations between PBDE concentrations and indicators of toxicity have been reported in marine mammals, although the indicators may be influenced by co-exposure to other toxicants such as PCBs (Shaw *et al.* 2009). One consequence of higher PBDE concentrations in embayments is marine animals that are a resident of or frequent the urbanized coast may be more highly exposed (Meng *et al.* 2009). We see four lines of future inquiry related to PBDEs in the SCB that may help determine/quantify the risk and determine the effect of regional restrictions and regulations. 1) Future monitoring to determine temporal trends. 2) Quantification of loads from urban watersheds. 3) The biological effects of PBDEs on marine mammals, especially those with habitats that include urban embayments, and perhaps in conjunction with other bioaccumulative contaminants. 4) The human consumption of sport fish, some of which are caught from urban embayments and other inshore locations.

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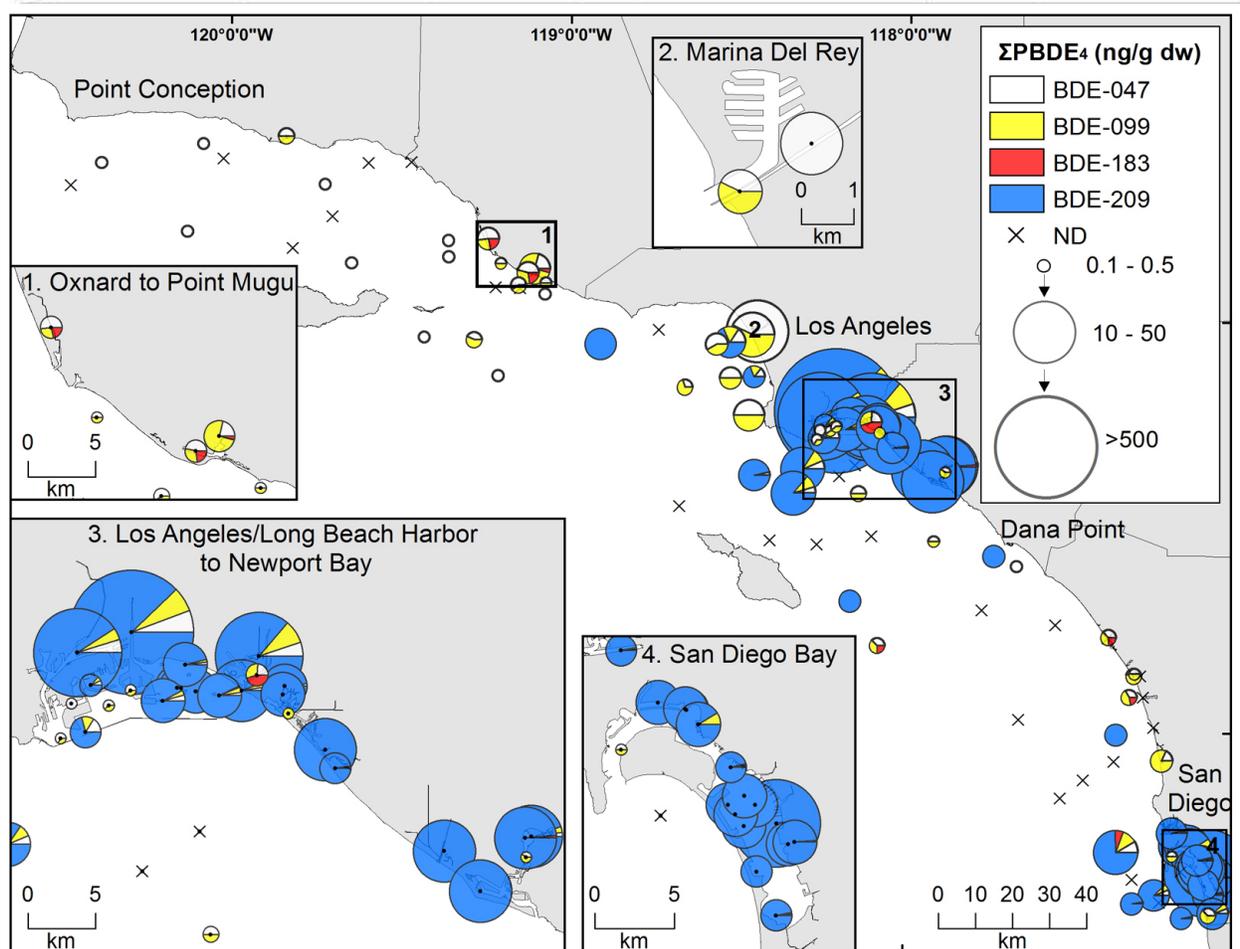
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Zhu, L.Y. and R.A. Hites, 2005. Brominated Flame Retardants in Sediment Cores from Lakes Michigan and Erie. *Environmental Science and Technology* 39, 3488-3494.

**Table 1. PBDE<sub>13</sub> sediment concentrations (ng/g dw) measured at 121 sites in the southern California Bight. The minimum measured concentration for all congeners was non-detect.**

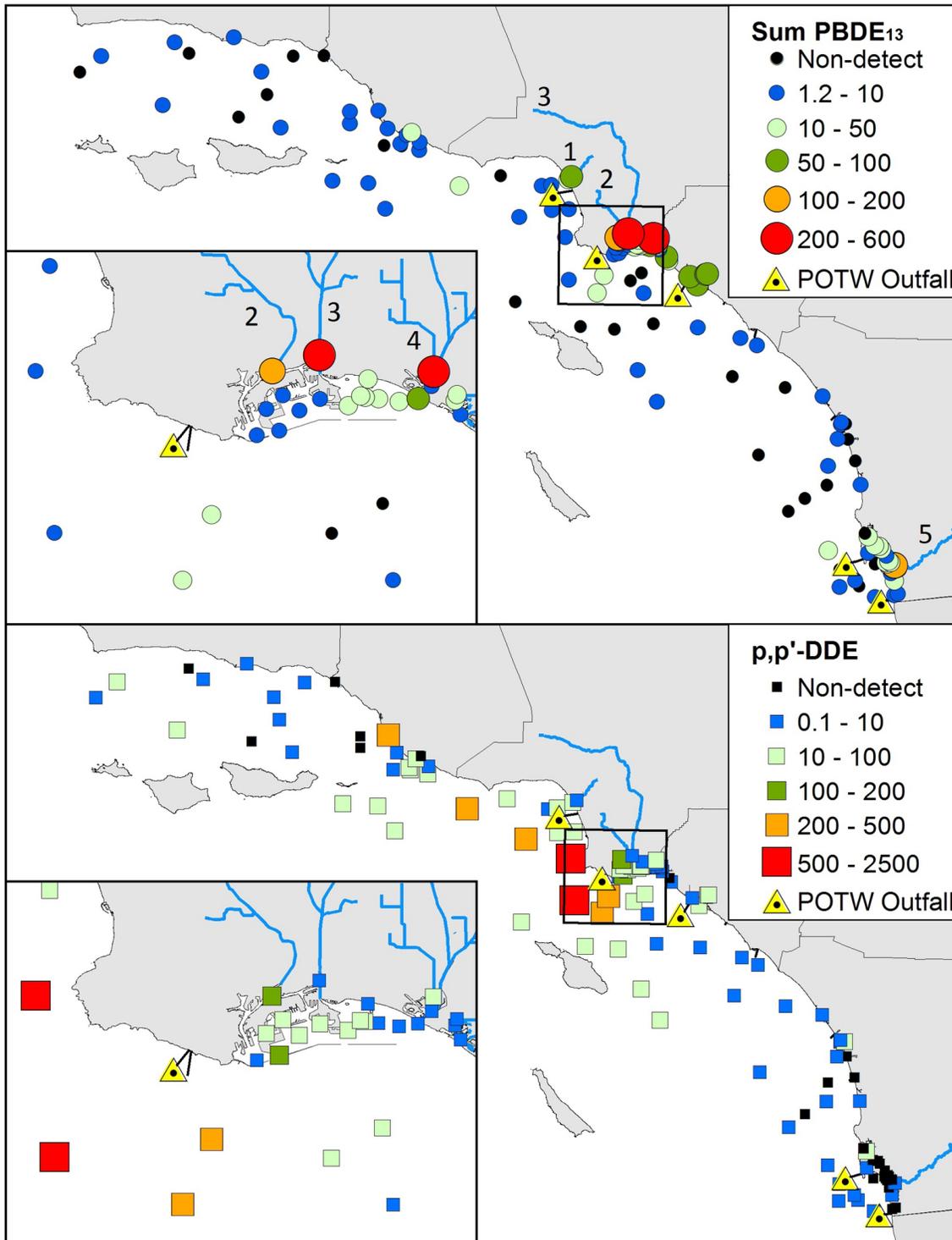
<b>Congener</b>	<b>No. Detects</b>	<b>Arithmetic Mean</b>	<b>Geometric Mean</b>	<b>Median</b>	<b>90<sup>th</sup> Percentile</b>	<b>Maximum</b>
BDE017	29	0.170	0.073	<0.1	0.2	4.9
BDE028	20	0.088	0.061	<0.1	0.1	1.3
BDE047	86	1.500	0.210	0.2	1.4	88.0
BDE066	19	0.090	0.062	<0.1	0.1	1.6
BDE085	38	0.280	0.094	<0.1	0.8	4.5
BDE099	68	0.980	0.180	0.1	1.6	34.0
BDE100	40	0.240	0.088	<0.1	0.3	6.3
BDE138	14	0.130	0.063	<0.1	0.1	4.1
BDE153	31	0.200	0.080	<0.1	0.3	4.7
BDE154	37	0.180	0.080	<0.1	0.3	4.0
BDE183	27	0.120	0.072	<0.1	0.2	1.7
BDE190	31	0.100	0.071	<0.1	0.2	1.0
BDE209	49	16.000	2.100	<1.0	37.0	460.0
ΣPBDE <sub>13</sub>	92	20.000	4.700	2.7	42.0	560.0



**Figure 1. Spatial distribution of four PBDE congeners representative of the three technical mixtures. BDE-47 and BDE-99 represent the penta-BDE mixture, BDE-183 represents the octa-BDE mixture, and BDE-209 represents the deca-BDE mixture. Circle size shows the total concentration of the four congeners. The proportion of each congener is shown within the circles; proportions <1% are not shown.**

**Table 2. Estimates of the area weighted geometric mean concentrations (AWGM), mass of each congener in each stratum, and percent of total PBDE<sub>13</sub> mass in each stratum. The 95% lower confidence bounds and upper confidence bounds are given in parenthesis. There were 61 embayment sites and 60 offshore sites. Offshore BDE-183 was not detected at sufficient frequency to estimate summary statistics.**

<b>Congener</b>	<b>Stratum</b>	<b>No. Detects</b>	<b>AWGM (ng/g dw)</b>	<b>Mass (kg)</b>	<b>Percent Mass</b>
BDE-47	Embayments	54	0.25 (0.20, 0.32)	2.4 (1.9, 3.0)	2.2
	Offshore	32	0.12 (0.092, 0.15)	51 (40, 65)	5.9
BDE-99	Embayments	50	0.24 (0.18, 0.33)	2.3 (1.7, 3.2)	2.1
	Offshore	18	0.098 (0.074, 0.13)	42 (32, 55)	4.9
BDE-183	Embayments	24	0.086 (0.071, 0.10)	0.82 (0.69, 0.99)	0.74
	Offshore	3	NA	NA	NA
BDE-209	Embayments	36	7.9 (5.1, 12)	76 (49, 120)	68
	Offshore	13	0.90 (0.69, 1.2)	390 (300, 510)	45
ΣPBDE <sub>13</sub>	Embayments	56	12 (8.0, 17)	110 (77, 160)	
	Offshore	36	2.0 (1.6, 2.5)	860 (700, 1100)	



**Figure 2. The spatial distribution of total PBDE<sub>13</sub> and p,p'-DDE relative to urban rivers and marine outfalls of four major publically owned treatment works (POTWs). The five highest total PBDE concentrations occurred at the mouths of five urban rivers: 1) Ballona Creek, 2) Dominguez Channel, 3) Los Angeles River, 4) Los Cerritos Channel, and 5) Sweetwater River. The highest p,p'-DDE concentrations occurred near the POTW outfall off the Palos Verdes Peninsula.**

# Distribution and sources of polybrominated diphenyl ethers in the southern California Bight

## SUPPLEMENTAL INFORMATION

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Table SI-1: Surrogate standards, internal standard, and target PBDE congeners.

Table SI-2: PBDE<sub>13</sub> and PBDE<sub>minor</sub> concentrations (ng/g dw) measured in the SCB.

Figure SI-1: Detailed map of the southern California Bight and total PBDE concentrations (sum of all 52 congeners)

Table SI-1. Surrogate standards, internal standard, and target PBDE<sub>13</sub> congeners. BDE-71 was in the external calibration solution, but co-eluted with BDE-49 so is classified as PBDE<sub>minor</sub>. The quantification and confirmation ions for PBDE<sub>minor</sub> congeners (shown on Table SI-2) were *m/z* 79 and 81, respectively.

Analyte	CAS Number	Quantification Ion	Confirmation Ion
Internal Standard			
4'-Fluoro-2,3',4,6-tetrabromodiphenyl ether (PBDE-69)	NA	79	81
Polybrominated biphenyl-209 ( <sup>13</sup> C <sub>12</sub> )	NA	79	81
Surrogate Standards			
4'-Fluoro-2,3,3',4,5,6-hexabromodiphenyl ether (PBDE-160)	NA	79	81
Polybrominated diphenyl ether-209 ( <sup>13</sup> C <sub>12</sub> )	NA	494	492
Thirteen PBDE Congeners in External Calibration Solutions (PBDE <sub>13</sub> )			
BDE 17 (2,2',4-TriBDE)	147217-75-2	79	81
BDE 28 (2,4,4'-TriBDE)	41318-75-6	79	81
BDE 47 (2,2',4,4'-TetraBDE)	5436-43-1	79	81
BDE 66 (2,3',4,4'-TetraBDE)	189084-61-5	79	81
BDE 85 (2,2',3,4,4'-PentaBDE)	182346-21-0	79	81
BDE 99 (2,2',4,4',5-PentaBDE)	60348-60-9	79	81
BDE 100 (2,2',4,4',6-PentaBDE)	189084-64-8	79	81
BDE 138 (2,2',3,4,4',5'-HexaBDE)	182677-30-1	79	81
BDE 153 (2,2',4,4',5,5'-HexaBDE)	68631-49-2	79	81
BDE 154 (2,2',4,4',5,6'-HexaBDE)	207122-15-4	79	81
BDE 183 (2,2',3,4,4',5',6-HeptaBDE)	207122-16-5	79	81
BDE 190 (2,3,3',4,4',5,6-HeptaBDE)	68928-80-3	79	81
BDE 209 Decabromobiphenyl Ether	1163-19-5	486	488

Table SI-2. PBDE<sub>13</sub> and PBDE<sub>minor</sub> concentrations (ng/g dw) measured in the SCB. There is less certainty in the identity and concentration of the PBDE<sub>minor</sub> congeners. Detects is the number of sites (out of 121) at which the congener was detected. The minimum measured concentration for all congeners was non-detect. ΣPBDE is the sum of the 52 congeners. BDE-49 and BDE-71 co-eluted. It is suspected that an unknown compound interfered with the measurement of BDE-116 and lead to a false positive identification.

Congener	Category	No. detects	Arithmetic Mean	Geometric Mean	Median	90 <sup>th</sup> Percentile	Maximum
BDE001	PBDE <sub>minor</sub>	0	NA	NA	<0.1	<0.1	<0.1
BDE002	PBDE <sub>minor</sub>	4	0.052	0.051	<0.1	<0.1	0.20
BDE003	PBDE <sub>minor</sub>	0	0.050	NA	<0.1	<0.1	<0.1
BDE007	PBDE <sub>minor</sub>	9	0.056	0.053	<0.1	<0.1	0.30
BDE008	PBDE <sub>minor</sub>	2	0.053	0.051	<0.1	<0.1	0.40
BDE010	PBDE <sub>minor</sub>	0	NA	NA	<0.1	<0.1	<0.1
BDE011	PBDE <sub>minor</sub>	0	NA	NA	<0.1	<0.1	<0.1
BDE012	PBDE <sub>minor</sub>	9	0.060	0.055	<0.1	<0.1	0.40
BDE013	PBDE <sub>minor</sub>	9	0.060	0.055	<0.1	<0.1	0.40
BDE015	PBDE <sub>minor</sub>	6	0.10	0.055	<0.1	<0.1	5.5
BDE017	PBDE <sub>13</sub>	29	0.17	0.073	<0.1	0.2	4.9
BDE025	PBDE <sub>minor</sub>	2	0.053	0.051	<0.1	<0.1	0.40
BDE028	PBDE <sub>13</sub>	20	0.088	0.061	<0.1	0.1	1.3
BDE030	PBDE <sub>minor</sub>	11	0.10	0.058	<0.1	<0.1	4.9
BDE032	PBDE <sub>minor</sub>	15	0.056	0.054	<0.1	0.1	0.10
BDE033	PBDE <sub>minor</sub>	2	0.052	0.051	<0.1	<0.1	0.20
BDE035	PBDE <sub>minor</sub>	6	0.061	0.054	<0.1	<0.1	0.50
BDE037	PBDE <sub>minor</sub>	12	0.092	0.061	<0.1	<0.1	1.2
BDE047	PBDE <sub>13</sub>	86	1.5	0.21	0.2	1.4	88
BDE049/071	PBDE <sub>minor</sub>	35	0.25	0.083	<0.1	0.4	5.9
BDE066	PBDE <sub>13</sub>	19	0.090	0.062	<0.1	0.1	1.6
BDE075	PBDE <sub>minor</sub>	12	0.15	0.063	<0.1	<0.1	5.1
BDE077	PBDE <sub>minor</sub>	42	0.13	0.085	<0.1	0.4	0.60
BDE085	PBDE <sub>13</sub>	38	0.28	0.094	<0.1	0.8	4.5
BDE099	PBDE <sub>13</sub>	68	0.98	0.18	0.1	1.6	34
BDE100	PBDE <sub>13</sub>	40	0.24	0.088	<0.1	0.3	6.3
BDE116	PBDE <sub>minor</sub>	1	0.76	0.053	<0.1	<0.1	86
BDE118	PBDE <sub>minor</sub>	19	0.065	0.058	<0.1	0.1	0.50
BDE119	PBDE <sub>minor</sub>	6	0.20	0.055	<0.1	<0.1	17.4
BDE126	PBDE <sub>minor</sub>	0	NA	NA	<0.1	<0.1	<0.1
BDE138	PBDE <sub>13</sub>	14	0.13	0.063	<0.1	0.1	4.1
BDE153	PBDE <sub>13</sub>	31	0.20	0.080	<0.1	0.3	4.7
BDE154	PBDE <sub>13</sub>	37	0.18	0.080	<0.1	0.3	4.0
BDE155	PBDE <sub>minor</sub>	2	0.12	0.053	<0.1	<0.1	8.1

Congener	Category	No. detects	Arithmetic Mean	Geometric Mean	Median	90 <sup>th</sup> Percentile	Maximum
BDE166	PBDE <sub>minor</sub>	5	0.054	0.052	<0.1	<0.1	0.20
BDE181	PBDE <sub>minor</sub>	12	0.064	0.057	<0.1	<0.1	0.30
BDE183	PBDE <sub>13</sub>	27	0.12	0.072	<0.1	0.2	1.7
BDE190	PBDE <sub>13</sub>	31	0.10	0.071	<0.1	0.2	1.0
BDE194	PBDE <sub>minor</sub>	10	0.067	0.057	<0.1	<0.1	0.50
BDE195	PBDE <sub>minor</sub>	2	0.052	0.051	<0.1	<0.1	0.20
BDE196	PBDE <sub>minor</sub>	13	0.11	0.059	<0.1	0.1	5.4
BDE197	PBDE <sub>minor</sub>	12	0.063	0.056	<0.1	<0.1	0.50
BDE198	PBDE <sub>minor</sub>	15	0.078	0.058	<0.1	0.1	1.1
BDE201	PBDE <sub>minor</sub>	7	0.060	0.054	<0.1	<0.1	0.50
BDE202	PBDE <sub>minor</sub>	1	NA	NA	<0.1	<0.1	0.20
BDE204	PBDE <sub>minor</sub>	1	NA	NA	<0.1	<0.1	0.70
BDE205	PBDE <sub>minor</sub>	2	0.052	0.051	<0.1	<0.1	0.20
BDE206	PBDE <sub>minor</sub>	55	0.17	0.10	<0.1	0.3	2.5
BDE207	PBDE <sub>minor</sub>	40	0.15	0.083	<0.1	0.3	1.7
BDE208	PBDE <sub>minor</sub>	14	0.064	0.056	<0.1	0.1	0.50
BDE209	PBDE <sub>13</sub>	49	16	2.1	<1	37	460
ΣPBDE	all	117	24	8.7	5.0	44	560

Figure SI-1. Map of the southern California Bight and total PBDE concentrations (sum of all 52 congeners). Non-detects were set to zero.

