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Levels and Distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and Bivalves from the San Francisco Estuary

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Polybrominated diphenyl ethers (PBDEs) were found in water, surface sediments, and bivalve samples that were collected from the San Francisco Estuary in 2002. ΣPBDE concentrations in water samples ranged from 3 to 513 pg/L, with the highest concentrations found in the Lower South Bay (range 103−513 pg/L) region, which receives approximately 26% of the Estuary's wastewater treatment plant effluents. The ΣPBDEs in sediments ranged from below detection limits to 212 ng/g dry wt, with the highest concentration found at a South Bay station (212 ng/g dry wt), which was up to 3 orders of magnitude higher than other stations. The ΣPBDE concentrations ranged from 9 to 64 ng/g dry wt in oysters (*Crassostrea gigas*), from 13 to 47 ng/g dry wt in mussels (*Mytilus californianus*), and from 85 to 106 ng/g dry wt in clams (*Corbicula fluminea*). Only three PBDE congeners were detected in bivalves, BDE-47, BDE-99, and BDE-100; these are the most bioaccumulative congeners from the commercial Penta-BDE mixture.

Introduction

Separate studies recently conducted in the San Francisco Estuary have identified polybrominated diphenyl ethers (PBDEs) in harbor seals (*1*), in fish (*2*), and in local municipal wastewater treatment plant effluents (*3*). These data prompted further interest by the San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP) to determine PBDE occurrence in the Estuary ambient environment. California has the most stringent flame retardant standards in the United States; therefore, we hypothesized that their abundant use in consumer products would result in concomitant contamination in environmental and biological samples. The objective of this study was to determine PBDE concentrations in the Estuary water column, surface sediments, and bivalves (resident clams and transplanted oysters and mussels). Bivalves are a critical food source for fish and even humans and are an excellent sentinel species for determining contaminant bioavailability in the water column and for identifying potential hot spots of contamination and exposure.

PBDEs, which are composed of three commercial mixtures identified as Penta-BDE, Octa-BDE, and Deca-BDE, are used as flame retardants in manufactured products such as polymers, resins, electronic devices, building materials, textiles, and polyurethane foam padding used in furniture and carpets. The Penta-BDE mixture (e.g., Bromkal-70-5DE) is composed of the congeners BDE-47, -99, -100, -153, and -154. The Octa-BDE mixture contains several hexa- to nona-brominated congeners with BDE-183 as the major congener, while the Deca-BDE mixture is composed mostly of BDE-209 with some small amounts of nona-brominated congeners (*4*). Penta-BDE and Octa-BDE have been banned in Europe. California will phase out the use of Penta-BDE and Octa-BDE mixtures in 2006. In 2001, the market demand for PBDEs in North America was 33 100 t, which accounts for 49% of the world demand (*5*). Deca-BDE was the most commonly used commercial mixture (24 500 t) in North America followed by lesser amounts of Penta-BDE (7100 t) and Octa-BDE (1500 t).

Various studies have shown that PBDEs persist in the environment, bioaccumulate in marine biota, and biomagnify (*6*−*11*). PBDEs have been shown to induce neurotoxicity in mice (*4*). They can act as agonists of both estrogen Er^{α} and Er^{β} receptors and exhibit dioxin-like Ah-receptor-mediated induction of cytochrome P450 1A1 and 1A2 drug-metabolizing and carcinogen-activating enzymes (*12*). In North America, PBDE concentrations in the environment and in humans have doubled every 4−6 years (*13*).

In August 2003, California became the first state in the United States to ban the use of Penta-BDE and Octa-BDE, the two most mobile forms of commercially used PBDE mixtures. The law requires that these two PBDE mixtures be phased out of use in California by June 1, 2006. The Deca-BDE mixture was exempted from this ban; however, because it is photolytically and biologically debrominated to lower molecular weight congeners (*14*−*17*), its exemption does not entirely reduce concern over future PBDE occurrence (Deca-BDE and its debrominated products) in the San Francisco Estuary.

Experimental Methods

In 2002, the RMP began monitoring for PBDEs in water, surface sediments, and bivalve samples. The PBDE congeners (numbered according to IUPAC nomenclature used for PCBs) that were targeted for chemical analysis included BDE-17, -28, -33, -47, -66, -82, -85, -99, -100, -138, -153, -154, -166, -183, -190, -203, -204, -205, -206, -207, -208, and -209. The total PBDE (ΣPBDEs) concentrations in the three matrixes were calculated as the sum of these target analytes. Congener concentrations below their respective method detection limit (MDL) were assumed to be zero for the summation of ΣPBDEs in each sample.

Water Collection and Analysis. Water samples were collected during the dry season (July) of 2002 at 28 spatially randomized and 5 fixed or nonrandomly selected sampling stations located throughout the Estuary (Figure 1). The random sampling design applied for water and surface sediments is based on the Generalized Random Tessellation Stratified design (GRTS) used by the U. S. EPA's Environ-

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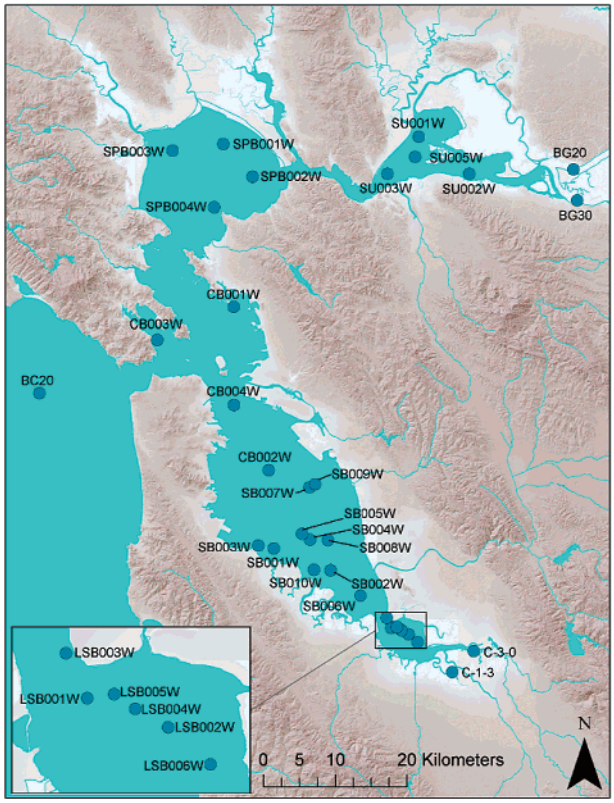

FIGURE 1. Map of San Francisco Estuary water sampling stations.

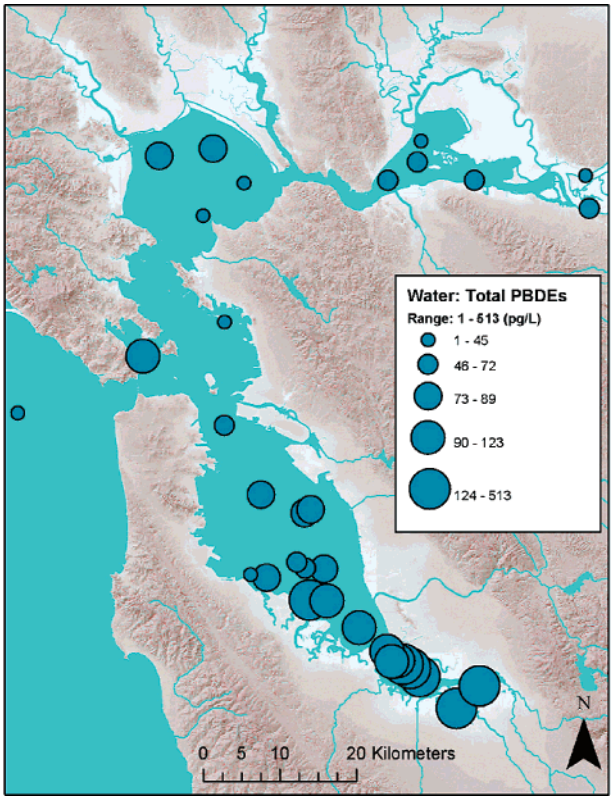

FIGURE 2. Bubble-map showing distribution of total PBDEs (pg/L) in San Francisco Estuary water sampling stations.

mental Monitoring and Assessment Program (EMAP). This design is appropriate for determining status and trends as it provides a spatially balanced random sample of the Estuary with increased resolution over time. After arriving at a sampling station, the vessel was anchored, and the engine was turned off. Whole water was sampled at approximately 1 m below the water surface through Teflon tubing that was attached to an aluminum pole oriented upcurrent from the vessel and upwind from equipment and personnel by pumping through a customized AXYS Infiltrex sampler (AXYS Environmental Systems, Ltd., Sidney, BC). Water was pulled first through a glass fiber filter (1.0 μm nominal pore size) to obtain a separate particulate fraction and then through two XAD-2 resin-filled Teflon columns mounted in parallel to obtain the dissolved fraction. Samples collected were approximately 100 L pulled at a flow rate of approximately 1.5 L/min. Caution was taken to minimize contamination at all levels of sample collection and handling. Samples were shipped to the laboratory on ice; filters were stored frozen, and XAD columns were maintained at 2−4 °C until analysis. Water quality measurements such as total suspended solids (TSS), temperature, conductivity, and salinity were also collected; this monitoring information is available from the RMP (*18*).

Prior to extraction, each sample was spiked with an aliquot of a ^{13}C-labeled PCB surrogate standard solution. XAD-2 resin and glass fiber filters were each extracted, fractionated on Florisil, further cleaned up by silica and alumina chromatography, and then reduced in volume. Independent analyses have shown that PCBs and PBDEs are collected in the same fraction of this analysis procedure. At this point, due to limited funding, the cleaned XAD-2 resin and glass fiber filter fractions from each individual sampling station were combined into a single composite sample, except for three stations (BC20, BG20, and C-3-0), which were kept separate to examine PBDE distribution between the dissolved (XAD-2 resin associated) and particulate (glass fiber filter associated) phases. The PCB fractions were spiked with ^{13}C-labeled PBDE internal standard and concentrated by evaporation under purified nitrogen to final volumes of 50 μL for analysis by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS).

Just prior to analysis, an aliquot (2 μL) of recovery standard solution containing additional ^{13}C-labeled analogues of PCBs was added to the autosampler vial. A 2 μL splitless injection was then analyzed on a Micromass Ultima mass spectrometer equipped with a Hewlett-Packard 6890 gas chromatograph and operating in the selected ion monitoring mode. Two masses from the molecular ion cluster were used to monitor each of the target analytes and ^{13}C-labeled internal standards. The GC was equipped with a fused silica capillary column coated with a DB-5HT capillary column (30 m, 0.25 mm i.d., 0.1 μm film thickness). The temperature program of the GC oven was as follows: held isothermal at 100 °C for 3 min, increased to 320 °C at 5 °C/min, and held isothermal at 320 °C for 5 min. Helium was used as the carrier gas.

Quantification of the suite of PBDEs in the samples was determined by the internal standard method, quantifying against the ^{13}C-labeled PBDEs that were added to the sample. The MDLs for the individual PBDE congeners in water ranged from 20 to 200 pg/L. Quantification was carried out using Micromass software. Recoveries of the ^{13}C-labeled PCB surrogates were monitored in a separate PCB analysis and used as general indicators of recovery through the analytical process.

Sediment Collection and Analysis. Sediments were collected during the dry season (July) of 2002 at 40 spatially randomized and 8 fixed sampling stations located throughout the Estuary (Figure 3). Sediments were collected using a modified Van Veen grab with a surface area of 0.1 m^2. The grab was made of stainless steel, and the jaws and doors were coated with Dykon to improve chemical inertness. All scoops, buckets, and stirrers used to collect and composite sediments were constructed of Teflon or stainless steel coated with Dykon. When the sampler was on deck, the top 5 cm

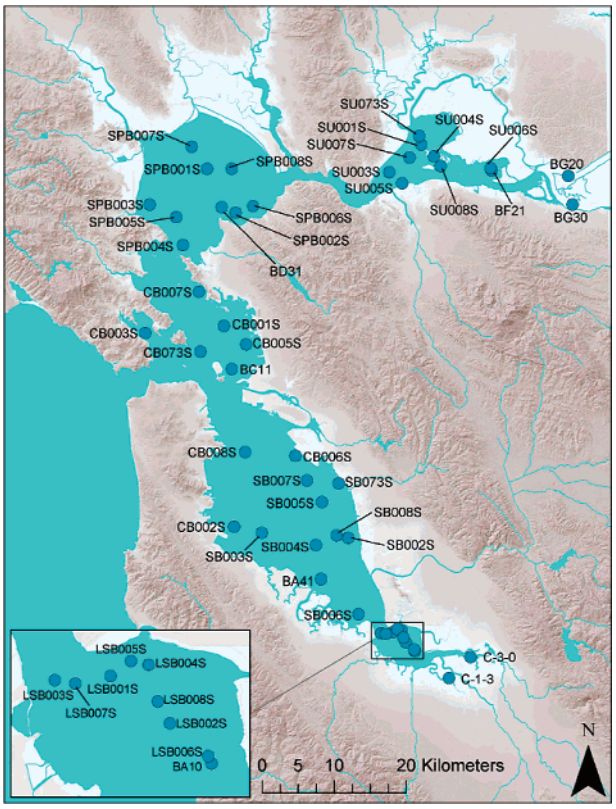

FIGURE 3. Map of San Francisco Estuary sediment sampling stations.

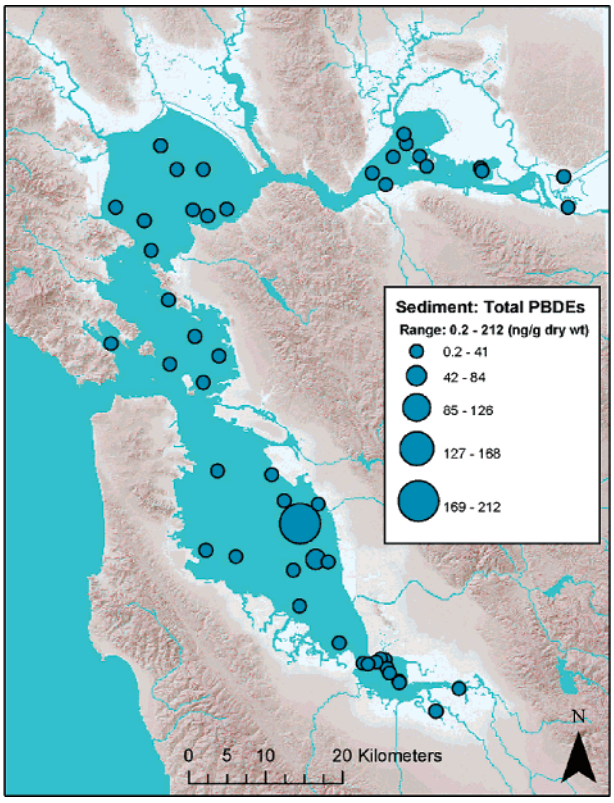

FIGURE 4. Bubble-map showing distribution of total PBDEs (ng/g dry wt) in San Francisco Estuary sediment sampling stations.

of sediment was scooped from each of two replicate grabs and homogenized in a bucket to provide a single composite sample for each station. Homogenized samples were placed into precleaned 250 mL wide mouth jars with Teflon-lined lids and stored in a cooler (4 °C) until shipment to the laboratory. At the laboratory any standing water in the samples was drained and discarded. The sample was then homogenized and a 20 g subsample was weighed for extraction. A surrogate recovery standard containing 2,2′,4,5′,6-pentachlorobiphenyl and 2,2′,3,3′,4,5,5′,6-octachlorobiphenyl was added to the subsample, which was then mixed with pelletized diatomaceous earth until a dry, free-flowing mixture was obtained. This mixture was placed into a Dionex Accelerated Solvent Extraction (ASE) System and extracted with dichloromethane (DCM) at 100 °C and 2000 psi for 30 min (EPA Method 3545). The sample extracts were dried with granular Na_2SO_4 and a Labconco Rapid Vap was used to reduce the extract volume to approximately 3 mL in DCM. Extracts were cleaned up with an alumina/copper column and then concentrated to a final extract volume of 1 mL in DCM.

A 5 μL splitless injection was then analyzed on a PerkinElmer Clarus 500 GC−MS, which was operated in the electron impact mode using selected ion monitoring (SIM). Two masses from the molecular ion cluster were used to monitor each of the target analytes and the surrogate standards. The mass scan was incremented over the run period to encompass scan ranges of 100−495 and 461−801 toward the end of the run. The GC was equipped with a DB5-MS fused silica capillary column (15 m length, 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific). The GC temperature program was as follows: held isothermal at 80 °C for 2 min, increased to 200 °C at 40 °C/min, increased to 325 °C at 10 °C/min, and held isothermal at 325 °C for 5 min. Helium was used as the carrier gas. Internal standard quantification was used to calculate all concentrations. The MDLs for the individual PBDE congeners in the sediments ranged from 0.1 to 1.5 ng/g dry wt.

Bivalve Collection and Analysis. Oysters (*Crassostrea gigas*) and mussels (*Mytilus californianus*) were initially collected from uncontaminated "background stations", which are located outside of the Estuary, and deployed in cages during the dry season (July−September) of 2002 at fixed sampling stations located throughout the Estuary (Figure 5). Mussels were collected from Bodega Head and Tomales Bay, which are coastal areas north of the Estuary, and deployed at 7 fixed (nonrandomly selected) stations. Oysters were collected from Tomales Bay and deployed at 5 fixed stations. Clams (*Corbicula fluminea*), which are resident species of the Estuary, were collected at 2 sampling stations. The total number of mussels and oysters deployed in cages at each station was 80, while resident clams were not deployed because they were dredged directly from sediments. The deployment duration was 90 days with a maintenance check occurring midway through the deployment. For the retrieval, once divers returned bivalves to the surface they were then observed for mortality. Dead bivalves were counted, recorded, and removed from the sample. The live samples allocated to organics analysis were wrapped in aluminum foil, placed in pre-labeled Ziploc bags, and stored in a cooler on dry ice for transport to the laboratory. The percent survival of retrieved bivalves was >95%, except for Davis Point and Napa River, which were 25% and 29%, respectively, due to high predation at those stations.

At the laboratory, the bivalves were rinsed with reagent grade water to remove extraneous material and shucked using a stainless steel knife into appropriate pre-cleaned homogenizing containers. The tissue was then homogenized using a Büchi B-400 homogenizer. A 1−5 g (tissue homogenate) sample was dried in a 70 °C oven for 48 h to determine moisture content. A 10 g sample was mixed with approximately 7 g of pre-extracted Hydromatrix until the mixture was free flowing. A surrogate recovery standard solution containing BDE-77 was added to the mixture in the extraction cell. The mixture was extracted using U.S. EPA

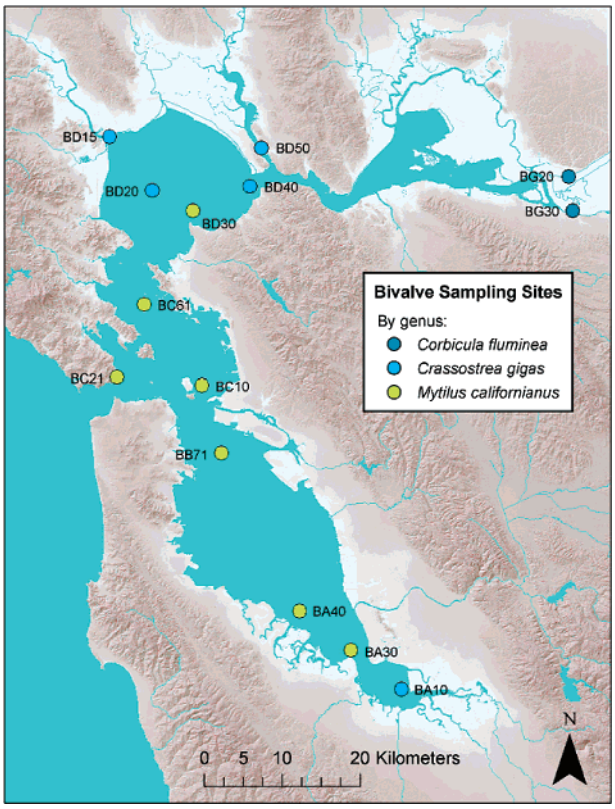

FIGURE 5. Map of San Francisco Estuary bivalve sampling stations. Twelve stations had transplanted bivalves (*Crassostrea gigas and Mytilus californianus*) deployed on submerged moorings for 3 months, and two stations were trawled for resident bivalves (*Corbicula fluminea*).

Method 3545 (Pressurized Fluid Extraction) with acetone: DCM (1:1) using heat (100 °C) and pressure (1500 psi). The samples were extracted a second time using the same conditions. The extracts were combined, evaporated to approximately 0.5 mL, and diluted to 10 mL with DCM. A 2 mL aliquot of the extract was removed for lipid determination. The remainder of the extract was cleaned up using gel permeation chromatography (70 g Bio-Beads SX-3 in 100% DCM) and fractionated using Florisil. The extract final volume was 2 mL in isooctane.

A 3 μL splitless injection was analyzed on a Hewlett-Packard 6890*plus* GC equipped with two ^{63}Ni micro-electron capture detectors and two fused silica capillary columns (DB-5 and DB-17MS, 60 m length, 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific). The temperature program of the GC oven was as follows: initial temperature 70 °C, increased to 210 °C at a rate of 15 °C/min, held isothermal for 10 min, increased to 280 °C at rate of 2 °C/min, and held isothermal for 11 min. Helium was used as the carrier gas, and nitrogen was used for the detector makeup at 30 mL/min. External standard quantification was used, and all analyte concentrations were adjusted for surrogate standard recoveries. The MDLs for PBDEs in tissues ranged from 1.4 to 2.8 ng/g dry wt.

Quality Assurance. Quality assurance followed the protocol outlined in the RMP's Quality Assurance Project Plan (*19*). For all matrices, cleaned sample extracts and blanks were spiked with surrogate recovery standards prior to solvent extraction to monitor methodological analyte losses. Recoveries between 50 and 120% were accepted. Concentrations of analytes in sediment and tissue were corrected for surrogate recoveries, while concentrations of analytes in water samples were not surrogate recovery corrected. Calibration curves using PBDE standard solutions (Cambridge Isotope Laboratories, Inc.) were generated at concentration ranges that were expected in each of the sample matrices. Laboratory fortified sediment and tissue matrix spikes were analyzed to evaluate the effects of the sample matrix on the recovery of the target analytes. Matrix spike recoveries within ±50% were accepted. To evaluate the precision of the sediment and tissue analysis, replicates of spiked matrix and field samples were analyzed. For sediment samples relative standard deviations (RSDs) of <35% were accepted, while for tissue samples RSDs of <20% were accepted. Laboratory check solutions were analyzed daily and with every batch of samples to confirm instrument accuracy and precision. Certified reference materials (CRMs) for PBDEs were not used since these are currently not available.

Results and Discussion

Water. The ΣPBDE concentrations in San Francisco Estuary water column samples ranged from 3 to 513 pg/L (Table 1), and their spatial distribution is shown in Figure 2. The highest ΣPBDE levels were concentrated around the Lower South Bay (range 103−513 pg/L) region of the Estuary. This region of the Estuary receives approximately 26% of the Estuary's total publicly owned treatment works (POTW) wastewater effluents and only 10% of the Estuary's freshwater inflow (*20*). It also has a shallow water depth, is surrounded on three sides by urban area, is minimally flushed by tides, and receives significant quantities of urban runoff. For the individual stations, ΣPBDE concentrations were highest at a Lower South Bay station (513 pg/L, LSB006W) with the next highest concentrations found at Sunnyvale (293 pg/L, C-1-3) and San Jose (238 pg/L, C-3-0). The ΣPBDE concentrations were generally lower in the South Bay segment (range 42−124 pg/L), which may be due to dilution as water is transported north toward the South Bay.

Lower ΣPBDE levels were found in the northern reach of the Estuary at the Sacramento River and San Joaquin River stations (range 3−43 pg/L), with the Sacramento River (3 pg/L, BG20) station showing the lowest ΣPBDE concentration. The lower levels of PBDEs at the River stations could be due to their location in a non-urbanized area of the Estuary since the urbanized portions of watersheds surrounding the Estuary have been shown to have sediment median contaminant concentrations (e.g., PCBs) that are over 100 times higher than non-urbanized areas (*21*). The northern reach also receives up to 90% of the Estuary's freshwater inflow (*20*), so the ΣPBDE concentrations at the river stations may be low due to dilution and short residence time.

The most abundant PBDE congeners in the water samples were BDE-47, BDE-99, and BDE-209 (Table 1). BDE-47 and BDE-99, along with BDE-100, BDE-153, and BDE-154, which were also detected in the samples, are major congeners of the Penta-BDE mixture, while BDE-209 is the predominant congener of the Deca-BDE mixture. The Penta-BDE mixture is most abundant at the Lower South Bay (LSB006W) and Sunnyvale (C-1-3) stations, while the Deca-BDE mixture was most abundant in a Lower South Bay (LSB006W) station. BDE-183, the predominant congener from the Octa-BDE mixture, was most abundant at the Sunnyvale (C-1-3) station and was also present in Lower South Bay water samples.

To determine the relative severity of PBDE contamination in the San Francisco Estuary water column, comparisons were made against other studies where water column PBDE concentrations have been measured. For example, the ΣPBDE (sum of BDE-47, -99, -153, and -209) concentrations in water samples collected from the Scheldt Estuary and the North Sea along the Dutch Coast (The Netherlands) ranged from 0.1 to 5.6 pg/L, with the highest concentration found in the Scheldt Estuary (*22*). The ΣPBDE (sum of BDE-47, -99, -100, -153, -154, and -183) concentrations in Lake Michigan water column samples were reported to have increased from an

TABLE 1. PBDE Concentrations (pg/L or ppq) in Water[a]

site code	station	ΣPBDEs	BDE-17	BDE-28/33	BDE-47	BDE-66	BDE-85	BDE-99	BDE-100	BDE-138/166	BDE-153	BDE-154	BDE-183	BDE-190	BDE-206	BDE-207	BDE-208	BDE-209	ΣPCBs/ΣPBDEs
BC20	Golden Gate	0.2	0.2	Q	Q	Q	Q	Q	Q	bdl	Q	Q	Q	bdl	Q	Q	Q	Q	240
BG20	Sacramento River	2.9	1.4	1.5	Q	Q	Q	Q	Q	Q	Q	Q	Q	bdl	Q	Q	Q	Q	31
BG30	San Joaquin River	43.1	2.2	2.1	37.4	1.4	Q	Q	Q	bdl	Q	Q	Q	bdl	Q	Q	Q	Q	5
SU001W	Suisun Bay	37.2	2.6	2.3	30.7	1.3	Q	Q	Q	0.3	Q	Q	Q	bdl	Q	Q	Q	Q	4
SU002W	Suisun Bay	62.6	3.0	2.7	45.4	1.8	Q	Q	9.4	0.4	Q	Q	Q	bdl	Q	Q	Q	Q	2
SU003W	Suisun Bay	60.4	2.8	3.2	42.9	2.5	Q	Q	9.0	bdl	Q	Q	Q	bdl	Q	Q	Q	Q	3
SU005W	Suisun Bay	59.8	2.7	3.0	43.1	1.4	Q	Q	9.2	0.4	Q	Q	Q	bdl	Q	Q	Q	Q	3
SPB001W	San Pablo Bay	86.0	3.7	2.2	35.9	1.6	1.9	Q	9.9	0.5	Q	Q	Q	0.3	9.3	13.5	7.1	Q	9
SPB002W	San Pablo Bay	45.4	3.3	2.6	38.2	1.3	Q	Q	Q	bdl	Q	Q	Q	bdl	Q	Q	Q	Q	3
SPB003W	San Pablo Bay	88.4	6.4	3.7	62.3	2.3	Q	Q	13.1	0.5	Q	Q	Q	bdl	Q	Q	Q	Q	12
SPB004W	San Pablo Bay	38.3	2.4	1.5	32.6	1.2	Q	Q	Q	0.2	Q	Q	Q	0.3	Q	Q	Q	Q	12
CB001W	Central Bay	3.9	2.5	1.1	Q	Q	Q	Q	Q	0.2	Q	Q	Q	bdl	Q	Q	Q	Q	158
CB002W	Central Bay	77.8	5.8	2.6	56.2	1.9	Q	Q	10.5	0.8	Q	Q	Q	bdl	Q	Q	Q	Q	10
CB003W	Central Bay	109.2	1.4	1.0	24.8	0.9	1.2	35.6	6.7	0.4	4.3	3.4	2.1	bdl	bdl	0.8	bdl	26.6	4
CB004W	Central Bay	71.8	2.2	0.9	20.6	0.9	0.8	24.0	4.8	0.2	2.9	2.3	Q	bdl	bdl	bdl	bdl	12.2	5
SB001W	South Bay	75.3	2.3	1.1	16.1	0.8	0.4	11.7	2.7	0.5	Q	1.3	0.8	bdl	bdl	0.9	bdl	36.8	9
SB002W	South Bay	99.3	5.8	2.0	24.4	Q	Q	17.5	4.4	bdl	2.3	2.0	Q	bdl	bdl	bdl	bdl	40.9	4
SB003W	South Bay	42.4	2.6	Q	19.3	Q	Q	15.3	3.6	Q	Q	1.6	Q	bdl	bdl	bdl	bdl	bdl	9
SB004W	South Bay	62.8	3.3	1.2	17.7	Q	Q	12.5	3.1	bdl	Q	1.4	Q	bdl	bdl	bdl	bdl	23.6	5
SB005W	South Bay	58.3	3.1	Q	17.7	Q	Q	14.5	3.2	bdl	Q	1.5	Q	bdl	bdl	1.6	bdl	16.7	13
SB006W	South Bay	123.4	5.7	1.8	18.9	Q	Q	13.1	3.2	Q	Q	1.2	Q	bdl	1.7	2.4	1.3	74.1	3
SB007W	South Bay	89.0	3.8	1.6	30.8	Q	Q	25.1	5.9	bdl	2.2	2.0	Q	bdl	0.7	1.1	bdl	15.7	6
SB008W	South Bay	85.1	4.0	1.4	24.4	Q	Q	23.3	5.2	bdl	2.6	2.1	Q	bdl	1.0	1.1	0.7	19.3	9
SB009W	South Bay	83.9	3.4	1.3	25.4	Q	Q	21.2	4.9	bdl	2.2	1.8	Q	bdl	0.8	1.1	0.8	21.1	6
SB010W	South Bay	124.1	5.2	2.0	30.5	Q	Q	25.1	6.1	bdl	2.6	2.2	Q	bdl	2.1	1.7	1.3	45.3	8
LSB001W	Lower South Bay	102.7	5.7	1.8	28.0	1.3	0.7	23.5	5.3	0.5	3.2	2.7	1.0	bdl	0.8	1.9	1.1	25.1	15
LSB002W	Lower South Bay	221.0	12.7	4.2	51.8	2.9	0.9	35.6	8.1	0.5	4.5	3.9	1.5	bdl	2.1	3.0	1.7	87.8	6
LSB003W	Lower South Bay	118.9	9.2	3.0	34.3	1.4	0.6	23.8	5.7	bdl	2.3	2.9	1.6	bdl	0.6	1.7	1.2	30.7	8
LSB004W	Lower South Bay	159.5	8.6	3.0	36.6	1.9	0.7	27.3	6.3	0.3	3.4	3.3	1.3	0.6	2.1	4.1	2.2	57.9	10
LSB005W	Lower South Bay	122.6	6.0	2.2	30.4	1.2	0.7	22.3	5.0	0.5	2.8	2.7	1.1	0.4	1.1	bdl	1.0	45.2	7
LSB006W	Lower South Bay	512.9	26.7	10.3	123.0	5.8	2.3	90.7	20.7	1.4	10.3	9.3	3.5	0.5	5.1	7.5	4.9	191.0	3
C-1-3	Sunnyvale	292.9	36.5	13.4	103.0	4.1	2.0	62.7	15.1	1.2	9.0	7.1	26.9	1.1	Q	10.8	Q	Q	9
C-3-0	San Jose	238.3	32.1	17.4	179.5	7.9	Q	Q	Q	1.0	Q	Q	Q	0.4	Q	Q	Q	Q	17

[a] ΣPBDEs is sum of the target parameters. BDE congeners that coelute include 28 with 33 and 138 with 166. Abbreviations: bdl, below detection limit; Q, outside QA limits, detected but not reportable. For data analysis, bdl = zero. BC20 Golden Gate is the background site located 2 mi offshore.

average of 31 pg/L in 1997 to 158 pg/L in 1999 (*23*). In comparison, the San Francisco Estuary ΣPBDE concentrations (range 3−513 pg/L) are much higher than those found in European estuarine waters, but are similar to those found in Lake Michigan.

It has been previously reported that PBDEs have a relatively high affinity for lipids (log K_{ow} 5−10) and particles (*24*, *25*). Therefore, the ΣPBDE distribution between the collected dissolved (XAD-2 resin associated) and particulate (glass fiber filter associated) fractions, which were kept separate for three water sampling stations (Golden Gate, Sacramento River, and San Jose) in this study, was examined to determine the relative abundances (%) of the ΣPBDE concentrations in each of the fractions. The results show that ΣPBDEs were predominantly partitioned into the filterable suspended particulate matter fraction (Golden Gate = 93%, San Jose = 87%, and Sacramento River = 78%). To determine if the observed ΣPBDE partitioning with particulate matter applied to the entire Estuary water column, total suspended solids (TSS) and ΣPBDE concentrations were examined using linear regression analysis. Results showed that there was a significant positive relationship ($r^2 = 0.38$, $p < 0.0005$, $n = 33$) between TSS and ΣPBDE concentrations in the Estuary. Hence, TSS in the water column represents an important substrate for transporting PBDEs among Estuary segments and biota (e.g., suspended particles can be ingested and filtered by biota).

To determine if ΣPBDE concentrations in Estuary water samples are present at levels similar to those of ΣPCBs, the ΣPCBs/ΣPBDEs ratio was calculated (Table 1). The results show that the ΣPCB concentrations were higher than ΣPBDEs for samples collected within the Estuary (ratio range 2−158). The lowest ratios (2−4) within the Estuary were found in Suisun Bay, which also had the lowest ΣPCB concentrations in the Estuary. The highest ΣPCBs/ΣPBDEs ratio was found in the open ocean background station (240, Golden Gate, BC20), which is located 2 mi offshore, followed by a Central Bay station (158, CB001W), which is heavily influenced by saltwater inflow through the Golden Gate Bridge. The ΣPBDE and ΣPCB concentrations at the Golden Gate station are both very low. The ΣPCB concentration (48 pg/L) at Golden Gate is similar to those reported in surface seawater from open oceans and seas; for example, a maximum of 63 pg/L was found in the North Pacific (*26*), while the ΣPBDE concentration is 1−3 orders of magnitude lower than Estuary stations. This suggests that proximity to potential sources of input (e.g., wastewater treatment plant discharges, stormwater runoff, and urban area atmospheric deposition) is an important factor that could influence water column contaminant concentrations within the Estuary boundary.

Sediments. ΣPBDE concentrations in San Francisco Estuary sediment samples ranged from below detection limits (bdl) to 212 ng/g dry wt (Table 2), and their spatial distribution is shown in Figure 4. The highest ΣPBDE concentration was

TABLE 2. PBDE Concentrations (ng/g dry wt or ppb) in Sediments[a]

site code	station	ΣPBDEs	BDE-47	BDE-99	BDE-183	BDE-204	BDE-205
BG20	Sacramento River	1.5	1.1	0.3	bdl	bdl	bdl
BG30	San Joaquin River	1.0	bdl	1.0	bdl	bdl	bdl
BF21	Grizzly Bay	1.6	bdl	1.6	bdl	bdl	bdl
SU001S	Suisun Bay	6.1	4.4	1.7	bdl	bdl	bdl
SU003S	Suisun Bay	0.2	bdl	0.2	bdl	bdl	bdl
SU004S	Suisun Bay	12.1	8.2	3.9	bdl	bdl	bdl
SU005S	Suisun Bay	9.7	9.7	bdl	bdl	bdl	bdl
SU006S	Suisun Bay	2.0	bdl	2.0	bdl	bdl	bdl
SU007S	Suisun Bay	2.1	bdl	2.1	bdl	bdl	bdl
SU008S	Suisun Bay	4.3	bdl	4.3	bdl	bdl	bdl
SU073S	Suisun Bay	3.7	2.5	1.2	bdl	bdl	bdl
BD31	Pinole Point	3.3	bdl	3.3	bdl	bdl	bdl
SPB001S	San Pablo Bay	0.6	bdl	0.6	bdl	bdl	bdl
SPB002S	San Pablo Bay	0.7	bdl	0.7	bdl	bdl	bdl
SPB003S	San Pablo Bay	4.2	2.7	1.5	bdl	bdl	bdl
SPB004S	San Pablo Bay	2.7	2.0	0.7	bdl	bdl	bdl
SPB005S	San Pablo Bay	2.5	1.8	0.6	0.2	bdl	bdl
SPB006S	San Pablo Bay	1.0	bdl	1.0	bdl	bdl	bdl
SPB007S	San Pablo Bay	1.5	1.5	bdl	bdl	bdl	bdl
SPB008S	San Pablo Bay	0.7	bdl	0.7	bdl	bdl	bdl
BC11	Yerba Buena Island	16.3	9.2	5.0	bdl	2.1	bdl
CB001S	Central Bay	2.8	1.9	0.9	bdl	bdl	bdl
CB002S	Central Bay	2.8	bdl	2.8	bdl	bdl	bdl
CB003S	Central Bay	bdl	bdl	bdl	bdl	bdl	bdl
CB005S	Central Bay	0.8	bdl	0.8	bdl	bdl	bdl
CB006S	Central Bay	5.4	3.2	2.2	bdl	bdl	bdl
CB007S	Central Bay	20.2	13.2	7.0	bdl	bdl	bdl
CB008S	Central Bay	1.0	bdl	1.0	bdl	bdl	bdl
CB073S	Central Bay	2.4	bdl	2.4	bdl	bdl	bdl
BA41	Redwood Creek	bdl	bdl	bdl	bdl	bdl	bdl
SB002S	South Bay	bdl	bdl	bdl	bdl	bdl	bdl
SB003S	South Bay	0.6	bdl	0.6	bdl	bdl	bdl
SB004S	South Bay	bdl	bdl	bdl	bdl	bdl	bdl
SB005S	South Bay	211.8	100.0	71.0	bdl	19.0	21.8
SB006S	South Bay	1.4	bdl	1.4	bdl	bdl	bdl
SB007S	South Bay	2.9	2.0	0.8	bdl	bdl	bdl
SB008S	South Bay	68.5	41.0	27.5	bdl	bdl	bdl
SB073S	South Bay	bdl	bdl	bdl	bdl	bdl	bdl
LSB001S	Lower South Bay	bdl	bdl	bdl	bdl	bdl	bdl
LSB002S	Lower South Bay	bdl	bdl	bdl	bdl	bdl	bdl
LSB003S	Lower South Bay	bdl	bdl	bdl	bdl	bdl	bdl
LSB004S	Lower South Bay	14.5	10.2	4.3	bdl	bdl	bdl
LSB005S	Lower South Bay	11.3	8.6	2.7	bdl	bdl	bdl
LSB006S	Lower South Bay	21.2	12.8	8.4	bdl	bdl	bdl
LSB007S	Lower South Bay	bdl	bdl	bdl	bdl	bdl	bdl
LSB008S	Lower South Bay	8.2	bdl	8.2	bdl	bdl	bdl
BA10	Coyote Creek	2.7	1.9	0.8	bdl	bdl	bdl
C-1-3	Sunnyvale	6.1	bdl	6.1	bdl	bdl	bdl

[a] ΣPBDEs is sum of the target parameters. Only congeners with 1 or more measurements above their detection limit are shown. Abbreviation: bdl, below detection limit. For data analysis, bdl = zero.

found at a South Bay station (212 ng/g dry wt, SB005S), which was 1−3 orders of magnitude higher than other sampling stations.

Only five PBDE congeners were detected in the sediment samples, with BDE-47 (range <0.5−100 ng/g dry wt) being the most abundant congener followed in decreasing abundance by BDE-99 (range <0.2−71 ng/g dry wt), BDE-205 (range <0.5−22 ng/g dry wt), BDE-204 (range <0.5−19 ng/g dry wt), and BDE-183 (range <0.1−0.2 ng/g dry wt). The highest concentrations of BDE-47 (100 ng/g dry wt) and BDE-99 (71 ng/g dry wt) were both found at a South Bay station (SB005S). BDE-209 was below its detection limit (<1.5 ng/g dry wt) in Estuary sediments, although it was detected in water. BDE-100 was also below its detection limit (<0.5 ng/g dry wt) in sediments, although it was detected in both water and bivalves (see Bivalves section). The lack of detection of expected congeners such as BDE-209 and BDE-100 suggests that a more sensitive spectrometric method (e.g., HRGC/HRMS) could be used to get a better representation of the concentrations and distributions of low-level PBDE congeners that are likely to be found in Estuary surface sediments.

To determine the relative severity of PBDE contamination in San Francisco Estuary sediments, comparisons were made against other studies where sediment PBDE concentrations have been measured. Surface sediments from the Cinca River (Spain) had ΣPBDE concentrations (sum of BDE-47, -100, -118, -153, -154, -183, and -209) that ranged from 2 to 42 ng/g dry wt (*27*), while two sites in the Viskan River (Sweden) had ΣPBDE concentrations (sum of BDE-47, -99, and -100) at 1.6 and 3.9 ng/g dry wt (*24*). Surface sediments collected from Japanese Rivers had ΣPBDE concentrations (sum of tetraBDE and pentaBDE congeners) ranging from 21 to 59 ng/g dry wt (*28*), while surface sediments from Virginia (USA) had total tetra to hexaBDE concentrations ranging from <0.5 to 52.3 ng/g dry wt (*9*). Sediments collected from the River Calder (United Kingdom) downstream of a sewage treatment plant had BDE-47 and BDE-99 concentrations at 24 and 46 ng/g dry wt, respectively (*29*). In comparison, the ΣPBDE

TABLE 3. PBDE Concentrations (ng/g or ppb) in Bivalves[a]

site code	station	bi-valve	ΣPBDEs (dry wt)	BDE-47 (dry wt)	BDE-99 (dry wt)	BDE-100 (dry wt)	ΣPBDEs (wet wt)	BDE-47 (wet wt)	BDE-99 (wet wt)	BDE-100 (wet wt)	ΣPBDEs (lipid wt)	BDE-47 (lipid wt)	BDE-99 (lipid wt)	BDE-100 (lipid wt)	ΣPCBs/ ΣPBDEs
BG20	Sacramento River	CFLU	85	48	13	25	12	6.4	1.7	3.4	13053	7301	1948	3804	0.8
BG30	San Joaquin River	CFLU	106	60	17	29	14	8.1	2.3	3.9	13950	7886	2246	3818	2
	mean	CFLU	95	54	15	27	13	7.3	2.0	3.7	13502	7594	2097	3811	1.5
	SD	CFLU	14	9	3	3	2	1.2	0.4	0.4	634	414	211	10	
BD50	Napa River	CGIG	48	29	12	6	6	4.0	1.6	0.8	11088	6814	2837	1437	1
BD40	Davis Point	CGIG	64	43	13	7	9	5.8	1.8	1.0	3770	2544	787	439	4
BD20	San Pablo Bay	CGIG	36	25	7	4	5	3.4	0.9	0.5	2993	2100	578	315	7
BD15	Petaluma River	CGIG	9	9	bdl	bdl	1	1.2	bdl	bdl	2654	2654	bdl	bdl	5
BA10	Coyote Creek	CGIG	23	19	5	bdl	3	2.5	0.6	bdl	3590	2859	731	bdl	16
T-0	Tomales Bay	CGIG	0	bdl	bdl	bdl	0	bdl	bdl	bdl	0	bdl	bdl	bdl	
	mean	CGIG	40	25	9	6	5	3.4	1.2	0.8	5358	3394	1233	730	7
	SD	CGIG	19	13	4	2	3	1.7	0.6	0.3	3620	1932	1073	615	
BD30	Pinole Point	MCAL	15	11	4	bdl	2	1.4	0.6	bdl	1369	972	397	bdl	10
BC60	Red Rock	MCAL	18	13	6	bdl	3	1.7	0.8	bdl	1498	1041	457	bdl	12
BC21	Horseshoe Bay	MCAL	13	10	4	bdl	2	1.3	0.5	bdl	855	605	250	bdl	11
BC10	Yerba Buena Island	MCAL	38	23	12	3	5	3.1	1.6	0.4	2304	1406	703	195	7
BB71	Alameda	MCAL	47	28	15	5	6	3.7	2.0	0.7	4265	2500	1327	438	11
BA40	Redwood Creek	MCAL	40	24	12	4	5	3.3	1.6	0.5	3330	2017	1017	296	8
BA30	Dumbarton Bridge	MCAL	20	15	5	bdl	3	2.0	0.7	bdl	1811	1349	462	bdl	16
T-0	Bodega Head	MCAL	0	bdl	bdl	bdl	0	bdl	bdl	bdl	0	bdl	bdl	bdl	
	mean	MCAL	29	17	8	4	4	2.4	1.1	0.5	2382	1413	659	310	11
	SD	MCAL	13	7	4	1	2	1.0	0.6	0.2	1158	650	386	122	

[a] ΣPBDEs is the sum of BDE-47, BDE-99, and BDE-100 since other congeners were not detected. ΣPCBs is the sum of 40 congeners found in the same sample. Abbreviations: bdl, below detection limit; SD, standard deviation. For data analysis, bdl = zero. $T - 0$ = time of bivalve deployment into the Estuary from the source indicated. CFLU, *Corbicula fluminea* (clam), is a resident species. CGIG, *Crassostrea gigas* (oyster). MCAL, *Mytilus californianus* (mussel). Tomales Bay and Bodega Head were the background sites. Total number of bivalves deployed in cages was 80 at each site.

concentrations in San Francisco Estuary sediments were slightly higher than European, Japanese, and Virginia river sediments. Only two of the San Francisco Estuary sediment stations (SB008S and SB005S), both in the South Bay, had BDE-47 and BDE-99 concentrations that were within range or above the concentrations found in River Calder sediments, which were collected downstream of a sewage treatment plant.

The majority of San Francisco Estuary sediment stations, except the South Bay station (SB005S), had BDE-47 (range <0.5−100 ng/g dry wt) and BDE-99 (range <0.2−71 ng/g dry wt) concentrations that were at or slightly above those reported in sediments from the Tweed Estuary (United Kingdom, BDE-47 <0.3 and BDE-99 0.6 ng/g dry wt), which was considered a background site (*29*). Sediments from the mouth of the Tees Estuary (United Kingdom) had BDE-47 (103 ng/g dry wt) and BDE-99 (201 ng/g dry wt) concentrations that were similar in range to the South Bay station only, while sediments collected in that same Estuary ~40 km downstream of a PBDE manufacturing plant had BDE-47 (368 ng/g dry wt) and BDE-99 (898 ng/g dry wt) concentrations that were much higher than the South Bay station (*29*).

Bivalves. The ΣPBDE concentrations in transplanted and resident (BG20 and BG30) bivalves are shown in Table 3, and their spatial distribution is shown in Figure 6. Three different genera of bivalves were deployed at different geographic locations within the Estuary. It is therefore not possible to make a direct Estuary-wide comparison of the PBDE distributions. However, comparisons of PBDE distribution are made within a single bivalve genus. Only three PBDE congeners were detected in bivalve samples: BDE-47, BDE-99, and BDE-100. These congeners all share the 2,2′,4,4′ substitution pattern and are major components of the Penta-BDE mixture. The most abundant PBDE congener in bivalves

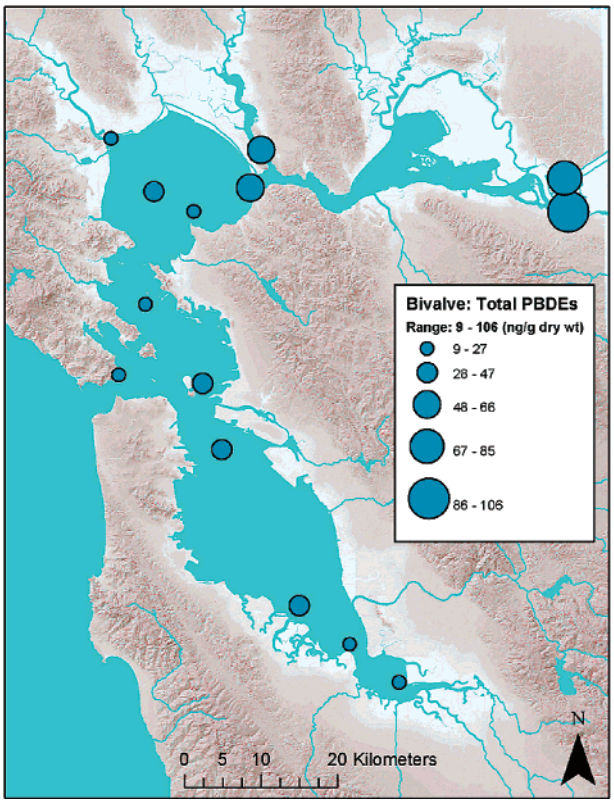

FIGURE 6. Bubble-map showing distribution of total PBDEs (ng/g dry wt) in San Francisco Estuary bivalve sampling stations.

was BDE-47, which was found above its MDL (2.4 ng/g dry wt) in all the bivalve samples, while BDE-99 (MDL = 2.4 ng/g

TABLE 4. Comparison of Total PBDEs between 2002 and 2001 Bivalve Samples[a]

site code	station	bivalve	ΣPBDEs (ng/g dry wt) 2001	2002
BG20	Sacramento River	CFLU	72	85
BG30	San Joaquin River	CFLU	63	106
	mean	CFLU	68	95
	SD	CFLU	6	14
BD50	Napa River	CGIG	24	48
BD40	Davis Point	CGIG	49	64
BD20	San Pablo Bay	CGIG	22	36
BD15	Petaluma River	CGIG	4	9
BA10	Coyote Creek	CGIG	41	23
T-0	Tomales Bay	CGIG	0.6	0
	mean	CGIG	28	40
	SD	CGIG	18	19
BD30	Pinole Point	MCAL	8	5
BC60	Red Rock	MCAL	15	18
BC21	Horseshoe Bay	MCAL	25	13
BC10	Yerba Buena Island	MCAL	37	38
BB71	Alameda	MCAL	22	47
BA40	Redwood Creek	MCAL	33	40
BA30	Dumbarton Bridge	MCAL	17	20
T-0	Bodega Head	MCAL	0.7	0
	mean	MCAL	22	29
	SD	MCAL	10	13

[a] ΣPBDEs is the sum of BDE-47, BDE-99, and BDE-100, since other congeners were not detected. $T-0$ = time of bivalve deployment into the Estuary from the source indicated. CFLU, *Corbicula fluminea* (clam) is a resident species. CGIG, *Crassostrea gigas* (oyster). MCAL, *Mytilus californianus* (mussel). Tomales Bay and Bodega Head were background sites.

dry wt) and BDE-100 (MDL = 1.9 ng/g dry wt) were less abundant and above their respective MDLs in >50% of all bivalve samples. BDE-47, BDE-99, and BDE-100 are the predominant congeners that bioaccumulate in wildlife and humans (*12*).

The ΣPBDE concentrations in transplanted oysters (*Crassostrea gigas*) ranged from 9 to 64 ng/g dry wt with the highest concentration found at Davis Point (BD40). For the individual PBDE congeners their concentration ranges in oysters were BDE-47 at 9−29 ng/g dry wt (76% of ΣPBDEs), BDE-99 at <2.4−13 ng/g dry wt (17%), and BDE-100 at <1.9−7 ng/g dry wt (7%).

In transplanted mussels (*Mytilus californianus*), the ΣPBDEs ranged from 13 to 47 ng/g dry wt with the highest ΣPBDE concentration found at Alameda (BB71). The concentrations of the individual PBDE congeners in mussels were BDE-47 at 10−28 ng/g dry wt (67% of ΣPBDEs), BDE-99 at 4−15 ng/g dry wt (29%), and BDE-100 at <1.9−5 ng/g dry wt (4%).

ΣPBDE concentrations in resident clams (*Corbicula fluminea*) from the San Joaquin River (BG30) were measured at 106 ng/g dry wt, while clams from the Sacramento River (BG20) had lower ΣPBDE concentrations (85 ng/g dry wt). The individual PBDE congener concentrations in clams were BDE-47 at 48−60 ng/g dry wt (56% of ΣPBDEs), BDE-99 at 13−17 ng/g dry wt (16%), and BDE-100 at 25−29 ng/g dry wt (28%).

PBDEs were previously measured in San Francisco Estuary bivalves in 2001 at the same sampling stations (unpublished data, Table 4). In comparison to the 2001 results, the ΣPBDE concentrations in 2002 samples were higher in all bivalves at all sampling stations except in Coyote Creek (BA10) oysters and Horseshoe Bay (BC21) mussels. The greatest differences in ΣPBDE concentrations were found in Petaluma River (BD15) oysters, Alameda (BB71) mussels, and Napa River (BD50) oysters.

To determine the relative severity of PBDE contamination in San Francisco Estuary bivalves, comparisons were made against other studies where bivalve PBDE concentrations have been measured. Mussels are compared to other studies since to our knowledge no other studies have reported PBDE concentrations in oysters or clams. San Francisco Estuary mussels had ΣPBDE (sum of BDE-47, -99, and -100) concentrations ranging from 13 to 47 ng/g dry wt or 1.3−3.7 ng/g wet wt) (Table 3), which is 11−34 times higher than the ΣPBDE (sum of BDE-47, -99, -100, and -153) concentrations found in blue mussels (0.11 ng/g wet wt) from Usuk, a nonpopulated, rural area of southern Greenland (*10*). San Francisco Estuary mussels had ΣPBDE concentrations that were higher than blue mussels (*M. edulis*) collected from Denmark (range 0.08−0.81 ng/g wet wt, sum of BDE-47, -99, -100, and -153) (*30*) and the Netherlands (1.7−3.2 ng/g dry wt) (*25*). In contrast, San Francisco Estuary ΣPBDE concentrations were slightly lower than mussels (7.4 ng/g wet wt, sum of BDE-47 and -99) collected from The Wash, United Kingdom (*29*).

To determine if PBDEs were accumulating in bivalves at levels similar to those of PCBs, the ΣPCBs/ΣPBDEs ratio was calculated (Table 3). The results show that on average oysters (ratio mean = 7, range 1−16) and mussels (ratio mean = 11, range 7−16) both had higher concentrations of PCBs than PBDEs, while in resident clams the concentrations were near unity (ratio mean = 1.5, range 0.8−2). Resident clams from the San Joaquin River and Sacramento River also had the highest ΣPBDE concentrations at 106 and 85 ng/g dry wt, respectively. Oysters from the Napa River, which had a ΣPCBs/ΣPBDEs ratio of 1.0, had the third highest ΣPBDE concentration (48 ng/g dry wt). These results show that in a few cases, in particular at river stations, bivalves are accumulating PBDEs at levels similar to PCBs.

Potential Sources and Loading of PBDEs. PBDEs in the Estuary could possibly originate from flame-retardant containing plastic products and polyurethane foams, as supported by an additional class of flame retardants, phosphorotriesters, previously found in the Estuary which have similar uses and sources as PBDEs (*31*). For example, tris(1,3-dichloro-2-propyl)phosphate (TDCPP), a fire retardant that is commercially used in flexible and rigid polyurethane foams and PVC, was found at concentrations ranging from 5 to 76 ng/L, with a maximum concentration in the South Bay region. In 1994, the U.S. EPA included TDCPP on its list of high production volume chemicals (chemicals that are manufactured or imported into the United States at >1 million lb/yr). In addition, a recent study found that PBDE concentrations in water samples were well-correlated with TDCPP concentrations (*30*). The study suggested that washout and emissions from a refuse dump could have been the source of PBDE contamination to the marine environment near the refuse site. The occurrence of TDCPP in the San Francisco Estuary provides further support for the hypothesis that flame-retardant containing plastic products and polyurethane foams are likely the major materials that are contributing PBDEs to this environment.

A recent study conducted at the Regional Water Quality Control Plant, a tertiary sewage treatment facility in Palo Alto, CA that treats 25 million gal/day (9125 million gal/yr) showed that BDE-47, BDE-99, and BDE-209 were the major congeners in sludge and in effluent that is discharged into the Estuary at a ΣPBDE loading rate of 2 lb/yr (0.9 kg/yr) (*3*). Assuming that this loading rate applies to all local wastewater treatment plants that discharge effluents into the Estuary, which have a total discharge of 230 000 Mgal/yr (*32*), then the estimated ΣPBDE loading from discharged effluents could amount to 50 lb/yr (23 kg/yr). In comparison to the current level of ΣPCB loading to the Estuary from wastewater treatment plant discharge sources (2.3 kg/yr) (*32*), the estimated level of ΣPBDE loading (23 kg/yr) may be up to an order of magnitude higher and is not expected to decrease

soon. This could represent a significant amount of PBDE loading to the Estuary.

Implications. This first year of PBDE field monitoring provided preliminary indications of their concentrations and spatial distributions in San Francisco Estuary water, surface sediments, and bivalves. PBDEs are widely distributed throughout the Estuary water column. PBDEs are adsorbed to particulate matter (>78% of ΣPBDEs is bound) in the water column. The Penta-BDE, Octa-BDE, and Deca-BDE commercial mixtures are all present in the water column. The Penta-BDE and Octa-BDE mixtures were found in sediments, but Deca-BDE (BDE-209) was below its detection limit (<1.5 ng/g dry wt). Generally, the ΣPBDE concentrations in Estuary water and sediment samples are comparable to other areas where there are no major wastewater discharges from PBDE manufacturing plants.

PBDE congeners from the Penta-BDE mixture were found in bivalves, but congeners from Octa-BDE and Deca-BDE mixtures were not detected, which could be due to their large molecular size and limited bioavailability (*12*). Lower trophic level animals in marine/freshwater food webs such as bivalves tend to bioaccumulate PBDE congeners from the Penta-BDE mixture. The ΣPBDE concentrations in resident clams were 2−3 times greater than those found in transplanted oysters and mussels, which is possibly due to their longer exposure period (>90 days) within the Estuary boundary.

RMP monitoring in the San Francisco Estuary will continue to analyze for PBDEs in water, surface sediments, and bivalves on an annual basis to examine spatial distributions and temporal trends and to fill critical data gaps. Data gaps of immediate concern include the identification of major sources, transport pathways, effects thresholds on aquatic biota, biomagnification pathways through the Estuary food web including humans, and the residence time of these contaminants in the Estuary.

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Literature Cited

(1) She, J.; Petreas, M.; Winkler, J.; Visita, P.; McKinney, M.; Kopec, D. *Chemosphere* **2002**, *46*, 697−707.

(2) Holden, A.; She, J.; Tanner, M.; Lunder, S.; Sharp, R.; Hooper, K. *Organohalogen Compd.* **2003**, *61*, 255−258.

(3) North, K. *Environ. Sci. Technol.* **2004**, *38*, 4484−4488.

(4) Darnerud, P. O.; Eriksen, G. S.; Johannesson, T.; Larsen, P. B.; Viluksela, M. *Environ. Health Perspect.* **2001**, *109*, 49−68.

(5) BSEF, Bromine Science and Environmental Forum. *Total Market Demand*; 2001; www.bsef.com.

(6) Sellström, U.; Jansson, B.; Kierkegaard, A.; de Wit, C.; Odsjo, T.; Olsson, M. *Chemosphere* **1993**, *26*, 1703−1718.

(7) Alaee, M.; Luross, J.; Sergeant, D. B.; Muir, D. C. G.; Whittle, D. M.; Solomon, K. *Organohalogen Compd.* **1999**, *40*, 347−350.

(8) Gustafsson, K.; Bjork, M.; Burreau, S.; Gilek, M. *Environ. Toxicol. Chem.* **1999**, *18*, 1218−1224.

(9) Hale, R. C.; La Guardia, M. J.; Harvey, E. P.; Mainor, T. M.; Duff, W. H.; Gaylor, M. O. *Environ. Sci. Technol.* **2001**, *35*, 4585−4591.

(10) Christensen, J. H.; Glasius, M.; Pécseli, M.; Platz, J.; Pritzl, G. *Chemosphere* **2002**, *47*, 631−638.

(11) Ikonomou, M. G.; Rayne, S.; Fischer, M.; Fernandez, M. P.; Cretney, W. *Chemosphere* **2002**, *46*, 649−663.

(12) Meerts, I. A. T. M.; van Zanden, J. J.; Luijks, E. A. C.; van Leeuwen-Bol, I.; Marsh, G.; Jakobsson, E.; Bergman, A.; Brouwer, A. *Toxicol. Sci.* **2001**, *56*, 95−104.

(13) Hites, R. A. *Environ. Sci. Technol.* **2004**, *38*, 945−956.

(14) Watanabe, I.; Tatsukawa, R. *Bull. Environ. Contam. Toxicol.* **1987**, *39*, 953−959.

(15) Sellström, U.; Söderström, G.; de Wit, C.; Tysklind, M. *Organohalogen Compd.* **1998**, *35*, 447−450.

(16) Söderström, G., Sellström, U.; de Wit, C. A.; Tysklind, M. *Environ. Sci. Technol.* **2004**, *38*, 127−132.

(17) Stapleton, H. M.; Alaee, M.; Letcher, R. J.; Baker, J. E. *Environ. Sci. Technol.* **2004**, *38*, 112−119.

(18) SFEI, San Francisco Estuary Institute. Regional Monitoring Program for Trace Substances, 2002 Annual Monitoring Results, Oakland, CA, 2004.

(19) SFEI, San Francisco Estuary Institute. Regional Monitoring Program for Trace Substances, 1999 Quality Assurance Project Plan, RMP Contribution 33, Oakland, CA, 1999.

(20) Squire, S.; Scelfo, G. H.; Revenaugh, J.; Flegal, A. R. *Environ. Sci. Technol.* **2002**, *36*, 2379−2386.

(21) EOA. Joint Stormwater Agency Project to Study Urban Sources of Mercury, PCBs and Organochlorine Pesticides. Final Report, Oakland, CA, 2002.

(22) Booij, K.; Zegers, B. N.; Boon, J. P. *Chemosphere* **2002**, *46*, 683−688.

(23) Stapleton, H. M.; Baker, J. E. Comparing the temporal trends, partitioning and biomagnification of PBDEs and PCBs in Lake Michigan. Presented at the 3rd Annual Workshop on Brominated Flame Retardants in the Environment, Burlington, Canada; National Water Research Institute: 2001; pp 22−25.

(24) Sellström, U.; Kierkegaard, A.; de Wit, C.; Jansson, B. *Environ. Toxicol. Chem.* **1998**, *17*, 1065−1072.

(25) de Boer, J.; Wester, P. G.; van der Horst, A.; Leonards, P. E. G. *Environ. Pollut.* **2003**, *122*, 63−74.

(26) Iwata, H.; Tanabe, S.; Sakai, N.; Tatsukawa, R. *Environ. Sci. Technol.* **1993**, *27*, 1080−1098.

(27) Eljarrat, E.; De La Cal, A.; Raldua, D.; Duran, C.; Barcelo, D. *Environ. Sci. Technol.* **2004**, *38*, 2603−2608.

(28) Watanabe, I.; Kashimoto, T.; Tatsukawa, R. *Chemosphere* **1986**, *16*, 2389−2396.

(29) Allchin, C. R.; Law, R. J.; Morris, S. *Environ. Pollut.* **1999**, *105*, 197−207.

(30) Christensen, J. H.; Platz, J. *J. Environ. Monit.* **2001**, *3*, 543−547.

(31) Oros, D. R.; Jarman, W. M.; Lowe, T.; David, N.; Lowe, S.; Davis, J. A. *Marine Pollut. Bull.* **2003**, *46*, 1102−1110.

(32) CRWQCB. PCBs in San Francisco Bay Total Maximum Daily Load Project Report. California Regional Water Quality Control Board, San Francisco Bay Region: Oakland, CA, 2004.

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