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Brominated and chlorinated flame retardants in San Francisco Bay sediments and wildlife

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ABSTRACT

Restrictions on the use of polybrominated diphenyl ethers (PBDEs) have resulted in the use of alternative flame retardants in consumer products to comply with flammability standards. In contrast to PBDEs, information on the occurrence and fate of these alternative compounds in the environment is limited, particularly in the United States. In this study, a survey of flame retardants in San Francisco Bay was conducted to evaluate whether PBDE replacement chemicals and other current use flame retardants were accumulating in the Bay food web. In addition to PBDEs, brominated and chlorinated flame retardants (hexabromocyclododecane (HBCD) and Dechlorane Plus (DP)) were detected in Bay sediments and wildlife. Median concentrations of PBDEs, HBCD, and DP, respectively, were 4.3, 0.3, and 0.2 ng g^{-1} dry weight (dw) in sediments; 1670, <6.0, and 0.5 ng g^{-1} lipid weight (lw) in white croaker (*Genyonemus lineatus*); 1860, 6.5, and 1.3 ng g^{-1} lw in shiner surfperch (*Cymatogaster aggregata*); 5500, 37.4, and 0.9 ng g^{-1} lw in eggs of double-crested cormorant (*Phalacrocorax auritus*); 770, 7.1, and 0.9 ng g^{-1} lw in harbor seal (*Phoca vitulina*) adults; and 330, 3.5, and <0.1 ng g^{-1} lw in harbor seal (*P. vitulina*) pups. Two additional flame retardants, pentabromoethylbenzene (PBEB) and 1,2-bis(2,4,6 tribromophenoxy)ethane (BTBPE) were detected in sediments but with less frequency and at lower concentrations (median concentrations of 0.01 and 0.02 ng g^{-1} dw, respectively) compared to the other flame retardants. PBEB was also detected in each of the adult harbor seals and in 83% of the pups (median concentrations 0.2 and 0.07 ng g^{-1} lw, respectively). The flame retardants hexabromobenzene (HBB), decabromodiphenyl ethane (DBDPE), bis(2-ethylhexyl) tetrabromophthalate (TBPH), and 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), were not detected in sediments and BTBPE, HBB and TBB were not detected in wildlife samples. Elevated concentrations of some flame retardants were likely associated with urbanization and Bay hydrodynamics. Compared to other locations, concentrations of PBDEs in Bay wildlife were comparable or higher, while concentrations of the alternatives were generally lower. This study is the first to determine concentrations of PBDE replacement products and other flame retardants in San Francisco Bay, providing some of the first data on the food web occurrence of these flame retardants in a North American urbanized estuary.

1. Introduction

Studies conducted over the last decade have revealed that polybrominated diphenyl ether (PBDE) concentrations in humans and wildlife in California, and the San Francisco Bay Area in particular, are among the highest reported in the world (recently reviewed by Shaw and Kannan, 2009). PBDEs, sold commercially as penta-BDE, octa-BDE, or deca-BDE, have been added to a wide variety of consumer products, including upholstered furniture, electronics, and textiles since the 1970s. Studies suggest that PBDEs migrate out of these products over time and accumulate in both indoor and outdoor environments, where wildlife and humans are exposed to them (Hale et al., 2006; Van den Eede et al., 2011). It has been hypothesized that the elevated exposures in California are the result of California's unique flammability standard for the polyurethane foam used in upholstered furniture, Technical Bulletin 117 (TB117) (Zota et al., 2008). Penta-BDE was used to comply with TB117, and the PBDE congeners in penta-BDE are the same congeners that bioaccumulate in the highest concentrations (Hites, 2004). Though TB117 is a standard pertaining only to upholstered furniture sold in California, polyurethane foam manufactured and sold in furniture throughout the United States (US) often complies with TB117, thus likely explaining the often similarly high concentrations of PBDEs observed in other parts of the country (Shaw and Kannan, 2009). Due to environmental and human health concerns (Eriksson et al., 2001; Stoker et al., 2005; Viberg et al., 2003), the penta- and octa-BDE mixtures have been

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banned or phased out of use in the US and Europe, and are also listed as persistent organic pollutants under the Stockholm Convention on Persistent Organic Pollutants (http://chm.pops.int/). The deca-BDE mixture was banned in Europe in 2008, and in 2009 chemical companies in the US agreed to phase out its production by 2013.

Restrictions on the use of PBDEs have resulted in the use of alternative flame retardants to comply with TB117 and other flammability standards. A number of compounds have been identified as penta-BDE replacements in polyurethane foam collected from furniture and baby products purchased since the phase-out of PBDEs in the US (Stapleton et al., 2009, 2011). These include bis(2-ethylhexyl) tetrabromophthalate (TBPH) and 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), the brominated compounds in the commercial mixture Firemaster 550®. Deca- and octa-BDE, which were primarily added to thermoplastics used in electronics and electrical equipment, are being replaced by decabromodiphenyl ethane (DBDPE) and 1,2-bis(2,4,6 tribromophenoxy) ethane (BTBPE), respectively (Covaci et al., 2011). With the exception of perhaps TBB, these replacement compounds are high production volume chemicals that have been used for a decade or more. Few studies have investigated and reported the occurrence of DBDPE and BTBPE in wildlife and other environmental matrices, though the number has increased in recent years (Covaci et al., 2011). The toxicological effects resulting from long-term exposure to DBDPE and BTBPE are still largely unknown. A very limited number of studies have investigated the occurrence and fate of TBB and TBPH in the environment. TBB and TBPH have been detected in US house dust and sewage sludge (Davis et al., 2012; La Guardia et al., 2010; Stapleton et al., 2008) and marine mammals in China (Lam et al., 2009). DNA damage was observed by Bearr et al. (2010) in laboratory exposed flathead minnows.

Prompted by the phase-out of PBDEs in the US, a survey of San Francisco Bay sediment and wildlife was conducted to evaluate whether PBDE replacement compounds (TBPH, TBB, DBDPE, and BTBPE), and other current use flame retardants were accumulating in the Bay food web (target compounds listed in Table 1). The additional current use flame retardants analyzed in this study were hexabromocyclododecane (HBCD), Dechlorane Plus® (DP), pentabromoethylbenzene (PBEB), and hexabromobenzene (HBB). HBCD is a high production volume flame retardant that has been identified as a persistent, bioaccumulative, and toxic (PBT) substance by the US EPA, classified as a 'substance of very high concern' by the European Chemicals Agency, and detected in environmental samples worldwide (ECHA, 2008; USEPA, 2010). DP, PBEB, and HBB have been used historically in a wide variety of applications and have been detected in the environment (Covaci et al., 2011; Gauthier and Letcher, 2009). PBDEs were included in the analysis as a point of reference following their production ban.

2. Materials and methods

2.1. Samples

Sediment, shiner surfperch (*Cymatogaster aggregata*), white croaker (*Genyonemus lineatus*), and double-crested cormorant (*Phalacrocorax auritus*) eggs were collected as part of routine chemical contaminant monitoring conducted by the Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP; http://www.sfei.org/rmp). Sample sites are shown in Fig. 1. Surface sediments (top 5 cm) were collected in 2007 via Van Veen Grab from ten sites spatially distributed

Table 1
Flame retardant chemicals analyzed in this study.

Chemical	CAS#	Log K_{ow}	Production/import volume in US[a] (million lbs)		Description/primary applications
			2002	2006	
Polybrominated diphenyl ethers (PBDEs)					Three commercial mixtures: penta-BDE, octa-BDE, deca-BDE
Penta-BDE mixture	32534-81-9	6.58[b]	10–50	0	Predominantly BDEs 47, 99, 100, 153, 154; polyurethane foam in furniture, automobiles
Octa-BDE mixture	32536-52-0	6.29[b]	1-10	0	Predominantly BDEs 183, 196, 197, 207; thermoplastics
Deca-BDE mixture	1163-19-5	6.3,12.6[b]	50-100	50-100	Typically >90% BDE 209; thermoplastics, <10% textiles
Hexabromocyclododecane (HBCD)	3194-55-6; 25637-99-4	5.6[c]	10-50 (3194-55-6)	10-50 (3194-55-6)	Contains α-, β-, γ-HBCD; expanded and extruded polystyrene foam in thermal insulation boards (~0.5% by weight) (Morose, 2006), textiles
α-HBCD	134237-50-6	5.1[d]	–	–	10–13% of technical mixtures (Covaci et al., 2006)
β-HBCD	134237-51-7	5.1[d]	–	–	1–12% of technical mixtures (Covaci et al., 2006)
γ-HBCD	134237-52-8	5.5[d]	–	–	75-89% of technical mixtures (Covaci et al., 2006)
Dechlorane Plus (DP)	13560-89-9	9.3[c]	1-10	1-10	Contains syn-DP, anti-DP isomers; Electrical and electronic products
Anti-DP	–	–	–	–	65–80% of technical mixtures (Gauthier and Letcher, 2009)
Syn-DP	–	–	–	–	20–35% of technical mixtures (Gauthier and Letcher, 2009)
Pentabromoethylbenzene (PBEB)	85-22-3	6.4[e]	No reports	No reports	Thermoset polyester resins (circuit boards, textiles, adhesives, wire and cable coatings, polyurethane foam)[e]
Decabromodiphenyl ethane (DBDPE)	84852-53-9	11.1[e]	No reports	10-50	Deca-BDE replacement; high-impact polystyrene, acrylonitrile butadiene styrene, polypropylene, textiles[e]
Bis(2,4,6-tribromophenoxy)ethane (BTBPE)	37853-59-1	7.9[e]	1-10	1-10	Octa-BDE replacement; high-impact polystyrene, acrylonitrile butadiene styrene, thermoplastics, thermoset resins, polycarbonate and coatings [e]
Hexabromobenzene (HBB)	87-82-1	5.9, 6.1[e]	No reports	No reports	Paper, woods, textiles, electronic and plastic goods; produced in Japan, China [e]
Bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH or BEHTBP)	26040-51-7	10.1[e], 11.95[c]	1-10	1-10	Component of Firemaster 550, a penta-BDE replacement; PVC, neoprene, wire and cable insulation, film and sheeting, carpet backing, coated fabrics, wall coverings, adhesives
2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB or EHTBB)	183658-27-7	NA	No reports	No reports	Component of Firemaster 550, a Penta-BDE replacement

[a] USEPA Inventory Update Reporting (http://www.epa.gov/iur/).
[b] Hardy, 2002.
[c] USEPA HPV database (http://www.epa.gov/hpvis/).
[d] ECHA, 2008.
[e] Covaci et al., 2011; NA = not available.

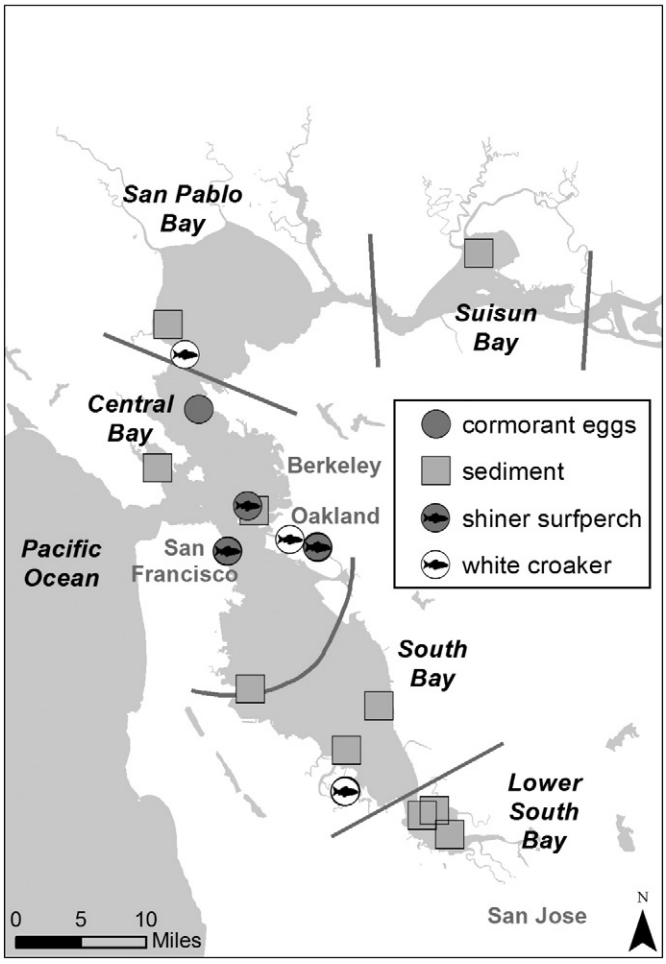

Fig. 1. San Francisco Bay sample sites.

throughout the Bay (SFEI, 2008). Shiner surfperch (n = 8 composite samples, 20 fish per composite) and white croaker (n = 6 composite samples, five fish per composite) were collected in 2006 from popular recreational fishing sites in three Bay segments (San Pablo Bay, Central Bay, and South Bay (Hunt et al., 2008)). Though the RMP monitors chemical contamination in several species of sport fish, white croaker and shiner surfperch have historically contained the highest concentrations of PBDEs and other organic chemical contaminants (Davis et al., 2006; Hunt et al., 2008) and were therefore the focus of this study. Three composites of cormorant eggs (seven eggs per composite) were collected in 2008 from a nesting site near the Richmond Bridge (Richmond, CA, USA). Eggs were collected from active nests by hand (one from each nest) and aged by flotation. An effort was made to collect the freshest eggs possible. Eggs were stored at 4 °C until analysis (25 days).

Harbor seal (*Phoca vitulina*) blubber was sampled from fresh dead or freshly euthanized stranded seals that were admitted to The Marine Mammal Center from locations in the Central Bay segment of San Francisco Bay in 2007 and 2008. Seals that reside in San Francisco Bay are known to forage within 1 to 5 km of a land-based rest area (haul-out); however, Bay seals have been located outside of the Bay and likely use multiple haul-out and foraging locations (Grigg et al., 2009; Harvey and Goley, 2011). By selecting seals that stranded in the Bay, the likelihood that some of their contaminant exposure occurred within the Bay was increased. Five adults (four female, one male) and 12 pups (6 female, 6 male) were sampled. Full thickness samples of blubber from the ventral axilla were wrapped in solvent-rinsed teflon sheeting and stored at −20 °C until chemical analysis.

2.2. Chemicals

Internal and surrogate standards were purchased from Chiron (Trondheim, Norway) and Wellington Laboratories (Guelph, Ontario). Native PBDE standards were purchased from AccuStandard (New Haven, CT); TBB, TBPH, and HBCD diastereoisomer (α-, β-, γ-HBCD) native standards were purchased from Wellington Laboratories. Solvents used in the sediment PBDE analysis were pesticide grade. All other solvents used were HPLC grade.

2.3. Analytical methods

Analytical methods used in this study are briefly described below. Method details are provided in the Supporting Information (SI).

PBDEs in sediments were analyzed by the RMP using a modified EPA 1614 method (USEPA, 2007). Samples (10 g wet weight) were mixed with diatomaceous earth, spiked with a ^{13}C-labeled PBDE surrogate standard solution, and extracted using dichloromethane (DCM) and accelerated solvent extraction (ASE). Extracts were dried by passing through a sodium sulfate (40 g) column and then high molecular organic compounds and sulfur were removed using size exclusion chromatography (SEC). The extracts were further purified using alumina chromatography (10 g, activated) eluted with DCM. The solvent was exchanged to hexane and a ^{13}C-labeled PCB internal standard solution was added to each extract. PBDEs (50 congeners total) were analyzed using high-resolution gas chromatography/high resolution mass spectrometry and quantified using isotope dilution.

PBDEs in biota samples, and DP, DBDPE, BTBPE, HBB, PBEB, TBB, and TBPH in all samples were analyzed at Duke University, North Carolina, USA. DBDPE in the wildlife samples and TBPH in seal samples were not reportable due to low recovery of standards in matrix spike tests. TBPH was not analyzed in fish samples because it was not detected in bird egg or sediment samples. Samples were spiked with two internal standards, (4′fluoro-2,3′,4,6-tetrabromodiphenyl ether (F-BDE 69) and ^{13}C-labeled decabromodiphenyl ether (^{13}C-BDE 209), and extracted with 50:50 DCM:hexane using ASE. For sediment analyses, each ASE extract was purified by elution through a column containing 8.0 g of 2.5% deactivated Florisil. For biota samples, post-ASE extracts were purified by SEC. Prior to SEC, an aliquot of each biota extract was removed for gravimetric lipid analysis. Biota extracts were further cleaned using alumina chromatography (6.0 g, 4.0% deactivated) eluted with 50:50 DCM:hexane. To quantify the recovery of F-BDE 69 and ^{13}C-BDE 209, ^{13}C-labeled 2,2′,3,4,5,5′-hexachlorodiphenyl ether was added to each sample prior to analysis. Extracts were analyzed using gas chromatography and mass spectrometry operated in electron capture negative ionization mode (GC/ECNI-MS).

Analysis of TBB in seal extracts was confounded by apparent matrix interferences when analyzed by GC/ECNI-MS. These extracts were solvent exchanged to methanol and re-analyzed by UPLC-high resolution mass spectrometry (UPLC/HRMS) using a LTQ-Orbitrap Velos tandem mass spectrometer (ThermoFisher Scientific, Bremen, Germany) with a Thermo Fisher Scientific Accela series UPLC system. Sample extracts (25 μL) were separated on a Hypersil Gold 50×2.1-mm C_{18} column with 1.9 μm particles (ThermoFisher Scientific) using a flow rate of 0.4 mL/min and a linear gradient from 25 to 95% methanol/water in 9 min, followed by a 1-min hold at 95% methanol before returning to initial conditions for 2 min. Sample extracts were analyzed using atmospheric pressure chemical ionization (APCI) to monitor molecular ions for TBB. The use of high resolution MS and APCI eliminated matrix interference previously observed by GC/ECNI-MS. TBB was not detected (<1 ng/g lipid) in the seal extracts using this method.

HBCD diastereomers were analyzed at the Virginia Institute of Marine Sciences, Virginia, USA. Freeze-dried homogenized samples were subjected to ASE. A surrogate standard of ^{13}C-labeled α-hexabromocyclododecane (^{13}C-α-HBCD) was added to each sample prior to extraction. After extraction, an aliquot of the extract was removed for gravimetric lipid analysis. The remaining extract was reduced, subjected to SEC, and purified using a silica glass extraction column. Deuterated α-hexabromocyclododecane (d18-α-HBCD) was added as an internal standard. The extracts were analyzed for HBCDs using liquid chromatography–mass spectrometry.

Total organic carbon (TOC) content in the sediment samples was determined by the RMP using a Carlo Erba 2500 Elemental Analyzer (SFEI, 2008). Sediment TOC content ranged from 1.0 to 1.6% (mean 1.3 ± 0.2). Sample-specific TOC content is provided in SI Table 3.

2.4. Quality control

Quality control measures included the analysis of blank, duplicate, matrix spike, and National Institute of Standards and Technology Standard Reference Materials (SRMs). For PBDEs in sediment samples, only values greater than three times the instrument signal to noise ratio were reported by the laboratory; results less than three times the average concentration in the blank samples were censored. Data for PBDEs in the wildlife samples and DP, BTBPE, HBB, PBEB, DBDPE, TBB, and TBPH in all samples were blank corrected by subtracting the average mass in the blank samples; detection limits for these samples represent three times the standard deviation of the lab blanks. The quantitation limit for the HBCD diastereomers was based on a five-point calibration curve constructed at time of analysis, and calculated using the lowest calibration standard and sample weight. HBCD was not detected in the blank samples. In the PBDE analysis of sediment samples, mean recoveries for all ^{13}C-PBDE standards ranged from 65% (^{13}C-BDE 3) to 155% (^{13}C-BDE 139). Mean recoveries of F-BDE 69 were 82% in sediment, 76% in fish, 103% in bird eggs, and 101% in seal blubber samples. Recoveries of ^{13}C-BDE 209 were very low (<50%) for the fish, bird eggs and seal samples, thus values for BDE 209 were only reported for the sediment samples. Mean recoveries of ^{13}C-α-HBCD were 114% in sediment, 94% in fish, 92% in bird eggs, and 97% in seal blubber samples. All data were corrected using surrogate recoveries. PBDE recoveries in SRM 1945 (whale blubber) ranged from 47% (BDE 153) to 95% (BDE 100). PBDE recoveries in SRM 1946 (fish tissue) ranged from 57% (BDE 153) to 107% (BDE 47) for the dominant congeners in this matrix, BDEs 47, 99, 100, and 153. Recovery of BDE 154 in SRM 1946 was high (169%) due to co-elution with BB 153, which is present in that matrix. The recoveries for compounds in the matrix spike samples are provided in SI Table 1.

2.5. Statistical analysis

Differences in flame retardant concentrations between harbor seal pups and adults and the two fish species were analyzed using Welch's two sample t-test. For the t-test, data were tested for normality using a Shapiro–Wilk test and log transformed when appropriate. Flame retardant concentrations in the sediment samples and each tissue matrix were also tested for normality, but were not found to be normally distributed, even after log transformation, so analysis of correlations among them were conducted using Spearman rank analysis. The correlation analyses were conducted only on compounds that were detected in at least 50% of the samples (PBDEs, HBCD, DP, PBEB). Half of the quantitation limit was used where concentrations were below the quantitation limit in the sample. For PBDEs, representative congeners (BDE 47 in wildlife and BDE 209 in sediment) were used in the analyses. The sum of the individual isomers was used for HBCD and DP, even when an isomer was detected in less than 50% of the samples. This was done to maintain consistency in analyses among sample types (e.g. γ-HBCD was detected in <50% of shiner surfperch but >50% in harbor seal pups). Statistical significance was determined using a p-value<0.05. All analyses were performed using R 2.10.1 (R Development Core Team, 2009).

3. Results and discussion

A summary of the flame retardant concentrations in sediments and wildlife is provided in Table 2. Sample-specific concentrations are provided in the Supporting Information (SI) Tables 2–7. PBDEs, HBCD, and DP were detected in sediments and all wildlife matrices. PBEB was detected in sediments and harbor seal samples. BTBPE was also detected in sediments but not in any wildlife samples. HBB, DBDPE, TBB, and TBPH were not detected. Percent lipid content in the biota samples is presented in SI Tables 4 and 5.

3.1. PBDEs

Sum PBDEs in sediments ranged from 2 to 8 ng g^{-1} dry weight (dw) (median 4 ng g^{-1}). BDE 209 was the dominant congener in each sample (range 1–5 ng g^{-1} dw; 38–68% of total PBDE). PBDE sediment concentrations were generally comparable or lower than values summarized in a recent review of North and South American coastal environments (Shaw and Kannan, 2009). San Francisco Bay sediments were also considered to be in the 'medium' range of PBDE concentrations among the 122 samples collected at US coastal sites in a recent NOAA Mussel Watch survey (Kimbrough et al., 2009). In particular, concentrations were comparable or lower than those in other urbanized US estuaries such as the Hudson–Raritan Estuary, Galveston Bay, and Narragansett Bay. Concentrations in San Francisco Bay were typically more than 100 times lower than sediments located close to wastewater outfalls receiving influent from

industrial and municipal sources (Klosterhaus et al., 2011; La Guardia et al., 2007).

Concentrations of PBDEs in Bay wildlife samples were at least one order of magnitude higher than the concentrations of any other flame retardant analyzed in this study. The highest median concentration was observed in the cormorant eggs (5500 ng g^{-1} lipid weight (lw)), followed by sport fish (1670 and 1860 ng g^{-1} lw for white croaker and shiner surfperch, respectively), and then harbor seal blubber (770 and 330 ng g^{-1} lw for adults and pups, respectively). Differences in PBDE concentrations between fish species and between seal pups and adults were not significant ($p = 0.20$ for fish species; $p = 0.29$ for seal pups and adults). Congener profiles in Bay wildlife samples (Fig. 2) reflected uptake of PBDEs in the penta-BDE mixture, consistent with observations in other aquatic species (Shaw and Kannan, 2009). BDE 209 was not detected in any wildlife sample. Species-specific variation in accumulation patterns was observed, and is likely the result of differences in metabolic capabilities for each species and those of their prey items. Compared to bird eggs and seals, both sport fish species exhibited higher ratios of BDEs 47:99 and 49:99, in addition to lower fractions of BDE 153. These profiles for white croaker and shiner surfperch are in agreement with previous observations of metabolic debromination of BDEs 153 and 99 to 47 and BDE 99 to 49 in carp, salmon and trout (Browne et al., 2009; Roberts et al., 2011; Stapleton et al., 2004). In general, the PBDE concentrations observed for the wildlife samples in this study were comparable to those reported previously for San Francisco Bay and support the premise that PBDE concentrations in wildlife living along the California coast are among the highest in the world (Greig et al., 2011; Meng et al., 2009; Shaw and Kannan, 2009). Further study is needed to understand the discrepancy between PBDE concentrations in Bay wildlife that are considered to be among the highest in the world, yet sediment concentrations that are only considered in the 'medium' range compared to other urban US estuaries. Although inter-laboratory variation could cause a similar apparent pattern, recovery samples for the laboratories showed an opposite tendency (i.e., often <100% for tissues and >100% for sediment). Alternatively, a possible cause is that some of the Bay wildlife analyzed in the present study and in previous studies, terns in particular (She et al., 2008), foraged near localized hotspots of contamination along the Bay margins where PBDE sediment concentrations were higher compared to sediments analyzed by the RMP, which were generally obtained from open waters of the Bay.

3.2. HBCD

HBCD was frequently detected in San Francisco Bay sediments and wildlife. Total HBCD concentrations in sediments ranged from 0.1 to 2 ng g^{-1} dw (median 0.3 ng g^{-1} dry) and the isomer profile was dominated by γ-HBCD (51–100%), followed by α-HBCD (0–36%), and β-HBCD (0–27%). This isomer profile is similar to the profile in HBCD commercial mixtures, as well as sediments in other locations (Covaci et al., 2006). To our knowledge, this is the first report of HBCD in marine sediments in the US, though other studies have detected HBCD in household dust (Stapleton et al., 2008) and municipal wastewater sludge (La Guardia et al., 2010) in the US. Most studies of HBCD occurrence in the environment have been conducted in Europe and Asia, where HBCD has historically been used in volumes two to three times higher than in the US (de Wit, 2002). Concentrations in San Francisco Bay sediments were generally one to three orders of magnitude lower then sediments in Europe and are consistent with locations where industrial users of HBCD are not known to be present (Covaci et al., 2006).

In San Francisco Bay wildlife, HBCD was detected at concentrations that were one to three orders of magnitude lower than PBDEs in the same samples. Cormorant eggs contained the highest concentrations of sum HBCD (22–39 ng g^{-1} lw), followed by shiner surfperch (3–25 ng g^{-1} lw), harbor seal adults and pups (4–19 and 2–12 ng g^{-1} lw, respectively), and white croaker (<6–5 ng g^{-1} lw). Similar to PBDEs, sum HBCD concentrations in seal adults and pups were not significantly different ($p = 0.29$). In white croaker, HBCD was detected in only one third of the samples and at the lowest concentrations (sum of all HBCD isomers <5–5 ng g^{-1} lw). Previous studies have reported biomagnification of HBCD in aquatic food webs (Covaci et al., 2006). The increase in concentration between harbor seal adults and one of its prey items, white croaker, suggests biomagnification of HBCD may be occurring in the San Francisco Bay food web.

Concentrations reported for HBCD in wildlife around the world vary widely by species, tissue, geographic region, and proximity to sources (Covaci et al., 2006; de Wit et al., 2010; Law et al., 2008). Relative to PBDEs, few studies have reported on the occurrence of HBCD in wildlife living in marine ecosystems, particularly in the US. In this study, concentrations of HBCD in San Francisco Bay fish were comparable to those reported for fish in the Northwest Atlantic, Canadian lakes, and the coastal waters of Europe and China, but were generally one to two orders of magnitude lower than concentrations reported for freshwater fish in Europe, most of which were located near suspected point sources (Covaci et al., 2006; Ismail et al., 2009; Shaw et al., 2009; Xia et al., 2011). Concentrations of HBCD in San Francisco Bay cormorant eggs were comparable to those reported for aquatic bird eggs in the Arctic and South Africa but were typically one to two orders of magnitude lower than concentrations in the Great Lakes and Europe (Covaci et al., 2006; de Wit et al., 2010; Gauthier et al., 2007; Lundstedt-Enkel et al., 2006; Morris et al., 2004; Polder et al., 2008). HBCD has also been detected in osprey eggs collected from Seattle, Washington and the lower Columbia River in Oregon and Washington (Henny et al., 2009). HBCD was not detected frequently in these samples, but when detected, concentrations in eggs from the Seattle area were comparable to those in cormorant eggs from San Francisco Bay, while those from the lower Columbia River were much higher (maximum 1640 ng g^{-1} lw). Similar to the cormorant eggs, concentrations in San Francisco Bay harbor seal blubber samples were comparable to those reported in remote regions, such as the Arctic (de Wit et al., 2010; Law et al., 2008; Letcher et al., 2009; Morris et al., 2004; Tomy et al., 2009), but were as much as one to three orders of magnitude lower than the concentrations for marine mammals in Europe and Asia (Covaci et al., 2006; Law et al., 2008). The median concentration of HBCD in the San Francisco Bay adult seal blubber samples in this study (7 ng g^{-1} lw) was also comparable to the mean HBCD concentrations determined for the blubber of California sea lions collected from the California coast between 1993 and 2003 (9 ng g^{-1} lw) (Stapleton et al., 2006) and dolphins collected from Florida coastal waters between 1991 and 2004 (7 ng g^{-1} lw) (Johnson-Restrepo et al., 2008), but was lower than the median concentration of HBCD in the blubber of dolphins collected from coastal waters of the eastern US between 1993 and 2004 (100 ng g^{-1} lw) (Peck et al., 2008).

Despite higher concentrations of γ-HBCD in sediments, α-HBCD clearly dominated the HBCD isomer profile in San Francisco Bay wildlife. The contribution of α-HBCD to the total HBCD concentration varied within each fish species and the harbor seals, and for all wildlife samples was highly dependent on detection of the β-HBCD and γ-HBCD isomers. When detected, the contribution of α-HBCD was 65 and 100% for white croaker, 62–100% (median 100%) for shiner surfperch, 90–100% (median 100%) for cormorant eggs, and 59–100% (median 97%) and 53–100% (median 74%) for harbor seal adults and pups, respectively. Enrichment of the α-HBCD isomer in upper trophic level organisms in this study is consistent with studies conducted in other locations and has been hypothesized to be the result of variation in physicochemical properties among isomers that influence partitioning, uptake, and metabolism. In particular, a higher water solubility for α-HBCD compared to the other isomers,

Table 2
Summary of flame retardant chemicals in the San Francisco Bay sediments (ng g^{-1} dry) and wildlife (ng g^{-1} lipid) analyzed in this study. Sample-specific concentrations and detection limits are presented in the Supporting Information.

	Sediments (n = 10)			White croaker (n = 6)			Shiner surfperch (n = 8)			Double-crested cormorant egg (n = 3)[a]			Harbor seal blubberadults (n = 5)			Harbor seal blubberpups (n = 12)		
Compound	% detect	Range	med	% detect	Range	med	% detect	Range	med	% detect	Range	med	% detect	Range	med	% detect	Range	med
PBDEs	100	2.1–8.0	4.3	100	470–2260	1670	100	730–3930	1860	100	3425–5550	5500	100	530–5075	770	100	70–1370	330
HBCDs	–	0.1–1.7	0.3	–	<6.0–4.5	<6.0	–	2.5–24.7	6.5	–	21.6–39.0	37.4	–	4.4–19.3	7.1	–	2.0–11.7	3.5
α-HBCD	70	<0.04–0.6	0.05	33	<2.0–4.5	<2.0	100	2.5–19.6	5.3	100	21.6–39.0	33.6	100	2.8–19.3	7.1	100	1.3–10.2	2.7
β-HBCD	80	<0.04–0.2	0.03	0	<2.0	–	25	<5.0–5.1	–	33	<4.0–1.1	–	20	<0.6–0.4	–	25	<0.6–0.4	–
γ-HBCD	100	0.1–1.0	0.2	17	<2.0–1.4	–	13	<5.0–2.5	–	33	<4.0–2.7	–	40	<0.6–2.0	–	92	<0.6–1.6	0.9
Total DP	–	0.1–0.9	0.2	–	<1.0–1.8	0.5	–	<8.0–3.7	1.3	–	0.9–1.1	0.9	–	0.2–7.1	0.9	–	<0.1–0.1	<0.1
Anti-DP	100	0.06–0.6	0.2	83	<0.2–1.8	0.5	75	<2.0–3.7	1.3	0	<1.0	–	100	0.06–3.3	0.4	8	<0.08–0.06	–
Syn-DP	100	0.03–0.3	0.1	0	<0.8	–	0	<6.0	–	100	0.9–1.1	1.0	100	0.08–3.8	0.5	42	<0.03–0.07	<0.03
PBEB	50	<0.03–0.1	0.01	0	<3.0	–	0	<11.0	–	0	<0.8	–	100	0.07–0.5	0.2	83	<0.08–0.2	0.07
DBDPE	0	<24	–	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
BTBPE	50	<0.03–0.06	0.02	0	<3.0	–	0	<20	–	0	<2.0	–	0	<0.1	–	0	<0.1	–
HBB	0	<0.02	–	0	<3.0	–	0	<24	–	0	<8.0	–	0	<0.3	–	0	<0.7	–
TBB	0	<0.01	–	0	<30	–	0	<203	–	0	<8.0	–	0	<1.0	–	0	<1.0	–
TBPH	0	<0.20	–	NA	NA	NA	NA	NA	NA	0	<12	–	NR	NR	NR	NR	NR	NR

[a] 3 egg composites from same site; med = median; NA = not analyzed; NR = not reportable; <DL = less than method detection limit.

faster metabolism of the γ-HBCD and β-HBCD isomers compared to α-HBCD, and bioisomerization of γ-HBCD and β-HBCD to α-HBCD have been reported (Covaci et al., 2006; Law et al., 2006; Szabo et al., 2010; Zegers et al., 2005). Previous studies in other locations have also generally observed an increasing proportion of the α-HBCD isomer with increasing trophic level in the food web (Covaci et al., 2006); however, differences in the proportion of α-HBCD among species in this study were not substantial.

3.3. DP

All sediment samples contained detectable concentrations of DP. Total DP concentrations (syn- and anti-DP) ranged from 0.1 to 0.9 ng g^{-1} dw (median 0.2 ng g^{-1} dry) and were comparable to concentrations of HBCD in these sediments. To our knowledge, this is the first report of DP in marine sediments in the US. DP, manufactured by OxyChem in Niagara Falls, New York, has been studied most extensively in the Great Lakes, where its occurrence in the environment was first reported (Hoh et al., 2006). Concentrations in San Francisco Bay sediments were generally one to three orders of magnitude lower than sediments in Lake Ontario, which is downstream of the manufacturing facility, but were comparable to concentrations in Lakes Superior, Michigan, and Huron, where average concentrations ranged from 0.3 to 0.9 ng g^{-1} dw (Sverko et al., 2011). Concentrations in Bay sediments were comparable or lower than those observed in marine and freshwater sediments in China, where DP is also reportedly produced (Sverko et al., 2011). The fractional abundance of the syn-DP isomer (f_{syn}) in the San Francisco Bay samples was variable, ranging from 0.2 to 0.6, and the mean (0.35) resembled the f_{syn} in DP commercial mixtures (Sverko et al., 2008).

DP was detected in most San Francisco Bay wildlife samples, but at concentrations that were lower than HBCD and often approaching detection limits. The highest DP concentrations were detected in adult harbor seals (0.2–7 ng g^{-1} lw), but median concentrations among all wildlife samples were relatively similar (0.5–2 ng g^{-1} lw). The exception was harbor seal pups, in which DP was detected in less than half of the samples, and at concentrations ranging from below detection limits to 0.1 ng g^{-1} lw. Previous studies have suggested that DP undergoes biomagnification, but that it may not occur in all food webs as a result of species-specific variation in biotransformation and other factors (Sverko et al., 2011). As mentioned previously, biomagnification potential could not be directly assessed in this study. The high molecular weight and estimated octanol–water partition coefficient (log K_{ow} ~11, Table 1) indicate that the bioavailability of DP is likely low; however, biotransformation may also be influencing the concentrations observed in the Bay wildlife.

Similar to occurrence data for DP in sediments, reports for DP concentrations in wildlife are limited, with the majority conducted in the Great Lakes region and Asia. Concentrations of DP in San Francisco Bay fish were very similar to those reported for fish in the Great Lakes and Lake Winnipeg, which ranged between 0.1 and 4 ng g^{-1} lw, with most measurements ≤1 ng g^{-1} lw (Shen et al., 2011; Sverko et al., 2011). In contrast, concentrations in San Francisco Bay fish were typically one to three orders of magnitude lower than fish in Asia, particularly those in fish collected near e-waste recycling sites (Sverko et al., 2011). Concentrations of DP in the San Francisco Bay cormorant eggs were generally more than an order of magnitude lower than concentrations in herring gull eggs in the Great Lakes and other parts of Canada (0.2–15 ng g^{-1} wet weight; sample-specific lipid weight concentrations not provided) and falcon eggs in Canada (38–65 ng g^{-1} lw), presumably due to closer proximity to the chemical manufacturing facility in the region. Concentrations of DP in Bay cormorant eggs were more comparable to stork and falcon eggs in Spain (Sverko et al., 2011). To our knowledge the detection of DP in San Francisco Bay harbor seals is the first report of DP occurrence in marine mammals.

Because DP isomer concentrations were near detection limits in most of the San Francisco Bay fish, bird egg, and seal pup samples, f_{syn} could only be determined for adult seal samples. In adult seals, f_{syn} was very consistent, ranging from 0.51 to 0.57 with a mean (±one standard deviation) of 0.54 ±0.03. This enrichment of syn-DP in the seals relative to Bay sediments (f_{syn} 0.35) is consistent with previous studies suggesting that syn-DP may be more bioaccumulative than anti-DP (Shen et al., 2011; Wu et al., 2010a). DP data for marine mammals in other studies is not available, though the f_{syn} for seals in this study are comparable or somewhat higher to the f_{syn} observed in fish in other studies (Hoh et al., 2006; Shen et al., 2011; Tomy et al., 2007; Wu et al., 2010a). The limited data available indicate that f_{syn} can vary substantially by species, foodweb, and trophic level and that a number of environmental fate processes, including species-specific biotransformation efficiencies, may be influencing these observations (Shen et al., 2011; Sverko et al., 2011; Tomy et al., 2007).

3.4. PBEB

PBEB was detected in half of the San Francisco Bay sediment samples, at maximum and median concentrations of 0.1 and 0.01 ng g^{-1} dw, respectively. Detection of PBEB in sediments did not appear to correspond with known sources (e.g., outfalls) or higher population densities compared to the other sample sites. Along with BTBPE, median concentrations of PBEB were two orders of magnitude lower than PBDEs and one order of magnitude lower than HBCD and DP in these samples. To our knowledge, this study is the first report of PBEB in sediments in the US. PBEB has been detected in sediments near a metal recycling area in Norway at a concentration of 0.03 ng g^{-1} dw (Arp et al., 2011) and in river sediments in Spain at concentrations as high as 10 ng g^{-1} dw (Guerra et al., 2010). In the US, Hoh et al. (2005) detected low concentrations of PBEB in Chicago air samples, but it was not detected in the Lake Michigan sediment core in the same study. Presumably the lack of occurrence data for PBEB in sediments is due to a decrease in worldwide production volumes over the last few decades (Hoh et al., 2005).

PBEB was detected in all adult harbor seal samples (range 0.07–0.5 ng g^{-1} lw) and the majority of seal pup samples (<0.08–0.2 ng g^{-1} lw) from San Francisco Bay. Concentrations in adult seals (median 0.2 ng g^{-1} lw) were not significantly different from concentrations in pups (median 0.07 ng g^{-1} lw) ($p = 0.10$). PBEB was not detected in fish or cormorant egg samples, likely due to higher detection limits for these samples (1–11 ng g^{-1} lw).

Few studies have reported on the occurrence of PBEB in wildlife living in aquatic environments (recently reviewed by Arp et al., 2011; Covaci et al., 2011). The highest concentrations have been reported for lake trout collected between 1979 and 2004 from Lake Ontario (17–320 ng g^{-1} lw). Concentrations of PBEB in the harbor seal blubber samples from San Francisco Bay were generally lower than those reported for marine mammals in the Gulf of Maine (<0.02–7 ng g^{-1} lw) (Montie et al., 2010).

3.5. BTBPE

BTBPE was detected in half of the San Francisco Bay sediment samples, at maximum and median concentrations of 0.06 and 0.02 ng g^{-1} dw, respectively. Similar to PBEB, detection of BTBPE in sediments did not appear to correspond with known sources (e.g., outfalls) or higher population densities compared to the other sample sites. Though BTBPE and PBEB were both detected at half the sample sites, they were not detected at the same sites (SI Table 3). Along with PBEB, median concentrations of BTBPE were two orders of magnitude lower than PBDEs, and one order of magnitude lower than HBCD, and DP in these samples. Concentrations of BTBPE in the San Francisco Bay sediment samples were most similar to sediments in the Western Scheldt estuary in the Netherlands (below detection limits to 0.3 ng g^{-1} dw) (López et al., 2011), but were two orders of magnitude lower than the concentrations previously detected in sediment cores from Lake Ontario and Lake Michigan and three orders of magnitude lower than concentrations reported for sediments from southern China (Covaci et al., 2011).

Despite detection in Bay sediments, BTBPE was not detected in any of the Bay wildlife samples analyzed in this study (detection limits 0.03–20 ng g^{-1} lw). Occurrence studies conducted worldwide have reported BTBPE accumulation in fish, bird eggs, and marine mammals, but at concentrations that were generally less than 5 ng g^{-1} lw (Covaci et al., 2011). In the only study conducted on species inhabiting US coastal waters, BTBPE was not detected (<0.1 ng g^{-1} lw) in marine mammals from the Gulf of Maine (Montie et al., 2010). Previous studies have suggested that BTBPE has the potential for biomagnification in aquatic food webs, however, this may be lower compared to PBDEs

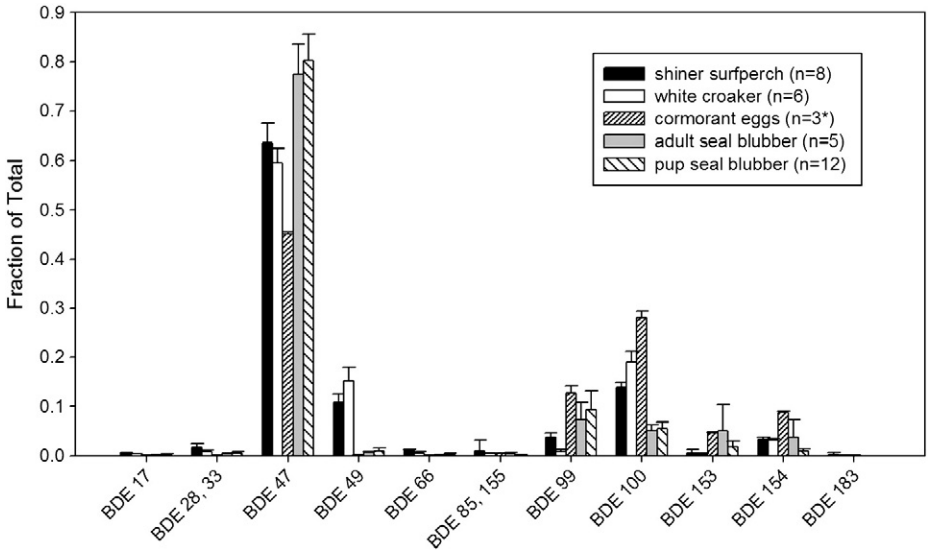

Fig. 2. PBDE profile of the predominant congeners detected in the San Francisco Bay wildlife samples analyzed in this study. *The three cormorant egg composites were collected from the same nesting site.

and HBCD (Covaci et al., 2011) because of the higher hydrophobicity of BTBPE (log K_{ow} 7.9, Table 1).

3.6. HBB, DBDPE, TBB, TBPH

HBB and DBDPE were not detected in the San Francisco Bay samples. TBB and TBPH were also not detected; however, detection may have been compromised by matrix interferences in all samples, particularly the wildlife samples. A small number of studies have reported the occurrence of HBB in sediments in Europe and Asia, with most concentrations <5 ng g^{-1} dw (Arp et al., 2011). In wildlife, HBB has been detected at concentrations mostly <5 ng g^{-1} lw in fish in France, bird eggs from the Great Lakes and Norwegian Arctic, and marine mammals from the Gulf of Maine and the Arctic (Covaci et al., 2011; Montie et al., 2010). Much higher concentrations of HBB (means range from 200 to 3100 ng g^{-1} lw) have been detected in a freshwater food web near an electronic waste recycling facility in South China, where biomagnification of HBB was observed (Wu et al., 2010b). Studies conducted in Europe have reported DBDPE sediment concentrations ranging from 0.2 to 11 ng g^{-1} dw (López et al., 2011; Ricklund et al., 2010), and the highest concentrations reported in wildlife are for herring gull eggs in the Great Lakes (range 1–288 ng g^{-1} wet weight) and prawn and fish species living near an electrical waste recycling site in South China (<4–340 ng g^{-1} lw). TBB and TBPH have been previously detected in wildlife. Fish collected from the Great Lakes contained TBB and TBPH at concentrations ranging from 0.01–0.04 and 0.04–0.08 ng g^{-1} (unit basis not provided), respectively (Zhou et al., 2010). In coastal waters of Hong Kong, South China, finless porpoise contained TBB and TBPH at concentrations ranging from <0.04–70 and <0.04–3859 ng g^{-1} lw, respectively (Lam et al., 2009). In the same study, dolphin TBB concentrations were below detection limits (<0.04 ng g^{-1} lw), but TBPH ranged from <0.04 to 5 ng g^{-1} lw.

3.7. Correlations among flame retardants

Correlation analyses were conducted for all flame retardants detected in each of the matrices analyzed in this study to investigate possible similarities in sources and fate of these compounds in the Bay. The resulting correlation matrices are shown in Supporting Information Tables 8–12. A significant correlation was only observed for BDE 47 and sum HBCD in shiner surfperch (Spearman's $r = 0.88$, $p = 0.007$). BDE 47 and HBCD are both highly bioaccumulative, persistent, brominated compounds, which suggests that their fate in aquatic organisms may be similar. Given that Penta-BDE and HBCD are both associated with urban sources, it is not clear why a significant correlation between BDE 47 and HBCD in sediments was not also observed.

3.8. Spatial patterns in sediment concentrations

Flame retardant concentrations in sediments were compared among Bay segments to investigate any spatial patterns and thus provide insight into possible source areas of contamination. For the flame retardants most frequently detected in sediments (i.e. PBDEs, HBCDs, and DPs), the highest concentrations tended to be in samples from the Central and Lower South segments of San Francisco Bay and the lowest concentrations tended to be in the northern segments (Fig. 3). This spatial pattern is likely a reflection of the differences in the extent of urbanization among Bay segments and the hydrodynamics of the Bay system. Urbanization is higher in the Central and Lower South Bays compared to San Pablo, Suisun, and South Bays. In addition, the Central Bay contains the highly populated cities of San Francisco and Oakland, and their waterfronts include the majority of the industrial, port, and shipping activities in the Bay Area. In general, San Francisco Bay experiences a high volume of tidal exchange with the Pacific Ocean (Conomos, 1979). However, the Bay segments exhibit varying degrees of tidal mixing and freshwater inflow, which influence the extent of dilution of chemical contaminants present in urban runoff and wastewater effluent that enters Bay surface waters. In the Lower South Bay, surface waters experience the least amount of mixing with non-effluent flow, particularly in the dry season, and have the highest hydraulic residence time compared to other segments. South Bay surface waters therefore often have higher contaminant concentrations compared to other Bay segments (http://www.sfei.org/tools/wqt).

3.9. Implications

The potential impacts to San Francisco Bay wildlife due to chronic exposure to the concentrations of flame retardants observed in this study are for the most part unknown. PBDEs were detected in the highest concentrations by far and have been associated with a wide variety of reproductive, developmental, and neurobehavioral effects, including those related to disruption of the endocrine system. However, only a relatively small number of studies have investigated PBDE toxicity in wildlife, and many of these have been conducted at concentrations higher than those typically observed in the environment (reviewed in Shaw et al., 2010). In studies with fish, increased susceptibility to pathogenic microorganisms (Arkoosh et al., 2010) and altered locomotion behavior (Chou et al., 2010) have been observed at concentrations comparable to those found in fish samples in this study. In birds, PBDEs have been associated with various reproductive effects in American kestrels (McKernan et al., 2009) and osprey (Henny et al., 2009) at concentrations within range of those found in San Francisco Bay tern eggs in previous studies (She et al., 2008; RMP unpublished data), but higher than those observed in cormorant eggs in the present study. Though PBDEs have been or are in the process of being phased out, continued monitoring in San Francisco Bay is warranted given their potential for toxicity, the reservoir in current-use consumer products, and the anticipated time lag between decreased use in consumer products and accumulation in the environment.

Relative to PBDEs, concentrations of the other flame retardants detected in the San Francisco Bay wildlife samples were generally low. A few studies have investigated the potential human health effects of these compounds, though toxicity threshold data for wildlife are extremely limited and only a small number are available in the peer-reviewed literature (Shaw et al., 2010). Though not detected in this study, TBB, TBPH, and DBDPE should be considered for continued monitoring in San Francisco Bay and other aquatic systems because of their high volume use as PBDE replacements and anticipated persistence in the environment. Future studies should also examine the fate and distribution of the organophosphate flame retardants in the Bay. Further study of tris(1,3-dichloro-2-propyl) phosphate in particular is needed, considering it is a known replacement for penta-BDE (Stapleton et al., 2009, 2011) and has the potential to act as a mutagen, carcinogen, neurotoxin, and endocrine disruptor (Dishaw et al., 2011; Meeker and Stapleton, 2010; Shaw et al., 2010). Because the samples in this study were collected soon after the US phase-out of PBDEs began, results from this study may be considered a baseline for PBDE replacement products in San Francisco Bay.

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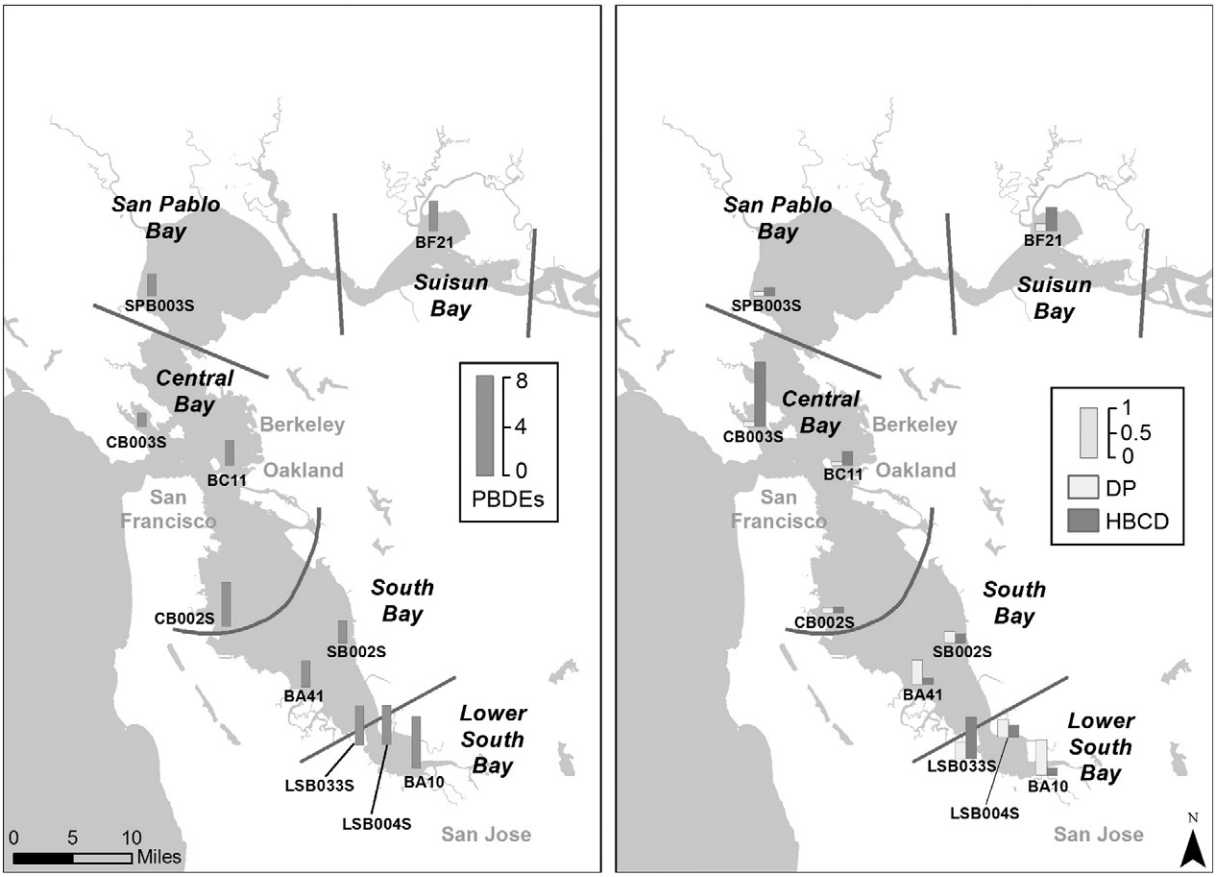

Fig. 3. Concentrations of PBDEs, HBCD, and DP in San Francisco Bay sediments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.envint.2012.06.005.

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