Environmental Science & Technology
Article
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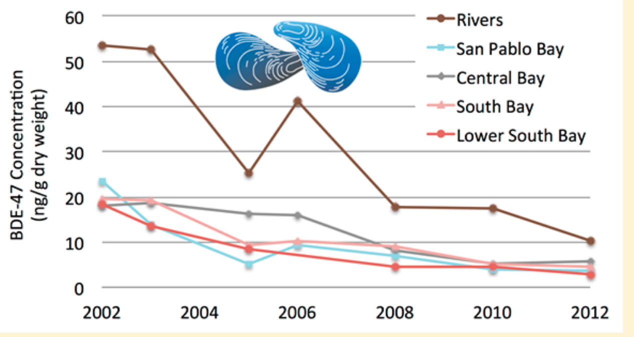
Declines in Polybrominated Diphenyl Ether Contamination of San Francisco Bay following Production Phase-Outs and Bans

Rebecca Sutton,*,† Margaret D. Sedlak,† Donald Yee,† Jay A. Davis,† David Crane,‡ Richard Grace,§ and Nirmela Arsem∥

†San Francisco Estuary Institute, 4911 Central Avenue, Richmond, California 94804, United States
‡California Department of Fish and Wildlife, 2005 Nimbus Road, Rancho Cordova, California 95670, United States
§AXYS Analytical Services Ltd., 2045 Mills Road West, Sidney, British Columbia V8L 5X2, Canada
∥East Bay Municipal Utility District, 375 11th Street, Oakland, California 94612, United States

S *Supporting Information*



ABSTRACT: California has implemented unique consumer product flammability standards. Polybrominated diphenyl ether (PBDE) flame retardants were once widely incorporated into products to meet these standards, but concerns regarding toxicity and accumulation in humans and biota led to nationwide phase-outs and state bans. A decade of PBDE monitoring in San Francisco Bay has resulted in a data set that covers periods during and after PBDE use and consists of hundreds of measurements of water, sediment, and biota. While PBDEs remain widely detected in biota, levels have declined by nearly half in sport fish and 74−95% in bivalves and bird eggs. Concentrations of BDE-47 in sediment have dropped by over one-third from 2002 to 2012; in water, a decline is not yet evident. The dominant congener in sediment, DecaBDE component BDE-209, showed no temporal trend. U.S. production of DecaBDE ended in 2013; future monitoring may reveal declines. Overall, the data indicate that reduced production can result in relatively rapid reductions in the concentrations of some hydrophobic contaminants in biota and sediment, particularly when implemented after only a few decades of heavy use. Recent changes to California's flammability standards may lessen the use of other flame retardants and similarly reduce Bay contamination.

INTRODUCTION

The state of California has established a number of unusual regulations originally thought to improve fire safety. The California Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation ("the Bureau") develops Technical Bulletins (TBs) describing flammability standards for consumer products, such as TB 117 for upholstered furniture.[1] Products that meet California's unique standards are sold throughout the United States.[2] Manufacturers have typically incorporated chemical flame retardants into products to ensure compliance.

Widespread commercial production and use of polybrominated diphenyl ethers (PBDEs) as flame retardants in consumer goods began in the 1970s.[3] PBDEs are diphenyl ethers with one to ten bromine atoms. The commercial mixture PentaBDE, composed primarily of congeners BDE-99 and BDE-47, was the primary flame retardant used for upholstered furniture.[3] OctaBDE, composed predominantly of BDE-183, BDE-197, and BDE-203, was used primarily in thermoplastic (acrylonitrile butadiene styrene) resins and often found in housings of electronic office equipment and computer casings, among other items.[3] DecaBDE, composed primarily of BDE-209, was added to many plastics and textiles, with particularly common use in electronics.[3,4]

Extensive use in consumer goods led to unusually high PBDE exposure in San Francisco residents[5,6] and contamination of San Francisco Bay ("the Bay") and its wildlife.[5,7−10] Samples of Forster's tern eggs collected in the Bay in 2002 exhibited the highest level of PBDE contamination in biota reported at the time: 63 300 ng/g of lipid.[10]

In response to increasing concerns regarding accumulation and toxicity,[3,11,12] the major manufacturer of PentaBDE and OctaBDE ceased production in 2004, preceding a California ban that would take effect in 2006. The U.S. Environmental Protection Agency (EPA) issued a significant new use rule for these mixtures in 2006, requiring notification from companies 90 days before manufacture or import. In 2013, U.S. manufacturers of DecaBDE phased out production; however, the mixture may still be present in goods produced in other

Received: July 31, 2014
Revised: October 31, 2014
Accepted: November 7, 2014
Published: December 28, 2014

DOI: 10.1021/es503727b
Environ. Sci. Technol. 2015, 49, 777−784

countries as well as in goods manufactured prior to the phase-out but still in use or in the waste stream. To address concerns over the use of chemical flame retardants in general, the Bureau issued TB 117-2013, a revised flammability standard that went into effect in 2014 and eliminated the need to incorporate these substances into upholstered furniture and many items for infants and young children.[13] As a result, chemical flame retardants are expected to disappear from many new consumer goods.

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP), administered by the San Francisco Estuary Institute, is a monitoring program initiated in 1993 that provides the information needed to manage Bay water quality. The RMP has conducted PBDE monitoring over the past decade to determine the impact of reduced production on environmental contamination. The RMP monitors Bay water and sediment, the latter being an especially important matrix for hydrophobic contaminants such as PBDEs.

In addition, the RMP monitors bioaccumulative pollutants such as PBDEs in Bay biota, including bivalves, sport fish, and aquatic piscivorous birds. Bivalves are exposed to PBDEs through food, water, and sediment, providing an integrated measure of contaminant exposure over time. They also act as transfer vectors of contaminants to higher trophic levels of aquatic food webs. Similarly, sport fish can transfer contaminants to human consumers. Aquatic bird eggs represent accumulation typical of higher trophic levels and have been found to be among the most PBDE-contaminated of Bay matrices.[10] Unlike most PBDE congeners, BDE-209 has a relatively short half-life in organisms and is often found at lower levels in tissue samples from aquatic biota.[3]

The RMP data set is unique in its long-term, comprehensive characterization of an urban estuary via multiple matrices. All of the data are publicly available via the California Environmental Data Exchange Network (www.ceden.org). An examination of contaminant levels during and after PBDE production indicates the apparent rapid water quality benefit of policies to reduce the use of these persistent, bioaccumulative, and toxic compounds in consumer goods.

■ METHODS

Sampling and PBDE Analyses. The RMP has conducted extensive PBDE monitoring of San Francisco Bay for over a decade, producing data for the following matrices and years: sediment (2002–2003, 2007–2012) and water (2002–2011); transplanted and resident bivalves (2002, 2003, 2005, 2006, 2008, 2010, 2012); sport fish (2000 (semiquantitative), 2003, 2006, 2009); and the eggs of cormorants (2002, 2004, 2006, 2009, 2012) and terns (2009, 2012).

Sediment and water samples were spatially distributed throughout the Bay using a generalized random tessellation-stratified (GRTS) statistical design. Sediment was sampled at 40 random sites and seven historical sites in the summer; biennial winter sampling commenced in 2010 using at least 20 random and seven historical sites. Surface sediment samples were collected at a depth of 0 to 5 cm using a Young-modified Van Veen grab with a surface area of 0.1 m^2. Sediment from two or more grabs taken at each site was composited, homogenized by hand mixing, and provided to the East Bay Municipal Utility District (EBMUD) Laboratory (Oakland, CA, USA) for extraction and analysis.

Water samples were collected annually in the summer at 17 random locations and five historical sites. Solid-phase-extracted water samples were collected 1 m below the surface using the AXYS Infiltrex 300 system by pumping 100 L through a 1 μm glass fiber cartridge particulate filter and columns filled with XAD-2 resin. Samples were extracted and analyzed by AXYS Analytical (Sidney, BC, Canada); filters were extracted by ambient-temperature sonication in acetonitrile and hexane, and XAD-2 columns were Soxhlet-extracted in methylene chloride.

Transplanted bivalves (*Mytilus californianus*) were deployed at nine stations in the Bay for 90 days during the summer. In 2002, Pacific oysters (*Crassostrea gigas*) were also deployed in some Bay locations. At two upstream river sites, resident freshwater bivalves (*Corbicula fluminea*) were collected. Bivalves were retrieved, processed using clean techniques, and aliquoted for analysis. Generally, 30–40 bivalves were composited from each site. Samples were homogenized, extracted, and analyzed by the California Department of Fish and Wildlife (CA-DFW; Rancho Cordova, CA, USA) in 2003 and prior and by AXYS Analytical since 2006. AXYS Analytical also analyzed archived samples collected in 2005 and prepared by CA-DFW.

Eight species of sport fish were collected at five popular recreational fishing areas within the Bay every three years. Most sites were located in the Central Bay. Fish were typically dissected skin-off, and only the fillet muscle tissue was analyzed. Some species that were too small to be filleted (e.g., shiner surfperch, *Cymatogaster aggregata*) were processed whole but with the head, tail, and viscera removed. Samples were typically composites of three or more fish and were analyzed by CA-DFW.

Prior to 2009, samples of white croaker (*Genyonemus lineatus*) were analyzed with skin, inconsistent with advice from the California Office of Environmental Health Hazard Assessment for preparation of fish fillets.[14] In 2009, the RMP began testing fillets without skin; as a result, the earlier measurements are not comparable to the white croaker measurements made in 2009.

Eggs of double-crested cormorants (*Phalacrocorax auritus*) were collected at three fixed locations within the Bay: Richmond Bridge (Central Bay), Wheeler Island (Suisun Bay), and Don Edwards Wildlife Refuge (South Bay). At each site, composites were formed from seven to ten eggs. Eggs of Forster's terns (*Sterna forsteri*) were collected from established colonies at variable locations within the Bay (most in South Bay). Eggs were composited, homogenized, and analyzed by CA-DFW.

PBDE analyses performed by EBMUD and AXYS Analytical used gas chromatography/high-resolution mass spectrometry (GC/HRMS) and lab-modified implementations of EPA method 1614.[15] PBDE analyses performed by CA-DFW prior to 2006 and from 2006 on were performed with GC/dual-electron-capture detection (GC/dual-ECD) and GC/tandem mass spectrometry (GC/MSMS), respectively, using methods described previously.[9,16] The results were generally good for quality-control samples, aside from sporadic contamination found in blank samples; sample results were censored if the signal found in the blank was one-third or more of a sample result. Further details regarding data quality are provided in the Supporting Information.

Statistical Analyses. Maps of PBDE congener concentrations in sediment and water were constructed using spatial interpolation techniques. Area-weighted mean sediment and water PBDE concentrations for the entire Bay were calculated to adjust for variation in the density of sampling stations among Bay regions;[17] means calculated for the five regions within the

DOI: 10.1021/es503727b
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Bay were not adjusted. Temporal trends were examined for statistical significance using t tests. A (two-sided) p value of <0.05 was considered statistically significant. Linear regressions were used to characterize the magnitudes of declines for sediment and bivalves; Anderson−Darling tests of standardized residuals indicated that these data were normally distributed. In contrast, the water BDE-47 data showed signs of non-normal distribution and were log-transformed to assess the temporal trend. For sport fish and bird eggs (time series with fewer data points), a comparison of the earliest and most recent measurements was considered sufficient.

■ RESULTS AND DISCUSSION

Sediment. Total PBDE concentrations in Bay sediment were typically less than 10 ng/g dry weight (maximum 50 ng/g) and often dominated by BDE-209, the primary component of the commercial mixture DecaBDE. The levels of BDE-209 (Figure 1) and BDE-47 (Figure 2) as well as total PBDEs were comparable to those measured in the Strait of Georgia, British Columbia, Canada[18] and to the area-weighted geometric means of PBDEs found in the offshore region of the Southern California Bight, as opposed to the more contaminated coastal embayment regions.[19]

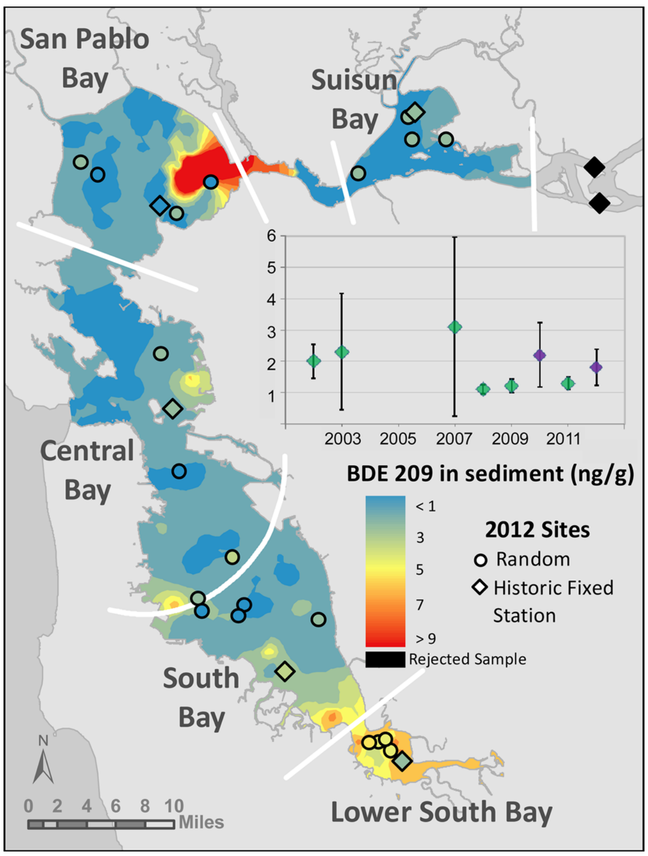

Figure 1. Concentrations of BDE-209 in sediment in San Francisco Bay (ng/g dry weight). The contour plot is based on RMP measurements from years sampled in the dry season (2002, 2003, 2007, 2008, 2009, and 2011). Colored symbols on the map show the most recent results (April 2012). Circles represent random sites, and diamonds represent historic fixed stations. The plot shows annual Bay-wide means with 95% confidence intervals. Green diamonds on the plot indicate dry-season samples, and purple diamonds indicate wet-season samples.

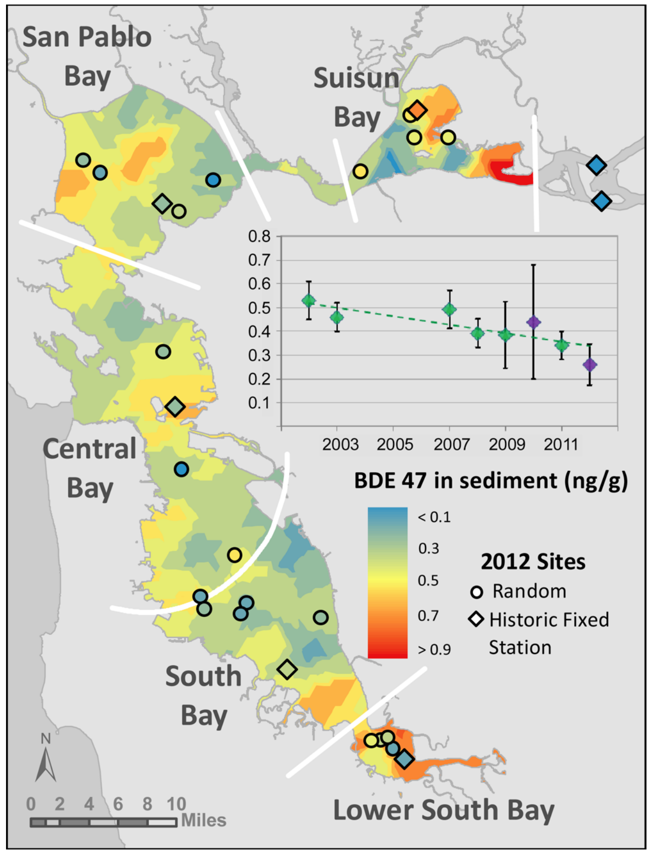

Figure 2. Concentrations of BDE-47 in sediment in San Francisco Bay (ng/g dry weight). The contour plot is based on RMP measurements from years sampled in the dry season (2002, 2003, 2007, 2008, 2009, and 2011). Colored symbols on the map show the most recent results (April 2012). Circles represent random sites, and diamonds represent historic fixed stations. The plot shows annual Bay-wide means with 95% confidence intervals. Green diamonds on the plot indicate dry-season samples, and purple diamonds indicate wet-season samples. The green line indicates the statistically significant regression for the dry-season data (see the Supporting Information for the equation).

BDE-209 is the dominant congener in sediment samples taken from several locations worldwide, including Asia, Europe, and the U.S. Great Lakes.[20] Because widespread background laboratory contamination makes BDE-209 particularly difficult to quantify, this congener is often excluded from sediment analyses, resulting in total PBDE values that do not fully represent the extent of contamination. A recent National Oceanic and Atmospheric Administration (NOAA) Mussel Watch Program survey quantified sediment PBDE levels, excluding the dominant congener BDE-209 and other highly brominated congeners, and found that San Francisco Bay samples were in the medium range for 122 sediment samples collected nationwide.[21]

Regionally, the long-term average dry-season concentrations of BDE-209 (2002, 2003, 2007, 2008, 2009, and 2011) were highest in the Lower South Bay (5.2 ng/g dry weight; Figure 1). The results observed in two years of wet-season sampling (2010 and 2012) were within the range of values measured during the dry seasons, with the highest concentrations (including samples at 16 ng/g dry weight in Lower South Bay and 8.4 ng/g dry weight in San Pablo Bay) occurring in areas previously shown to have relatively high concentrations. The averages for the 2010 and 2012 wet seasons (2.2 and 1.8

DOI: 10.1021/es503727b
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ng/g dry weight, respectively) were similar to the long-term average for the dry season (1.8 ng/g dry weight) and in the middle of the range of annual dry-season averages.

Similarly, the long-term mean dry-season concentrations of BDE-47 in sediment were highest in the Lower South Bay (0.65 ng/g dry weight; Figure 2), and the wet-season concentrations were within the range of values measured during the dry seasons.

The Bay-wide averages indicate a statistically significant decline in BDE-47 sediment contamination, with linear regression indicating that the levels dropped by over one-third from 2002 to 2012 (R^2 = 0.71; see the Supporting Information). Trends over time may be particularly difficult to detect in sediment samples as a result of compositing of the top 5 cm of sediment; the sediment accretion rate in most areas of the Bay is less than 0.5 cm/year and surface sediments are mixed by bioturbation and wind wave resuspension, so any recent trends can be obscured easily by mixing and compositing. For this reason, measurements indicating declining BDE-47 levels in sediment for recent years are especially notable and are probably related to the lack of domestic production and use of PentaBDE following the nationwide phase-out and state ban of this commercial mixture.

In contrast, the Bay-wide means of BDE-209 in sediment do not indicate a declining trend (see the Supporting Information). Because the nationwide phase-out of the source of this congener, DecaBDE, did not occur until 2013, a decline in contamination would not be expected at this time.

Surface Water. Concentrations of total PBDEs measured in San Francisco Bay surface waters were ≤1000 pg/L. While few measurements of PBDEs in seawater along urban coasts have been reported in the literature, the average Bay water concentrations were comparable to or greater than those measured near Hong Kong and an industrialized urban region of Turkey.[22,23] The San Francisco Bay levels have not demonstrated a clear trend over the last 10 years, with an interdecile range of total PBDEs (the sum of measurable congeners) from 65 to 603 pg/L (median 154 pg/L) in water. The maximum concentration of BDE-47, the dominant congener in water, was observed in 2004 (Figure 3).

Since 2004, the Bay-wide average levels of BDE-47 are suggestive of a decline, though this trend is not statistically significant (log-transformed BDE-47 values, p = 0.08; see the Supporting Information). The three lowest annual average concentrations were measured in 2008−2010. The mean BDE-47 concentration in Bay water in 2011 (43 pg/L) was higher than the averages for 2008−2010 (ranging from 18 to 23 pg/L), but this was largely due to one high value measured in the Central Bay (117 pg/L). The Bay-wide average BDE-47 concentration for the 10-year period from 2002 to 2011 was 45 pg/L.

The levels of PBDEs in water show considerable spatial variability within the Bay (Figure 3). The regional distribution of BDE-47 in water was distinctly different than that of BDE-47 in sediment (Figure 2), with the water samples suggesting a larger number of discrete hot spots of contamination. The highest long-term average concentration of BDE-47 from 2002 to 2011 was found in Suisun Bay (65 pg/L). The maximum concentrations (two samples greater than 300 pg/L) were observed at locations in Suisun Bay and San Pablo Bay, both in 2004. The high concentrations in Suisun Bay suggest the presence of PBDE inputs into the northern estuary. Although monitoring indicates regional differences in the concentration of PBDEs in Bay waters, the averages for all portions of the Bay show lower levels for the four most recent years of sampling (Figure 4).

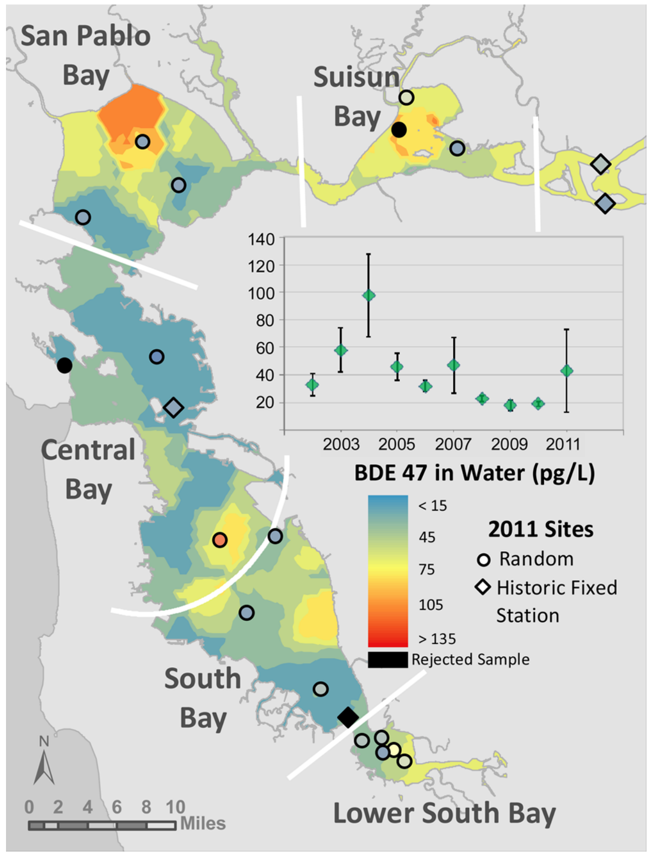

Figure 3. Concentrations of BDE-47 in water in San Francisco Bay (pg/L). Map plot based on RMP dry season data. Colored symbols on map show results for samples collected in 2011. Circles represent random sites, and diamonds represent historic fixed stations. Plot shows annual Bay-wide means with 95% confidence intervals.

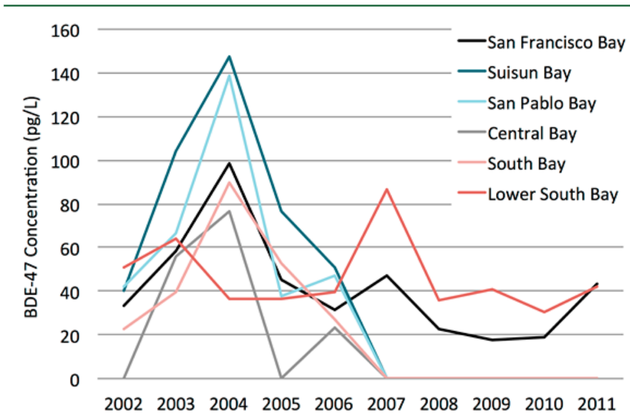

Figure 4. Regional trends in BDE-47 concentration (pg/L) in San Francisco Bay water over time.

Bivalves. The concentrations of total PBDEs in all bivalves were mostly between 6.2 and 62 ng/g dry weight (interdecile range), with a median across the monitored period of 20 ng/g dry weight. Resident bivalves located in the river stations had higher concentrations (median 61 ng/g), perhaps as a result of a longer exposure period or interspecies differences in

DOI: 10.1021/es503727b
Environ. Sci. Technol. 2015, 49, 777−784

bioaccumulation. In general, the more highly brominated congeners that constitute the DecaBDE formulation were not detected in bivalves. The most abundant congener was PentaBDE component BDE-47.

The levels of PBDEs and particularly BDE-47 have exhibited statistically significant declines at all sites across the Bay in both transplanted and resident bivalves (Figure 5). Linear regression

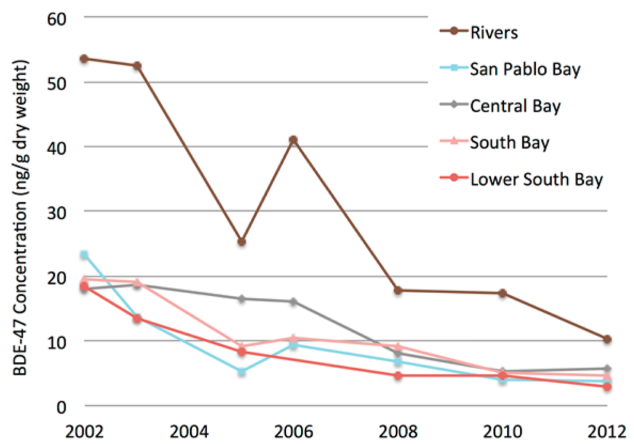

Figure 5. Concentrations of BDE-47 in bivalves (ng/g dry weight).

of the concentrations in each region with time indicated declines of 80−95% from 2002 to 2012 (R^2 range of 0.66 to 0.90; see the Supporting Information). Excluding river sites, the PBDE concentrations in bivalves did not exhibit a high degree of spatial variation within San Francisco Bay (Figure 5). These Bay-transplanted bivalve BDE-47 measurements were significantly higher than those found in bivalves from a nearby reference nonurban coastal site, Bodega Bay, the source of the transplanted bivalves (values ranging from nondetectable to 0.94 ng/g dry weight).

The BDE-47 levels for mussels reported by the RMP are generally lower than those reported by the NOAA Mussel Watch Program, which collects and composites resident mussels (*Mytilus* spp.) from San Francisco Bay sites.[24] Because NOAA uses resident mussels rather than transplants, the higher levels reported by the agency are likely due to longer exposure periods.

A comparison of nationwide bivalve PBDE measurements (sum of 38 congeners) conducted by NOAA from 2004 to 2007 revealed the highest levels to be from samples located near urban, industrialized regions.[21] A San Francisco Bay sample obtained at the Dumbarton Bridge had the seventh highest lipid-normalized level in the nation: 900 ppb lipid weight (63 ng/g dry weight). All of the Bay samples analyzed by NOAA were considered high in PBDEs on the basis of a cluster analysis of nationwide measurements.

Sport Fish. PBDEs were widely detected in fish samples from San Francisco Bay. The dominant congener found in fish tissues was BDE-47, followed by BDE-100 and BDE-154; BDE-209 was not detected in any fish samples examined by the RMP. The levels in Bay fish were comparable to those found in other urban coastal regions of North America and typically higher than those found in fish from less urban regions along the coasts of California and the Pacific Northwest.[25−27]

In 2009, the average PBDE concentrations were highest in shiner surfperch and northern anchovy, two of the smallest species sampled (both at 8 ppb or ng/g wet weight; Table 1).

Table 1. PBDE Concentrations (ppb) in Sport Fish Species in San Francisco Bay in 2009

species	composite *n*	PBDE conc. (ppb)[b]	average length (mm)
California halibut	3	1.8 ± 0.5	663
jack smelt	4	1.5 ± 0.4	263
leopard shark	3	5.0 ± 1.2	1095
northern anchovy	9	7.9 ± 1.0	89
shiner surfperch	15	8.3 ± 2.9	112
striped bass	6	5.0 ± 2.6	609
white croaker[a]	12	4.3 ± 2.5	256
white sturgeon	4	2.8 ± 1.3	1322

[a]White croaker data are for fillets without skin. [b]Values are reported as mean ± standard deviation.

The highest single concentration found was 14 ppb in a shiner surfperch sample. Other species averaged 5 ppb or less. Sampling in earlier years showed somewhat different distributions of contamination. In 2006, the average PBDE levels were highest in white croaker (fillet with skin; mean 57 ppb, standard deviation ± 22 ppb), white sturgeon (21 ± 9 ppb), and shiner surfperch (13 ± 5 ppb). The highest concentration in 2006 was 95 ppb in a white croaker sample (fillet with skin). Because white croaker samples were analyzed without skin after 2006, these measurements are not comparable with white croaker measurements made in 2009. The species with the next highest concentration measured in 2006 was a white sturgeon sample containing 31 ppb. In 2003, the average PBDE levels were highest in white sturgeon (42 ± 37 ppb) and anchovies (37 ± 27 ppb). The highest concentration measured in 2003 was 88 ppb in a white sturgeon sample.

Shiner surfperch is a species known for high site fidelity and thus is a useful indicator of localized levels of contamination. Significant spatial variation was detected in the 2009 levels of PBDEs in shiner surfperch samples obtained in different regions of the Bay. Oakland had the highest average concentration (13 ppb), which was not significantly different from that of the South Bay (10 ppb), the second highest concentration. Both of these levels were significantly higher than those found for Berkeley (8 ppb), San Francisco (6 ppb), and San Pablo Bay (5 ppb).

In contrast, Brown et al.[25] collected two shiner surfperch composite samples each from four Bay locations in 2000 and found the average sum of five major PBDE congeners (BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154) to be highest in the South Bay (16 ppb), followed by Berkeley (10 ppb), San Francisco (9 ppb), and finally Oakland (7 ppb). It is possible that this apparent difference in the spatial distribution of PBDEs in shiner surfperch was caused by the relatively small sample size of this study relative to that of the RMP.

The combination of high site fidelity and relatively high PBDE concentrations makes shiner surfperch a good indicator of trends in contamination through time. Consistent with the other matrices sampled, the Bay-wide average PBDE concentration for shiner surfperch in 2009 (8 ± 3 ppb) was significantly lower than the averages observed in 2003 (15 ± 4 ppb) and 2006 (13 ± 5 ppb), indicating a decline in contamination by almost half.

Aquatic Bird Eggs. A Forster's tern egg sample collected from the South Bay in 2002 by California Environmental Protection Agency scientists contained the highest concen-

DOI: 10.1021/es503727b
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Table 2. Mean Concentrations of Total PBDEs in Cormorant Eggs (ng/g of lipid)[a]

year (composite n)	Suisun Bay (Wheeler Island)	Central Bay (Richmond Bridge)	South Bay (Don Edwards)
2002 (2)	19000 ± 4000	9100 ± 2200	4200 ± 400
2004 (2)	n/a	3700 ± 500	3300 ± 300
2006 (3)	6100 ± 5200	1800 ± 400	4400 ± 2100
2009 (3)	440 ± 170	1800 ± 300	2100 ± 1200
2012 (3)	1300 ± 900	1100 ± 200	1100 ± 100

[a]Values are reported as mean ± standard deviation.

trations of PBDEs in biota reported at the time, 63 300 ng/g of lipid.[10] The mean of 20 egg samples collected the same year was 9420 ± 13 400 ng/g of lipid.[10] Follow-up sampling conducted by the RMP in 2009 and 2012 signaled a dramatic decline in PBDE levels for eggs of this piscivore. The highest concentration of PBDEs in 2009 Forster's tern egg samples was 2400 ng/g of lipid, and the mean of 18 samples was 1400 ± 500 ng/g of lipid. In 2012, the highest concentration of PBDEs was 3600 ng/g of lipid, and the mean of 19 samples was 1600 ± 700 ng/g of lipid, indicating a decline of more than 80% from the peak measurements in 2002. While there are some methodological differences between the earlier study[10] and the present study, the analytical quality-control performance of each method indicates that the significant declines cannot be explained by these changes.

The RMP has conducted more extensive and regular analyses of the eggs of another piscivorous species, the double-crested cormorant. The major congeners observed in these eggs were BDE-47, BDE-100, and BDE-99; no BDE-209 was detected.

A comparison of PBDE profiles in birds and bird eggs worldwide indicated that terrestrial-feeding birds are more likely to have detectable levels of BDE-209 than piscivores such as terns and cormorant.[28] Eggs of the terrestrial-feeding peregrine falcon collected in the Bay Area contained detectable levels of BDE-209,[29] consistent with this finding.

Two of the Wheeler Island cormorant egg samples, collected in 2002, contained extremely high PBDE levels, with total PBDEs of 24 000 and 15 000 ng/g of lipid. These measured values were greater than those typically found in eggs of other fish-eating birds of North America but lower than the most extreme value measured in San Francisco Bay tern eggs in 2002.[10,28,30]

Since 2002, the concentrations of total PBDEs in cormorant eggs generally suggested declines (Table 2). Eggs from Suisun, Central, and South Bays collected in 2012 had PBDE levels indicating declines of 93%, 88%, and 74% respectively, relative to eggs collected in 2002.

Consistent Declines in PBDE Contamination. Monitoring of wildlife for PBDEs indicated a decline in PBDE levels for all of the San Francisco Bay organisms under study. Bivalves collected during the three most recent sample years (2008, 2010, and 2012) showed lower levels of contamination than those collected when the RMP first began testing for PBDEs in 2002 (Figure 5). The Bay-wide average PBDE level in one of the most contaminated fish species, shiner surfperch, was significantly lower in 2009 than in 2006 and 2003. Cormorant eggs showed reductions in PBDE contamination in 2012 compared with 2002 (Table 2), and Forster's tern eggs exhibited significantly less contamination in 2009 and 2012 than they did in 2000–2003.[10]

The recent decline in PBDE levels found in San Francisco Bay biota is likely a consequence of the nationwide phase-out of PentaBDE and OctaBDE, effective in 2004, as well as the state ban, effective in 2006. Chemical bans and phase-outs do not immediately remove all sources of contaminants to the environment, as the chemicals remain present in products in use or entering the waste stream and in some cases may be imported via products manufactured in other countries. Nevertheless, these results suggest that policies designed to reduce the use of persistent, bioaccumulative, and toxic chemicals can lead to rapid reductions in contaminant concentrations in biota. In this case, substantial changes occurred just a few years after the bans were implemented.

This rapid response to reduced usage and loads is consistent with forecast modeling results based on a PBDE mass budget for San Francisco Bay.[31] This simplified one-box model predicted that if annual PBDE inputs to the Bay were reduced to zero, the total load of BDE-47 in the Bay would drop by 90% within 10 years. Under the same conditions, the total load of BDE-209 would decline by 50–90% depending on the degradation rate used; a lower rate results in better agreement between the model and empirical data, while a higher value was predicted in the literature.[31] These predictions differ from those for polychlorinated biphenyls (PCBs), legacy contaminants that exhibit greater persistence than PBDEs and were in use for a longer time period before their manufacture was banned in 1979. A one-box PCB model predicted that if annual inputs were reduced to zero, it would take 10 years for a 50% reduction in Bay PCB contamination.[32]

The RMP data provide the most compelling evidence to date for a recent decline in PBDE levels consistent over a broad variety of organisms. This analysis expands on other studies noting apparent PBDE declines in single species from regions likely impacted by the U.S. production phase-outs, including osprey eggs in the Pacific Northwest,[30] sockeye salmon from the northeast Pacific Ocean,[26] and trout in the Great Lakes.[33] The RMP's large bioaccumulation monitoring data set, covering multiple species and collected consistently for many years, has proven to be of great value in establishing the environmental outcomes associated with PBDE pollution prevention policies.

Consistent with trends seen in Bay wildlife, the concentrations of BDE-47 in sediment display a declining trend over the period of record despite compositing and mixing processes that would tend to obscure recent temporal trends in this matrix (Figure 2). Bay-wide averages of the dominant congener in water, BDE-47, are suggestive of a nonsignificant decline since 2004 (Figure 3). Contamination of sediment with BDE-209, the dominant congener for this matrix, showed little change (Figure 1), which is not surprising since the DecaBDE mixture was only phased out of U.S. production in 2013.

The absence of a decline in BDE-209 also suggests that a potential confounding factor, the drier regional climate after water year 2006,[34] is not a cause of the observed BDE-47 declines. The estimated annual BDE-209 loads from stormwater to San Francisco Bay are more than five times greater than the estimated annual BDE-47 loads,[31] so the potential impact of a drier climate and reduced runoff would be more likely to be observed in declines in BDE-209 than BDE-47. Analysis of suspended sediments in the Detroit River, with its different climatic regime, similarly indicated a decline in total PBDEs but the absence of a decline in BDE-209 from 1999 to 2009.[35]

Continued monitoring will track the expected continuing declines of less-brominated PBDE congeners and may identify declines in BDE-209 as a result of the nationwide phase-out of DecaBDE. However, as PBDE flame retardants are removed from use through bans and phase-outs, manufacturers have found different flame retardants to take their place. Pilot studies have detected several of these alternative flame retardants in San Francisco Bay water, sediment, and biota,[8,36] and their increased use in manufacturing may lead to higher concentrations. On the other hand, state efforts to change flammability standards to maintain fire protection without necessitating the use of chemical flame retardants may result in reduced chemical use and decreases in environmental pollution. In 2013, a key California flammability standard, TB 117, was modified to eliminate the incentive to incorporate these substances into upholstered furniture and many items for infants and young children (TB 117-2013).[13] Additional monitoring of alternative flame retardants, particularly those used as substitutes for PBDEs, will be critically important in evaluating the effect of changes in manufacturing practices and regulatory requirements on water quality in the Bay.

■ ASSOCIATED CONTENT

Supporting Information

Data quality information and temporal-trend regression equations described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: RebeccaS@sfei.org.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank E. Willis-Norton for assistance in preparing this manuscript. Data were formatted by J. Ross and A. Wong, and maps were constructed by M. Klatt, P. Kauhanen, and P. Frontiera. E. Agus, R. Chiu, and I. Lui-Wong are acknowledged for their contribution to sediment analysis. W. Arnold, D. Chen, D.L. Sedlak, and anonymous reviewers provided constructive comments on the manuscript. This synthesis article was funded by the Regional Monitoring Program for Water Quality in San Francisco Bay.

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DOI: 10.1021/es503727b
Environ. Sci. Technol. 2015, 49, 777−784