REGIONAL MONITORING PROGRAM
FOR WATER QUALITY IN THE SAN FRANCISCO BAY

Polybrominated Diphenyl Ethers (PBDEs) in San Francisco Bay

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Executive Summary

Polybrominated diphenyl ethers (PBDEs) are a group of flame retardant additives used in thermoplastics, polyurethane foam, and textiles. These diphenyl ethers possess one to ten bromine atoms; although 209 congeners are possible, only some of these are manufactured or result as degradation products. The three commercial mixtures of PBDEs, each named for the bromination level of its dominant components, are "PentaBDE," "OctaBDE," and "DecaBDE."

Flame retardant use has become widespread in large part due to unusually strict flammability standards in the state of California. California Environmental Protection Agency (Cal/EPA) studies of PBDEs in people and wildlife in the San Francisco Bay Area have revealed extremely high levels relative to the rest of the world, indicating the region is a global PBDE contamination "hot spot."

State and federal governments have responded to the rising environmental and human health concerns over PBDEs by enacting bans and encouraging voluntary phase-outs on production and use. The major manufacturer of PentaBDE and OctaBDE ceased producing these mixtures by the end of 2004, and the California Legislature banned the same commercial mixtures as of 2006. Also in 2006, the United States Environmental Protection Agency (USEPA) issued a significant new use rule on these substances, ensuring any proposed uses of these chemicals would be reviewed for safety by the agency. American chemical manufacturers voluntarily phased out the DecaBDE formulation in 2013. Also in 2013, a key California agency revised a state flammability standard to eliminate the need to incorporate these substances into upholstered furniture and many items for infants and young children.

The Regional Monitoring Program for Water Quality in the San Francisco Bay (RMP), administered by the San Francisco Estuary Institute (SFEI), has undertaken a series of monitoring and research projects to investigate the impacts of PBDEs in San Francisco Bay. The findings of this body of work are summarized in this report.

The RMP has found that PBDEs are widely detected in San Francisco Bay matrices including water and sediment, as well as in small and large tributaries to the Bay. These contaminants are also ubiquitous in Bay biota including bivalves, fish, bird eggs, and seals.

At present, a state risk assessment suggests that PBDE contamination of the Bay does not impair the beneficial use of sport fish consumption. Contamination is also unlikely to impair reproduction and development of Bay birds, according to a recent RMP-sponsored study of the toxicity of PentaBDE to tern eggs. On the other hand, it is possible that current levels of contamination may impair the health of Bay harbor seal populations, though further research is necessary to elucidate potential impacts, particularly for young, highly exposed, weaning pups. In addition, limited toxicity information suggests Bay fish and benthic organisms may also be susceptible to low level adverse effects.

Likely in response to the phase-outs and bans described above, RMP monitoring indicates a decline in contaminant levels for Bay organisms under routine study. This decline is expected to continue, and should diminish any potential impacts of PBDEs on Bay biota. The RMP developed a PBDE mass budget model that indicates rapid recovery is possible with reduced contaminant loads expected as these compounds are removed from the market.

In contrast to trends seen in Bay wildlife, concentrations in abiotic Bay media such as water and sediment have shown fewer clear temporal trends. Bay-wide averages of the dominant congener in water, PentaBDE component BDE-47, suggest a decline in contamination since 2004, though the trend is not yet statistically signficant ($p > 0.05$). Bay-wide averages of the dominant congener in sediment, DecaBDE component BDE-209, show little change over time. Because the phase-out of DecaBDE is still ongoing, it may be some time before a clear trend emerges for this congener.

However, levels of BDE-47 in sediment display a significant declining trend over the last decade. Because sediment mixing and sample compositing can cloud any signal of recent changes to sediment contaminant loads, it is notable that a temporal trend has already emerged in average Bay BDE-47 sediment concentrations.

The evidence of declining PBDE levels in biota and the outcome of the RMP's mass budget forecast modeling together suggest that management actions to eliminate production and use of PBDEs should be sufficient to address the potential impacts of contamination of San Francisco Bay. The last section of this report includes recommendations for monitoring based on this review and the management actions taken to eliminate use of PBDE flame retardants.

1.0 RMP Monitoring of PBDEs in San Francisco Bay

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) is a long-term monitoring program that provides information needed to manage Bay water quality. The Program has conducted a series of PBDE monitoring efforts and special studies with an aim to answer the following management question: Are PBDE concentrations in the Estuary at levels of potential concern and are associated impacts likely?

In response to concerns over the possible impacts of PBDEs on beneficial uses of the Bay, in 2007 the Clean Estuary Partnership completed an initial Conceptual Model/Impairment Assessment of PBDEs in San Francisco Bay (Werme et al. 2007). The model and assessment revealed a number of data gaps and a need for ongoing monitoring of Bay media for contaminants.

Since the publication of the Werme et al. (2007) report, a substantial amount of new information has been generated. The present report summarizes work to date characterizing PBDE levels in Bay water, sediment, sediment cores, stormwater discharges, and large tributaries, as well as those found in Bay biota including bivalves, fish, bird eggs, and seals, with a focus on findings since 2007. Monitoring data combined with toxicity studies or risk assessments allow characterization of the Bay with respect to the potential for impairment at current PBDE levels. The RMP has conducted preliminary work to model pathways and loads of PBDEs to the Bay, and has analyzed trends in contamination over the past ten years.

Taken together, this broad set of data and analyses permits qualitative forecasting of future trends, especially in light of the management actions described above. The report concludes with recommendations regarding future flame retardant monitoring in the Bay.

1.1 PBDEs: Use as Flame Retardants

PBDEs are a group of flame retardant additives used in thermoplastics, polyurethane foam, and textiles. These materials are found in products in many applications, including within homes, offices, automobiles, and airplanes. PBDEs are diphenyl ethers with one to ten bromine atoms attached (Figure 1). Although 209 congeners are possible, only some of these congeners are manufactured or result as degradation products. A characterization of the congener profiles of the three commercial mixtures of PBDEs, each named for the bromination level of its dominant components (“PentaBDE,” “OctaBDE,” and “DecaBDE”), is provided in Table 1.

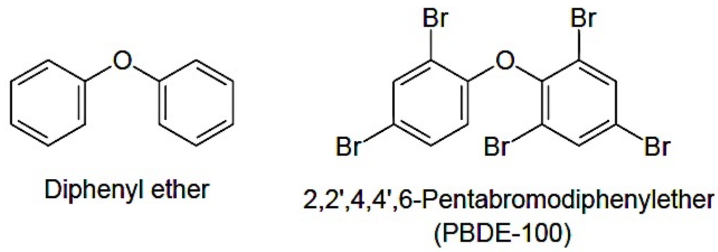

Figure 1. Diphenyl ether structure and structure of BDE-100 (Cal/EPA 2006).

Table 1. Commercial mixtures of PBDE flame retardants, their congeners, and major uses.

Commercial mixture	Congeners, listed from greatest to least[1]	Major use
PentaBDE[2] (commercially known as DE-71 and Bromkal 70-5DE)	BDE-99 (35-50%), 47 (25-37%), 100, 153, 154, possibly minor amounts of 17, 28, 66, 85, 138, 183	~95% used in polyurethane foam in furniture cushions, automobile seats and head rests, and mattresses; ~5% used in foam-based packaging and carpet padding
OctaBDE[2] (commercially known as DE-79)	BDE-183 (40%), 197 (21%), 203 (5-35%), 196, 208, 207, 153, 154	~95% used in ABS resins; ~5% used in other plastics for computers and kitchen appliances
DecaBDE[2] (commercially known as DE-83R and Saytex 102E)	BDE-209 (97.5%), 206, 207, 208	General purpose flame retardant used in virtually any type of polymer, including thermoplastics, textiles, back-coatings of consumer electronics like televisions, wire insulation, upholstery, electrical boxes, high impact polystyrene (HIPS) plastic

[1] Congener composition information from Alaee et al. 2010 and USEPA 2010.
[2] For this report, PentaBDE, OctaBDE, and DecaBDE refer to the commercial mixtures, not the homologue group.

California’s arid, fire-prone climate has given rise to some of the toughest fire regulations in the country. The California Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation is one of many state agencies that works to ensure that California residents are safe from fires that begin in the home. Since 1975, the Bureau has developed several flammability standards, set forth in a series of Technical Bulletins, defining tests for flammability in accordance with methods developed by the U.S. Consumer Product Safety Commission. Markets across the country sell products that meet California’s tough standards.

These flammability standards do not dictate the use of chemical flame retardants or other special materials. But because the standards are so strict, many manufacturers have turned to chemical methods to ensure compliance. As a result, widespread commercial production and use of PBDEs as flame retardants began in the 1970s (USEPA 2010). In particular, PentaBDE was the primary flame retardant used to comply with Technical Bulletin 117, which describes the standard for upholstered furniture (BHFTI 2000; USEPA 2010).

1.2 Growing Concerns: Contaminant Hot Spots, Toxicity Studies

Decades after PBDEs entered the marketplace, their production and use was found to have disturbing consequences for San Francisco Bay. A study by Cal/EPA scientists (She et al. 2002) found PBDE levels in blubber from Bay harbor seals that were among the highest found in wildlife. Bay data suggested that concentrations of PBDEs in seal blubber had doubled every 1.8 years throughout the 1990s. Another significant cause for concern, She et al. (2002) also found high levels of PBDEs in tissue samples from Bay Area women, the highest levels ever reported in humans.

Additional sampling of Bay wildlife amplified the alarm: samples of Forster's tern eggs collected by the same Cal/EPA team in 2002 revealed the highest levels of PBDE contamination in biota reported at the time, 63,000 ng/g lipid (She et al. 2008). This concentration remains one of the highest ever recorded in any organism. Clearly, San Francisco Bay had become a global PBDE contamination "hot spot."

Meanwhile, a growing body of literature suggested exposure to PBDEs could cause harmful effects. Studies of PBDEs in laboratory animals have tied PBDEs to developmental neurotoxicity, reproductive toxicity, endocrine disruption, and for DecaBDE, liver and thyroid toxicity as well as possible carcinogenicity (reviewed in USEPA 2008a,b). There is concern over human exposure to PBDEs, especially for young children receiving higher exposures through ingestion of PBDE-laden indoor dust via high amounts of hand-to-mouth activity (USEPA 2010).

Investigations of health concerns linked to PBDEs have also extended to wildlife. For example, in birds, PBDEs have been associated with various reproductive effects in American kestrels (Fernie et al. 2008; McKernan et al. 2009) and ospreys (Henny et al. 2009) at concentrations within the range of those found in San Francisco Bay tern eggs (She et al. 2008). Laboratory studies probing the effects of a PBDE-laden diet on fish suggest, for example, that juvenile Chinook salmon become more susceptible to infection (Arkoosh et al. 2010), juvenile zebrafish display altered locomotion behavior (Chou et al. 2010), and adult fathead minnows display altered thyroid status and thyroid-hormone regulated gene expression in the pituitary and brain (Lema et al. 2008). In addition, PBDE-contaminated sediment can impact the larval settlement and growth of polychaetes, common benthic organisms (Lam et al. 2010).

1.3 PBDE Sources, Pathways, and Fate

The pervasiveness and potential impacts of PBDE contamination on beneficial uses of the Bay suggested a closer look at the sources and pathways of contamination was necessary. Releases of PBDEs to the environment can occur during initial synthesis of the compounds, during their incorporation into polymers and products, during product use, and as the result of disposal, recycling or incineration of PBDE-containing products.

While PBDEs have never been manufactured in the Bay Area, notable Bay Area sources of PBDE contamination occurring during manufacture of products, as identified by USEPA's Toxic Release Inventory, include two Tyco Thermal Controls facilities in the Peninsula region (Redwood City and Menlo Park; McKee et al. *in prep*). At both locations, the majority of DecaBDE disposal has been done through landfilling and recycling. The Redwood City location also self-reported significant annual air emissions of 113 kg of DecaBDE for most years between 1991 and 2005 (McKee et al. *in prep*).

Because PBDEs are not chemically bound to substrate polymers, they may escape manufactured products through volatilization and via incorporation into dust. Indoor dust represents the primary exposure pathway for humans. PBDE-contaminated indoor dust can enter the outdoor environment through ordinary activities such as cleaning clothing and surfaces, which involves rinsing dust down the drain to sewage treatment plants, disposing of dust as refuse destined for landfill or incineration, and venting dust outside via dryer vents or open windows and doors. PBDEs are ubiquitous in the outdoor environment, with more densely populated urban areas generally containing higher concentrations than rural areas (with the exception of sewage sludge-applied lands [e.g., Strandberg et al. 2001]). Some facilities that may have a legacy of PBDE contamination as a result of leaching from manufactured products include carpet, upholstery and furniture manufacturers and warehouses; electronics manufacturers and distribution warehouses; and foam manufacturers and distributors (McKee et al. *in prep*).

The remaining pathway for PBDE release into the environment occurs during disposal of products – particularly via recycling, incineration, or use or disposal of sewage sludge. Environmental releases are expected or have been shown to result from all of the following sources: e-waste recycling facilities, autoshredders, carpet and foam recycling facilities, sewage sludge application to rural lands, and sewage sludge incinerators. There are few data to indicate the contribution of these sources to Bay contamination. However, the California Air Resources Board (CARB) has conducted ambient air monitoring in urban areas of California and near e-waste recycling and autoshredder facilities. BDE-209 near an e-waste recycling facility measured up to 11,000 pg/m^3 and near an unidentified California auto-shredding facility up to 1,900 pg/m^3 (Charles et al. 2005), versus an average of 23 pg/m^3 in seven San Francisco Bay Area and Southern California cities (and an average of 160 pg/m^3 for the sum of PBDEs in 2004 monitoring; CARB 2010). In addition, autoshredder waste sampled in the Bay Area contained approximately 50,000 ng/g of total PBDEs (Petreas and Oros 2009).

PBDEs enter the Bay primarily from stormwater runoff and wastewater treatment plant discharges (see Section 4.0), as well as in minor amounts from rainfall and direct atmospheric deposition. PBDEs on the terrestrial landscape are primarily atmospherically deposited after emissions from production, use, and disposal or recycling, as outlined above.

PBDEs are semivolatile organic compounds and have low water solubilities. Congener vapor pressures vary with bromination level, which affects their movement into and within environmental media (USEPA 2010). For example, at air temperatures of 25°C, more than 98% of the single, double, and triple brominated congeners may be found in air in the vapor phase. On the other hand, congeners with four or five bromines begin to partition to atmospheric particles, such that BDE-47 (four bromines) is 10% particle phase, and BDE-99 (five bromines) is 39% particle phase. Congeners with six or seven bromines are 87-99% particle phase, while the fully brominated BDE-209 is expected to be 99% associated with airborne particles. Differences in volatility and other chemical properties like octanol-water partitioning coefficients have important implications for how and where different PBDE congeners move and settle in the environment.

> **Air:** Lower-brominated congeners are volatile and persistent enough to permit long-range transport through the atmosphere. Higher-brominated congeners like BDE-209 may also be found in air samples, but are more likely to deposit closer to their sources as they are more prone to wet and dry atmospheric deposition. For example, in a study of atmospheric concentrations of PBDEs in urban and rural areas of the Great Lakes region, Strandberg et al. (2001) found that the dominant congeners in air samples were BDE-47, BDE-99, and BDE-100, while BDE-209 was only detected in the Chicago area, likely close to point sources. Likewise, ambient and near-source air monitoring by the CARB found that while all urban areas contained background levels of BDE-209 contamination, measurements taken near autoshredders were highly elevated (CARB 2010).
>
> **Soil and Sediment:** Adsorption of PBDEs increases with bromination and organic carbon content of soil and sediment. PBDEs in soils are therefore expected to be in greater concentrations nearest to point sources – most concentrated in urban areas, and source areas within the urban environment. In particular, BDE-209 is expected to deposit near its source and remain largely adsorbed to particles. For BDE-209, mobilization through the environment will primarily occur when the particles to which the compound adsorbs are moved, as occurs during stormwater discharges.
>
> **Water:** In water, greater proportions of the lower-brominated congeners will remain dissolved in the water column as compared to the higher-brominated congeners that are more likely to settle out on sediment particles. In the Bay, BDE-47 is the congener found in the highest concentrations in the water column, whereas BDE-209 is the dominant congener in the Bay's surficial sediment samples (Klosterhaus et al. 2012).
>
> **Organisms:** PBDEs are generally lipophilic, and therefore readily bioaccumulate in organisms. In contrast, BDE-209 is significantly less lipophilic due to its large size; while this fully brominated congener may be detected in human and animal lipid tissues, it does not necessarily bioaccumulate (USEPA 2010). It is frequently detected, however, in terrestrial organisms, particularly in top predators such as birds of prey (Chen and Hale 2010).

Once higher-brominated PBDEs enter the environment, they may undergo transformation through debromination via microbial, metabolic, or photolytic processes (reviewed by USEPA 2010). Debromination results in production of an array of lower-brominated congeners. Relative to the fully brominated BDE-209, many of these lower-brominated congeners (e.g., BDE-47) are considered more toxic and certainly more bioaccumulative, leading to the potential for increased risk to the environment (Darnerud 2003). Other lower-brominated products of debromination are not found in commercial mixtures and have not been subjected to toxicity tests.

1.4 Management Actions to Address PBDE Contamination

State and federal governments have responded to the rising environmental and human health concerns over PBDEs with a combination of encouraging voluntary phase-outs or instituting bans on production and use. PentaBDE and OctaBDE were the first commercial mixtures subject to action. At the federal level, the major manufacturers of these formulations agreed to cease production at the end of 2004, and the California Legislature banned them as of 2006. After production had halted, the USEPA issued a significant new use rule on PentaBDE and OctaBDE in 2006, which requires manufacturers and importers to notify the agency at least 90 days before commencing the manufacture or import of these chemical substances. This allows the USEPA to evaluate any intended new use and, if necessary, to prohibit or limit the activity before it occurs.

Improvements in analytical techniques leading to increasing detection of DecaBDE congener BDE-209 in people and wildlife, as well as a growing understanding of its potential to be a source of lower-brominated congeners via debromination, led to further management actions specific to this commercial mixture. Nationwide, major manufacturers agreed to a voluntary phase-out by the end of 2013. The USEPA has proposed extending its significant new use rule to cover DecaBDE as well.

The USEPA's Design for the Environment Program has encouraged use of PBDE alternatives that it considers safer. However, some of these chemicals have not been fully tested for safety and later have become chemicals of concern themselves (Hawthorne 2012). Initial studies indicate a number of non-PBDE flame retardants approved by this program, including those used to replace PBDEs, are present in Bay sediment and biota (Klosterhaus et al. 2012; Werme 2012).

To address concerns over the use of chemical flame retardants, the California agency largely responsible for their widespread use, the Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation, issued a revised flammability standard in 2013 to eliminate the incentive to incorporate these substances into upholstered furniture and many items for infants and young children (BEARHFTI 2013a). The Bureau determined that its previous standard did not "adequately address the flammability performance of the upholstery cover fabric and its interactions with underlying filling," and developed a new standard that is designed to better address fires caused by smoldering materials, the predominant source causing upholstered furniture fire deaths (BEARHFTI 2013b). As a result of this change, chemical flame retardants are expected to disappear from a variety of newly produced consumer goods.

2.0 Summary of PBDE Occurrence and Trends

2.1 PBDEs in San Francisco Bay: The Abiotic Environment

2.1.1 Water

Overall, 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 exist in the literature, average Bay water levels were comparable to or greater than those measured near Hong Kong and an industrialized, urban region of Turkey (Wurl et al. 2006; Cetin and Odabasi 2007). San Francisco Bay levels have not demonstrated a clear trend over the last ten years, with an interdecile range (the range between the first and ninth deciles [10% and 90%] of the measured values) 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 and an index of the sum of all compounds, occurred in 2004 (Figure 2). BDE-47 is a component of commercial mixture PentaBDE. Since 2004, Bay-wide average levels of BDE-47 are suggestive of a declining trend, though this trend is not yet statistically significant ($p > 0.05$). The three lowest annual average concentrations were measured in 2008-2010. The average 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 ten-year period from 2002 to 2011 was 45 pg/L, while the average for 2011 was 43 pg/L.

Levels of PBDEs in water show considerable spatial variability within the Bay (Figure 2). 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

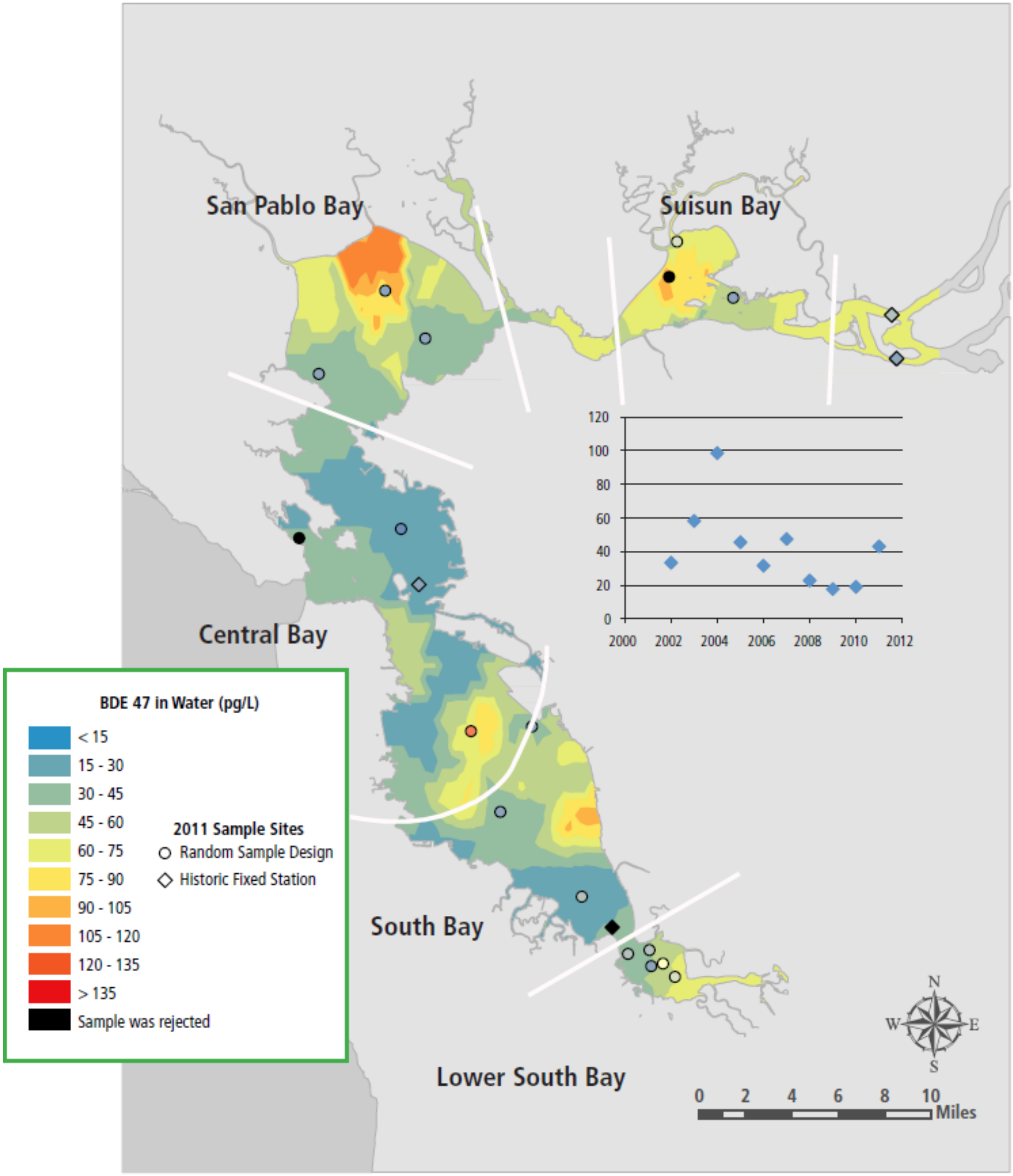

Figure 2: Concentrations of BDE-47 in water in San Francisco Bay (pg/L).

Map plot based on 206 RMP data points from 2002-2011. Trend plot shows annual Bay-wide averages. Colored symbols on map show results for samples collected in 2011: circles represent random sites, and diamonds represent historic fixed stations.

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, averages for all portions of the Bay show lower levels for the four most recent years of sampling (Figure 3).

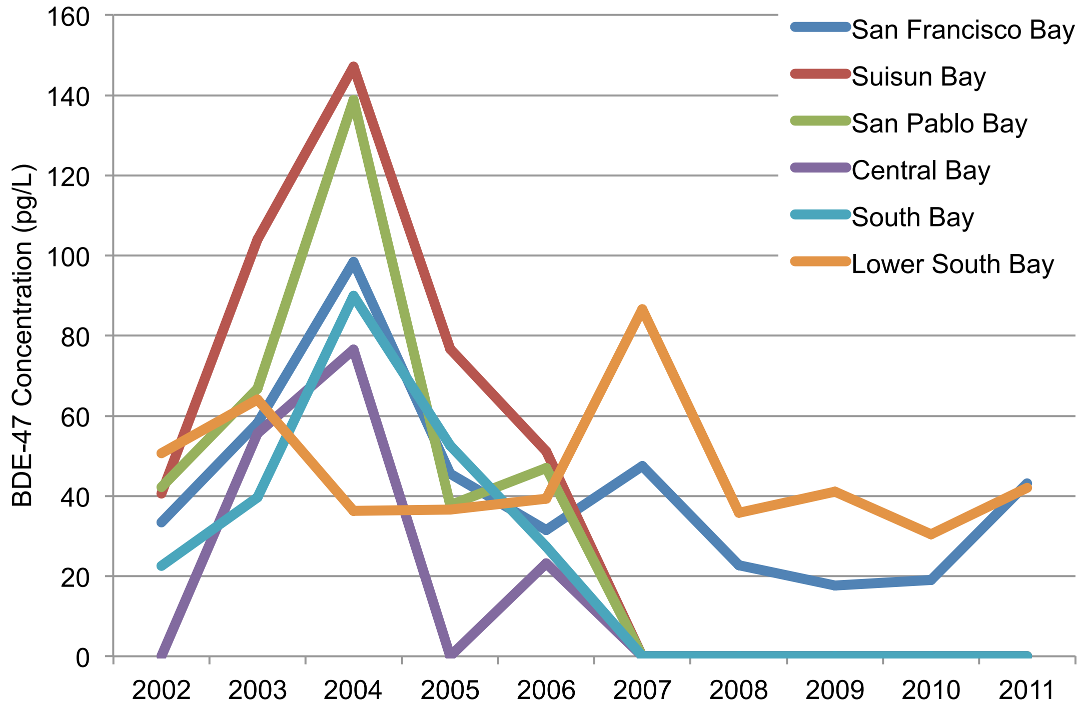

Figure 3: Regional distribution of BDE-47 in San Francisco Bay water over time (pg/L).

2.1.2 Sediment

Sediment concentrations in the Bay were typically less than 10 ng/g dry weight (maximum 50 ng/g), and were typically dominated by BDE-209 rather than BDE-47. BDE-209 is the primary component of commercial mixture DecaBDE. Levels of BDE-209 (Figure 4) and BDE-47 (Figure 5), as well as total PBDEs, were comparable to those measured in the Strait of Georgia, British Columbia, Canada (Grant et al. 2011). Levels measured within the Southern California Bight showed a greater degree of variability, with the greatest contamination found at or near river mouths, and a larger number of sites where no PBDEs were detected (Dodder et al. 2012). Overall San Francisco Bay sediment measurements for BDE-209 and BDE-47 were more similar to the area-weighted geometric means of the offshore region of the Southern California Bight than to the more contaminated coastal embayment regions.

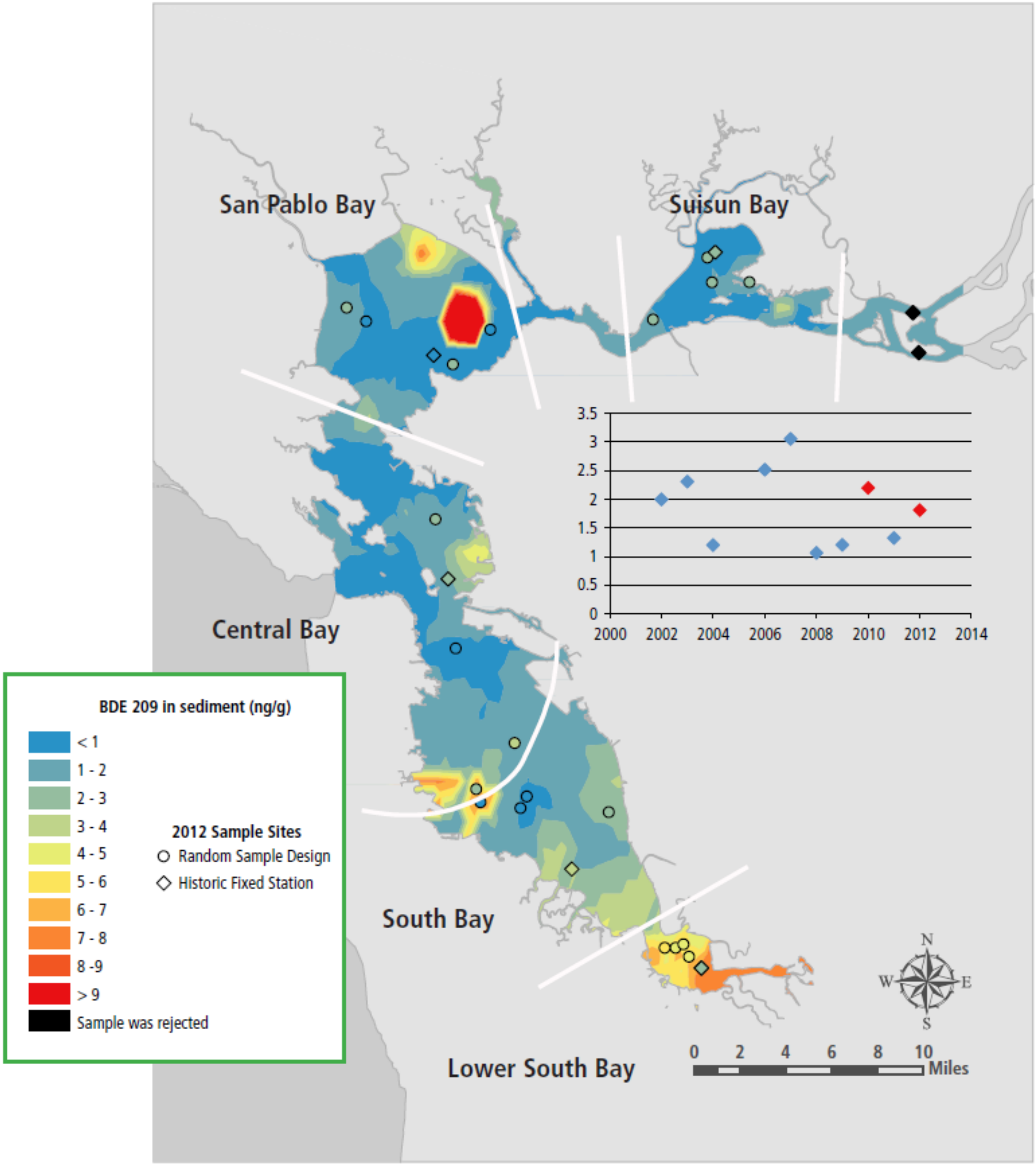

Figure 4: Concentrations of BDE-209 in sediment in San Francisco Bay (ng/g dry weight).

Contour plot based on 293 RMP data points from 2002, 2003, 2004, 2006, 2007, 2008, 2009 and 2011. Trend plot shows annual Bay-wide averages. Colored symbols on map show results for samples collected during the wet season (April) in 2012. Circles represent random sites. Diamonds represent historic fixed stations. Red diamonds on trend plot indicates wet season samples; blue diamonds indicate dry season samples.

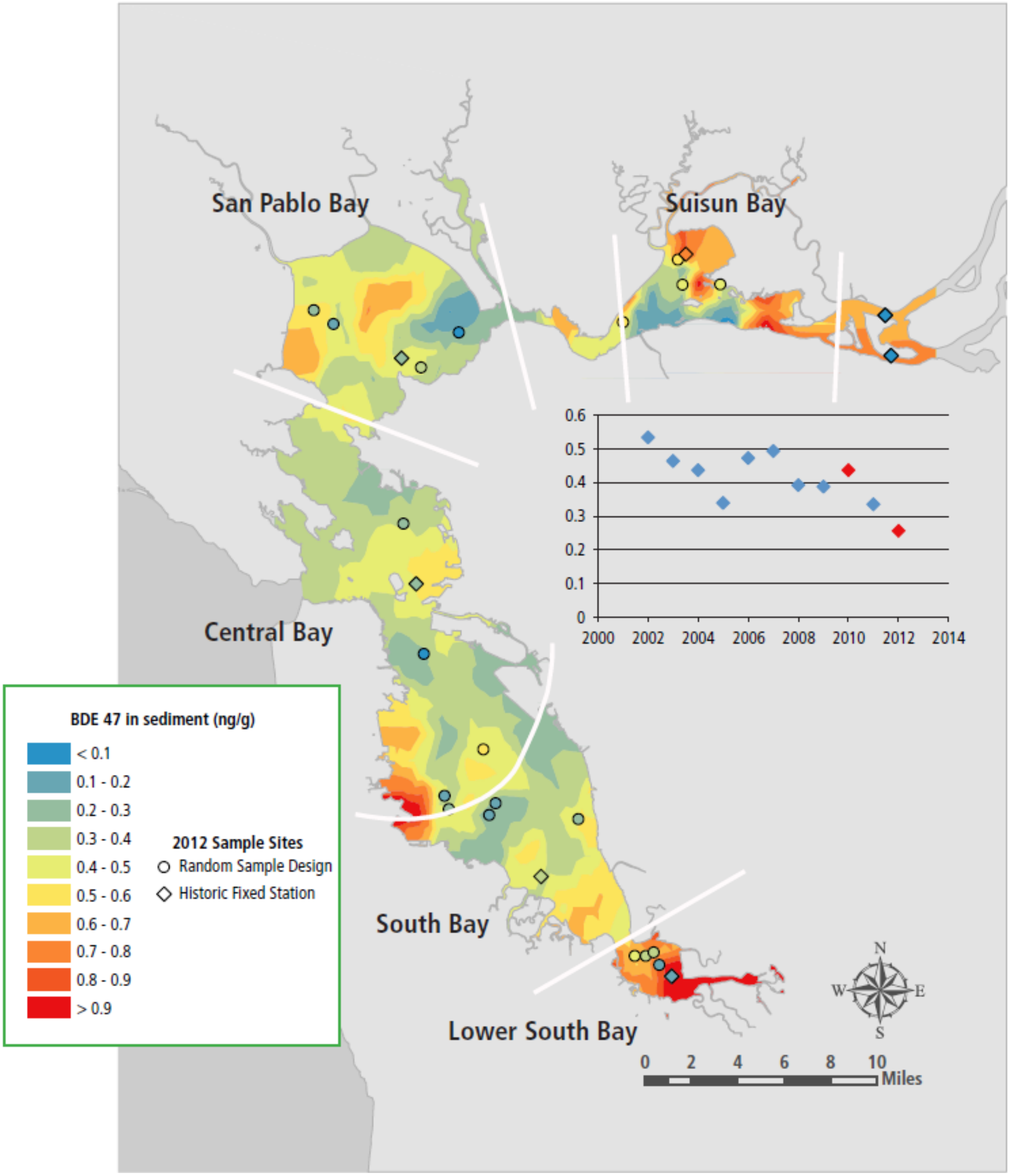

Figure 5: Concentrations of BDE-47 in sediment in San Francisco Bay (ng/g dry weight).

Contour plot based on 338 RMP data points from 2002–2009 and 2011. Trend plot shows annual Bay-wide averages. Colored symbols on map show results for samples collected during the wet season (April) in 2012. Circles represent random sites. Diamonds represent historic fixed stations. Red diamonds on trend plot indicates wet season samples; blue diamonds indicate dry season samples.

BDE-209 has been found to be the dominant congener in sediment samples taken from several other locations worldwide, including Asia, Europe, and the U.S. Great Lakes (Moon et al. 2006). However, because widespread background laboratory contamination makes BDE-209 particularly difficult to quantify, this congener is frequently excluded from sediment analyses. A recent National Oceanic and Atmospheric Administration (NOAA) Mussel Watch Program survey quantified sediment PBDE levels, excluding BDE-209 and other highly brominated congeners, and found that the San Francisco Bay samples they examined were in the middle of the range for all 122 sediment samples collected nationwide (Kimbrough et al. 2009).

Regionally, long-term average dry season concentrations of BDE-209 from 2002-2011 (excluding 2010) were highest in the Lower South Bay (5.4 ng/g dry weight; Figure 4). The spatial pattern observed from two years of wet-season sampling in 2010 and 2012 was consistent with the general pattern seen in dry season monitoring from 2002-2011 (excluding 2010), 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 average for the 2010 and 2012 wet seasons (2.2 and 1.8 ng/g dry weight, respectively) was similar to the long-term average for the dry season (1.9 ng/g dry weight) and in the middle of the range of annual dry season averages from 2002-2011 (excluding 2010).

Similarly, long-term average dry season concentrations of BDE-47 in sediment were highest in the Lower South Bay (0.71 ng/g dry weight; Figure 5). The regional distribution of BDE-47 in sediment was distinctly different than that of BDE-47 in water (Figure 2), with sediment samples indicating contamination that was broadly distributed over the Bay and displayed fewer, more dispersed hotspots. The spatial pattern observed in the wet season of 2010 and 2012 was consistent with the general pattern observed in dry season monitoring from 2002-2011 (excluding 2010). Three samples with relatively high concentrations were observed in northern Suisun Bay, a region that has been consistently elevated in past sampling.

Unlike BDE-209, for BDE-47 the Bay-wide averages from 2002 to 2012 indicate a statistically signficant trend of decreasing BDE-47 sediment contamination. Levels of BDE-47 measured in 2012 were frequently significantly lower than those indicated by the contour plot of the same location calculated using data points from 2002–2009 and 2011, consistent with an overall decline over the monitoring period (Figure 5). Trends over time may be particularly difficult to detect in sediment samples due to compositing of the top 5 cm of sediment; the sediment accretion rate in most areas of the Bay is less than 0.5 cm/yr, 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 suggesting declining BDE-47 levels in sediment over the last decade are especially notable, and may be caused by the lack of domestic production and use of PentaBDE following the nationwide phase-out and state ban of this commercial mixture.

In 2011, two additional sediment samples were collected from sites in Bay margins not typically monitored by the RMP, as an initial investigation into the hypothesis that margin sites may have greater levels of contamination than the overall Bay. In fact, sediment samples in San Leandro Bay and Mission Creek contained BDE-209 concentrations at least four times greater than any other site sampled that year. These findings suggest a need for further study of contamination of margin habitats, which are foraging sites for small fish and other prey items consumed by many species of Bay wildlife.

An inspection of some of the less dominant congeners revealed frequent detection of PBDEs not commonly found in commercial mixtures and most likely formed as a result of debromination. BDE-15, detected in 83% of 2012 sediment samples, is a major product of the photolytic debromination of heavier congeners (Fang et al. 2008). BDE-7 and BDE-17, detected in 86% and 90% of 2012 sediment samples, respectively, have been observed as products of the microbial debromination of heavier congeners (Tokarz et al. 2008). The widespread presence of these congeners suggests that PBDEs undergo measurable degradation in the environment. A detailed analysis of these data is presented in press (Rodenburg et al. *in press*).

There is no information available on the relative toxicity of BDE-7, BDE-15, and BDE-17, so the environmental implications of debromination for the Bay are unclear. However, a comparison of the congeners dominant in commercial mixtures suggests that less-brominated congeners like BDE-47 are more bioaccumulative and more toxic than the more-brominated congeners like BDE-209 (Darnerud 2003).

2.1.3 Sediment Cores

The RMP, in collaboration with the Clean Estuary Partnership, undertook a pilot study of PBDE distributions in sediment cores collected from three wetland sites in 2006 (Yee et al. 2011). Ages and contaminant concentrations of various layers in these cores were characterized in support of ongoing efforts to model Bay recovery.

Wetlands cores were obtained from sites in Point Edith and the Damon and Alviso Sloughs (Figure 6). Thickly rooted wetland surface sediments at the first two sites limited core depth to 30 cm. In contrast, the Alviso Slough core depth was one meter. Concentrations of total PBDEs (normalized to percent fines) ranged up to nearly 50 ng/g dry weight across the three cores (Table 2). Maximum concentrations were a factor of two or more greater than average Bay sediment concentrations, and were slightly greater than the maximum surface sediment concentrations for their respective Bay segments. BDE-209 was the dominant congener, accounting for 45-75% of total PBDEs at the three sites.

Table 2. Sediment core concentrations of BDE-209 and total PBDEs with depth, normalized to percent fines.

	Damon Slough		Point Edith		Alviso Slough	
depth cm	Sum PBDEs µg/Kg	BDE-209 µg/Kg	Sum PBDEs µg/Kg	BDE-209 µg/Kg	Sum PBDEs µg/Kg	BDE-209 µg/Kg
3.75	48	36	9.0	5.4	25	16
8.75	1.1	0.36	0.76	0.18		
13.75	0.33	Q	14	6.0	16	9.1
18.75	0.46	0.18	NRS	Q		
23.75	0.063	Q	NRS	Q	15	8.8
28.75	0.34	Q	NRS	Q		
38.75	NRS	Q	0.049	ND	4.9	4.0
48.75	NRS	Q	0.059	ND		
58.75					3.2	2.4
78.75					0.34	0.18
98.75					0.14	Q
118.75					0.13	Q

Q = results censored due to QA/QC issue (blank near measured concentration, poor recovery or precision; NRS = insufficient quantitative results to calculate sum; ND = analyte not detected above method detection limit.

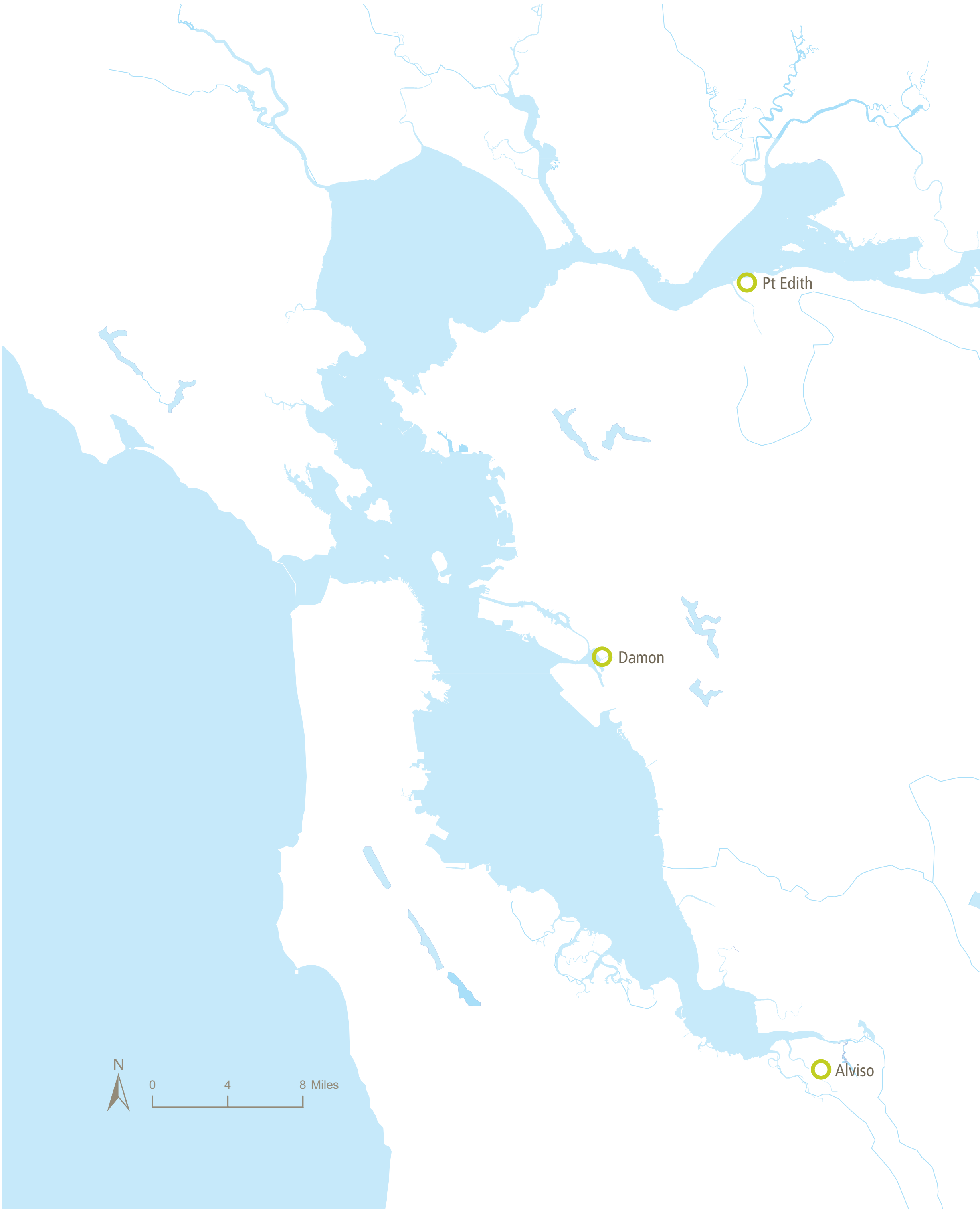

Figure 6. Locations of sediment core sample sites.

The dominance of BDE-209 was not as pronounced as in cores from Lake Erie and Lake Michigan, where it comprised 95-99% of total PBDEs measured (Zhu and Hites 2005). That study included a subset of the PBDEs analyzed by the RMP. However, even reducing the sum of PBDEs in the San Francisco Bay cores to the subset of congeners reported there, BDE-209 still only accounts for around 50-75% of total PBDEs in sediment. Another study of Great Lakes sediments reported somewhat more comparable results, with the sum of 20 PBDEs (other than 209) reported as often equaling or exceeding the BDE-209 measured (Li et al. 2006).

The wetland cores, being primarily depositional areas, showed patterns of PBDE concentration with depth suggestive of the expected history of increased local and national use. Concentrations in the deepest sections were below or near detection limits, or 3-0.4% of the maximum concentrations for BDE-209. Maximum concentrations were found in near-surface sections of the cores for two of the three wetland sites, which would be expected given ongoing use and continued loading of many PBDEs in 2006, when samples were collected. California began its ban on the use or sale of PentaBDE and OctaBDE on June 1, 2006. Although the major PBDE manufacturer ceased production of PentaBDE and OctaBDE by the end of 2004, sale, use, and disposal of products containing these materials continued through the period of core collection. Additionally, in 2006 no action had been taken on DecaBDE, so new releases of that mixture were likely ongoing.

This drastic rise in sediment concentrations of BDEs was also seen in cores from the Great Lakes (Zhu and Hites 2005), which showed a 100-fold increase in PBDEs in recent sediments from around 2000 compared to background levels from 1960, with concentrations starting to rise around 1970.

2.2 PBDEs in San Francisco Bay Bivalves

Living organisms can accumulate contaminants to levels much greater than those found in ambient water and sediment. Some contaminants bioaccumulate because they are not readily metabolized or excreted by exposed organisms, and some possess a high affinity for the lipid rich tissue commonly found in biota. Bivalves such as clams and mussels are excellent organisms for monitoring contaminants because they accumulate chemicals from the ambient environment, have limited mobility, and are fairly resistant to contaminant effects (O’Connor 2002).

Bivalves are exposed to contaminants through their food, by ingesting sediment and assimilating compounds sorbed to particles, and by filtering dissolved contaminants directly from the water column. Their body burden of contaminants reflects an integration of contamination levels over time. Bivalves also act as transfer vectors of contaminants to higher trophic levels of aquatic food webs. Biological monitoring using bivalves has been widely applied by the National Oceanic and Atmospheric Administration (NOAA) and California State Mussel Watch Programs (Phillips 1988; Rasmussen 1994; Kimbrough et al. 2009), among others.

The RMP has been analyzing bivalve tissue samples for trace contaminants since 1993. This ongoing effort continues the long-term monitoring of the California State Mussel Watch Program, which monitored sites throughout the Estuary beginning in 1976. The RMP began monitoring bivalves specifically for PBDEs in 2002.

To investigate the uptake of PBDEs and other contaminants into the foodweb, transplanted California mussels *(Mytilus californianus*) were deployed at up to nine stations in the Bay for 90 days during the summer. At the conclusion of deployments, bivalves were retrieved, processed using clean techniques, and aliquoted for analysis. Generally, 30-40 bivalves were composited from each site for each type of analysis, although high bivalve mortality sometimes reduces the number of organisms in a composite sample. In 2002, Pacific oysters (*Crassostrea gigas*) were also deployed in some locations. In addition, at two river sites, resident (non-native) Asian clams (*Corbicula fluminea*) were collected and analyzed.

Concentrations of total PBDEs in all bivalves were mostly between 6.2 to 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 when considered separately), perhaps as a result of a longer exposure period or interspecies differences. In general, the more highly brominated congeners that comprise the DecaBDE formulation were not detected in bivalves. The most abundant congener was BDE-47, a major ingredient in the PentaBDE formulation.

Excluding river sites, PBDE concentrations in bivalves did not exhibit a high degree of spatial variation within San Francisco Bay (Figure 7). However, levels of PBDEs and particularly the dominant congener, BDE-47, have exhibited statistically significant declines at all sites across the Bay in both transplanted bivalves and resident species (Figure 7). These Bay-based bivalve BDE-47 measurements were significantly higher than those found in bivalves from a reference non-urban coastal site to the north (Bodega Bay; values ranging from non-detect to 0.94 ng/g dry weight).

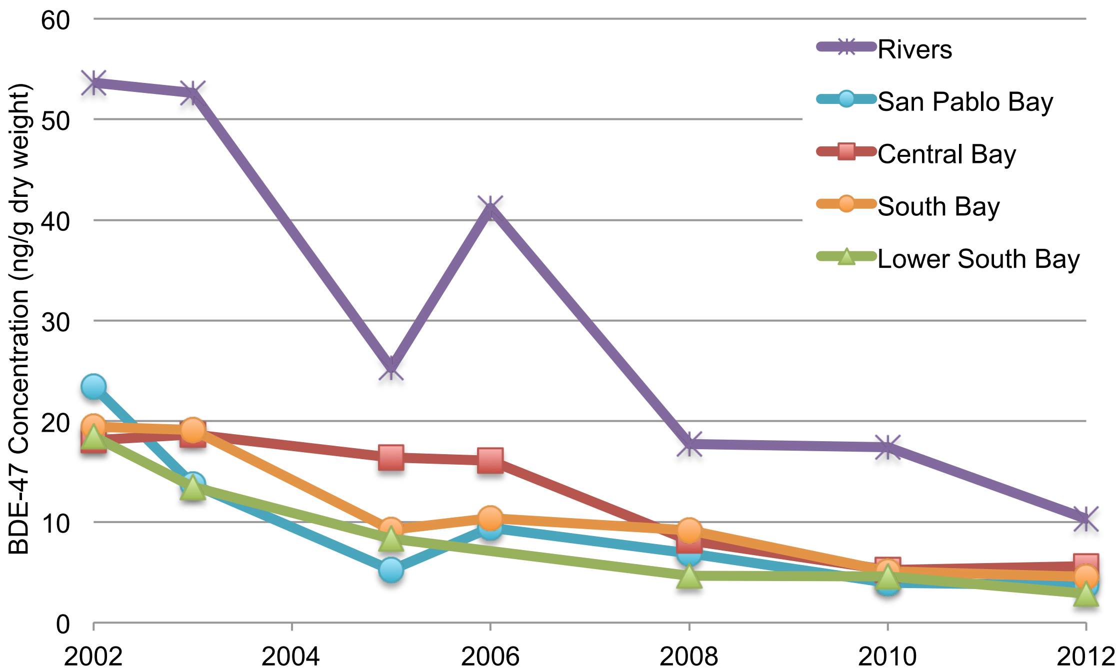

Figure 7: Concentrations of BDE-47 in bivalves (ng/g dry weight).

The BDE-47 levels for mussels reported by SFEI 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 (NOAA unpublished). Because NOAA uses resident mussels rather than transplanted ones, 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 measured by the agency to be from samples located near urban, industrialized regions (Kimbrough et al. 2009). The highest lipid-normalized level was found in a sample from Anaheim Bay, Calif., located near an industrialized area that included a military base. A San Francisco Bay sample obtained at the

Dumbarton Bridge contained the seventh highest lipid-normalized level in the nation, 900 ppb lipid weight (63 ng/g dry weight). All Bay Area samples analyzed by NOAA were considered high in PBDEs based on a cluster analysis of nationwide measurements.

2.3 PBDEs in San Francisco Bay Fish

Fish can be very sensitive to waterborne and sediment-bound contaminants. Exposure occurs via multiple routes, including ingestion, aquatic respiration, and regulation of osmotic pressure.

Contaminants in fish can also affect the people who eat them on a regular basis. The Cal/EPA's Office of Environmental Health Hazard Assessment (OEHHA) has evaluated the potential human health impacts of regularly consuming fish that contain PBDEs and other common contaminants. Their assessments provide guidance to public health agencies seeking to educate the public about safe fish eating practices.

Concern for the health of local fish and the people who eat them led the RMP to conduct triennial analysis of a number of chemical contaminants in Bay sport fish since 1993. Levels of PBDEs were quantified in fish collected in 2003, 2006 and 2009, with the final year of data considered the most robust following improvements in analytical techniques; semi-quantitative levels are also available for fish collected in 2000 (Klosterhaus et al. 2010). In addition, Cal/EPA's Hazardous Materials Laboratory tested fish samples collected in 1997 (stored at -20 °C for five years prior to analysis) and 2002 on behalf of Environmental Working Group (Lunder and Sharp 2003). These data have not been reviewed for quality assurance by the RMP and are not discussed here.

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 has not been detected in any fish samples examined by the RMP. 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 (Brown et al. 2006; Shaw and Kannan 2009; Ikonomou et al. 2011)

2.3.1 Variation in PBDE Levels Among Species

In 2009, 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; Figure 8 and Table 3). The highest single concentration found was 14 ppb in a shiner surfperch sample. Other species all averaged 5 ppb or less.

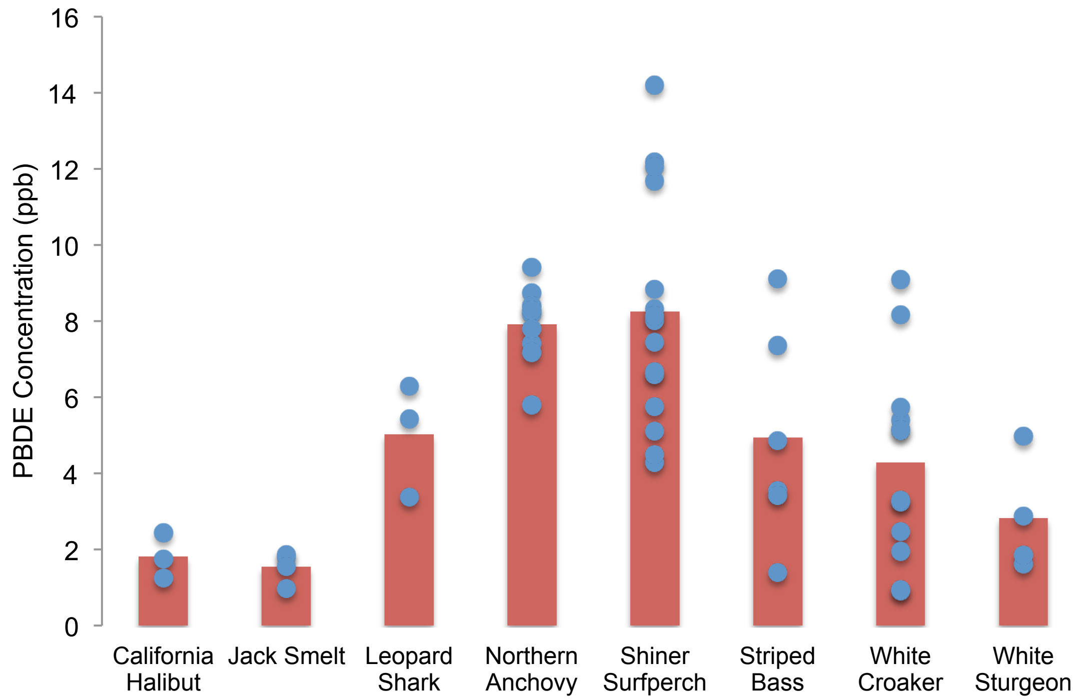

Figure 8. PBDE concentrations (ppb) in sport fish species in San Francisco Bay, 2009. Bars indicate average concentrations. Points represent individual samples (either composites or individual fish). White croaker data are for fillets without skin.

Sampling during earlier years showed somewhat different distributions of contamination. In 2003, the average PBDE levels were highest in white sturgeon (42 ppb) and anchovies (37 ppb). The highest concentration measured in 2003 was 88 ppb in a white sturgeon sample. In 2006, the average PBDE levels were highest in white croaker (fillet with skin; 57 ppb), white sturgeon (21 ppb), and shiner surfperch (13 ppb). The highest concentration in 2006 was 95 ppb in a white croaker sample (fillet with skin). The species with the next highest concentration measured was a white sturgeon sample containing 31 ppb.

Table 3. Average length (mm) and number of sport fish species sampled in San Francisco Bay, 2009.

Species	Average Length (mm)	Standard Deviation (mm)	n
White Sturgeon	1322	134	12
Leopard Shark	1095	105	9
California Halibut	663	55.7	9
Striped Bass	609	80.7	18
Jack Smelt	263	9.83	20
White Croaker	256	29	120
Shiner Surfperch	112	11.5	263
Northern Anchovy	89	9.8	338

Prior to 2009, the RMP had traditionally analyzed white croaker fillets with skin, as some anglers consume these fish with skin and this represents a conservative approach for estimating human exposure. Drawbacks in using this approach are that it is inconsistent with the advice provided by OEHHA for preparation of fish fillets; it is inconsistent with how white croaker samples are processed in other parts of the state; and skin is difficult to homogenize, leading to higher variance in the results. In 2009, the RMP began testing fillets without skin. Preparing white croaker fillets without skin is a very effective way to reduce exposure to organic contaminants. This alteration in sampling protocol makes it inappropriate to compare directly the levels of PBDEs in the most recently collected white croaker samples with earlier ones.

2.3.2 Spatial Variation in PBDE Levels in Fish

Shiner surfperch (*Cymatogaster aggregata*) is a species known for high site fidelity, and is thus a useful indicator of localized levels of contamination. Significant spatial variation was detected in 2009 levels of PBDEs in shiner surfperch samples obtained in different regions of the Bay (Figure 9). Oakland had the highest average concentration (13 ppb), which was not significantly different than 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). Overall, these averages spanned a 2.6 fold range from Oakland to San Pablo Bay.

In contrast, Brown et al. (2006) collected two shiner surfperch 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, BDE-154) to be highest in the South Bay, followed by Berkeley, San Francisco, and finally, Oakland. It is possible that this apparent difference in the spatial distribution of PBDEs in shiner surfperch is caused by the relatively small sample size of this study relative to that of the RMP.

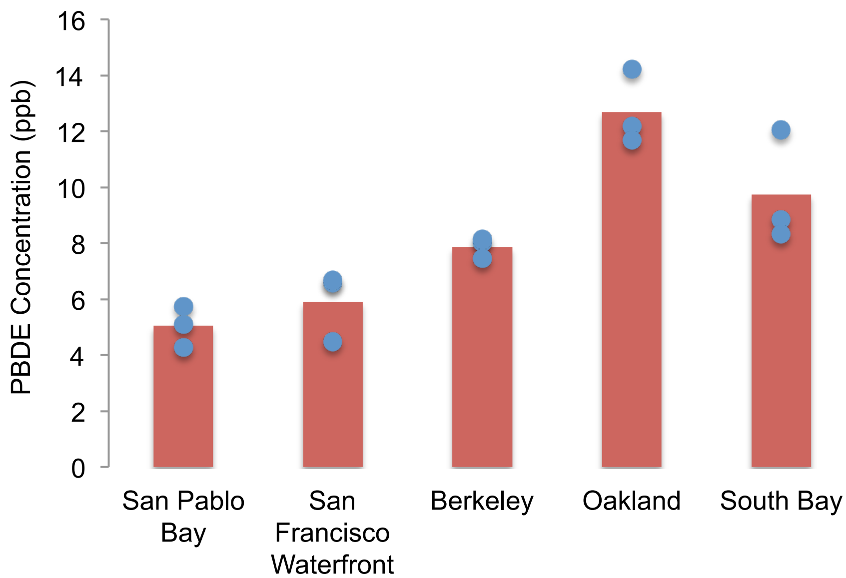

Figure 9. PBDE concentrations (ppb) in shiner surfperch in San Francisco Bay, 2009. Bars indicate average concentrations. Points represent composite samples.

2.3.3 Temporal Trends in PBDE Levels in Fish

The combination of high site fidelity and high PBDE concentrations also makes the shiner surfperch a good indicator of trends in contamination through time. The Bay-wide average for shiner surfperch in 2009 (8 ppb) was significantly lower than the averages observed in 2003 and 2006 (Figure 10).

A decline might be anticipated in response to the bans on PentaBDE and OctaBDE (the phase-out of DecaBDE would not be announced until later in 2009, after the fish sampling had occurred). However, given the short time series available and a potential lack of comparability due to the switch to a new analytical method in 2009, there is some uncertainty as to whether the lower concentrations in 2009 are a sign of a real decline or not. Continued monitoring of sport fish in the Bay will be needed to determine whether the bans on PentaBDE and OctaBDE and the phase-out of DecaBDE are indeed reducing PBDE concentrations in fish.

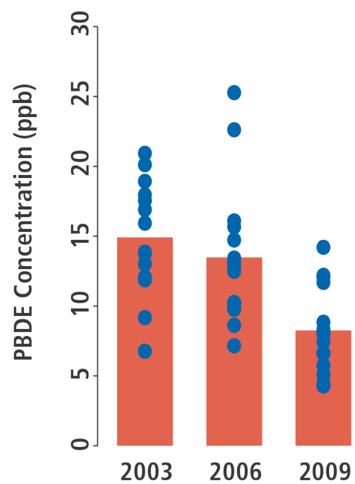

Figure 10. PBDE concentrations (ppb) in shiner surfperch in San Francisco Bay, 2003-2009. Bars indicate average concentrations. Points represent composite samples.

2.4 PBDEs in San Francisco Bay Aquatic Bird Eggs

2.4.1 PBDEs in Double-crested Cormorant Eggs

Double-crested cormorants (*Phalacrocorax auritus*) are used by the RMP as a sentinel species for the open waters of the Bay. Cormorants are piscivores, and while they prefer to forage in open Bay waters, they may also fish in a variety of shallow-water Bay habitats, including managed ponds (former salt ponds) and sloughs, as well as in deep water lakes and ponds (Hatch and Weseloh 1999; Ackerman 2013). Between 2002 and 2009, cormorant eggs were sampled Bay-wide every two to three years for PBDEs. Eggs were collected from three regions: the Central Bay (at the Richmond Bridge), the South Bay (at Don Edwards Pond or the South Bay Towers), and in the Delta-influenced Suisun Bay (at Wheeler Island). Each sample tested represents a composite of seven to ten eggs.

Two of these samples, collected in 2002, contained extremely high PBDE levels, with total PBDEs of 24,000 and 15,000 ng/g lipid, respectively. These samples were collected from

Wheeler Island in the Suisun Bay, an area that is relatively undeveloped but may be influenced by activities nearby and upstream in the Delta and Central Valley region. These measurements typically greater than those found in other fish-eating bird eggs of North America, though lower than the most extreme value measured in San Francisco Bay tern eggs at around the same time, 63,000 ng/g lipid (She et al. 2008; Henny 2009; Chen and Hale 2010).

Since 2002, concentrations of total PBDEs in cormorant eggs suggest overall declines (Figure 11). In particular, concentrations from eggs found in Wheeler Island and the Richmond Bridge in 2009 were significantly lower than those from eggs collected in 2002. Continued monitoring will be needed to detect a statistically significant declining trend. Reductions in PBDEs are expected as a result of the California Legislature's ban of PentaBDE and OctaBDE mixtures in 2006, and the voluntary halt to manufacture of DecaBDE in 2013.

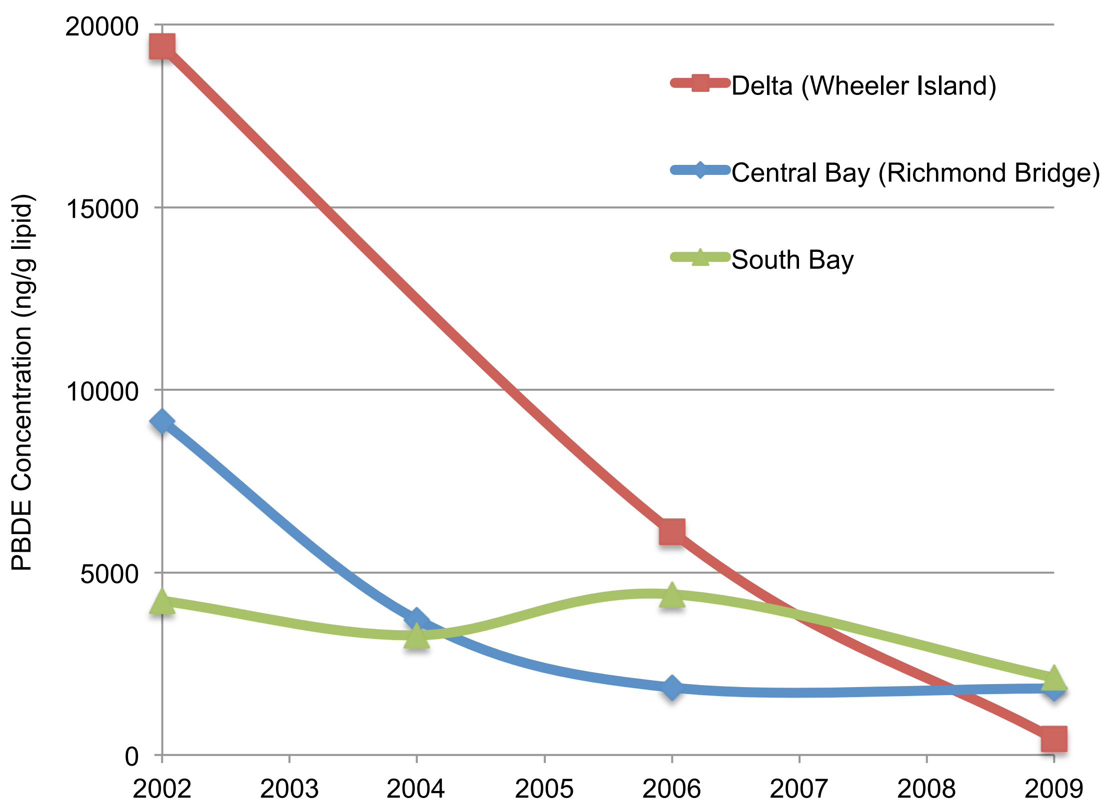

Figure 11. Average concentrations of total PBDEs in cormorant eggs (ng/g lipid). Values are averages of two or three composite samples, each obtained from seven to ten eggs.

Major congeners observed in 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 indicates that terrestrial-feeding birds are more likely to have elevated levels of BDE-209 than piscivores like the cormorant (Chen and Hale 2010). Eggs of the terrestrial-feeding peregrine falcon collected in the Bay Area contained detectable levels of BDE-209 (Newsome et al. 2010), consistent with this finding.

For cormorant eggs, the relative contribution of BDE-47 was consistently lower in the Delta-influenced Wheeler Island eggs (mean 26 ± 11%) as compared to eggs collected in the Central and South Bays (mean 43 ± 5% and 50 ± 8%, respectively), suggesting a difference in the types of PBDE contamination to which the birds are exposed. Contaminants in the Delta may experience a variety of physical, chemical, and biological processes as they move through the region, unlike contaminants directly discharged to the Bay.

2.4.2 PBDEs in Forster's Tern Eggs

A Forster's tern (*Sterna forsteri*) egg sample collected from the South Bay in 2002 by Cal/EPA scientists contained one of the highest concentrations of PBDEs in biota ever observed, 63,300 ng/g lipid (She et al. 2008). Forster's terns are piscivores that feed and breed primarily in and around managed ponds in San Francisco Bay. They are migratory, spending the winter months in Central and South America, and breeding from Baja California to British Columbia.

In 2009, the RMP analyzed tern eggs for PBDEs to determine whether contamination levels might be dropping for this species as well. Tern eggs were collected at various locations within the South, Lower South and San Pablo Bays, depending on where terns have established colonies, and eggs were composited for analysis. These more recent measurements show a dramatic decline in PBDE levels. The highest concentration of PBDEs in 2009 Forster's tern egg samples was 2,350 ng/g lipid, and the mean was 1,440 ng/g lipid, significantly lower than the 2002 mean of 9,420 ng/g lipid (Table 4).

Table 4. Total PBDE concentrations in Forster's tern eggs from San Francisco Bay (ng/g lipid).

Year	2000[1]	2001[1]	2002[1]	2003[1]	2009[2]
Samples (n)	5	29	20	22	18
Maximum (ng/g lipid)	3560	62400	63300	26000	2350
Minimum (ng/g lipid)	1080	1460	2590	666	668
Mean (ng/g lipid)	2160	7610	9420	5610	1440
Median (ng/g lipid)	1820	4380	5460	3600	1450
SD (ng/g lipid)	1010	11400	13400	5540	495

[1] Values from She et al. 2008
[2] Values measured by the RMP

2.5 PBDEs in San Francisco Bay Harbor Seals

The Pacific harbor seal (*Phoca vitulina richardii*) is a year-round resident of San Francisco Bay and the surrounding coastal waters. They can be found throughout the Bay and are the area's only permanent resident pinniped, the group that includes seals, sea lions, and walruses. Harbor seals are semi-aquatic, depending on beaches and other haul-out sites for daily rest and for giving birth during the spring pupping season.

Harbor seals are at the top of the Bay food chain, generally feeding close to shore on both bottom and schooling fishes as well as squid and crustaceans. Healthy harbor seals have thick blubber, used for insulation and energy reserves, and may live up to 30 years. These factors – year-round residency, feeding at the top of the food chain and close to the shore, and maintaining a large mass of fatty tissue over many years – put seals at special risk of accumulating toxic, lipophilic contaminants like PBDEs.

Harbor seals can be useful sentinels of water quality and have been used to identify regional contamination "hot spots." A growing body of literature from the world's five subspecies of harbor seals suggests that exposure to contaminants can reach levels that contribute to population declines (e.g., Marine Environmental Research Institute 2006).

When Cal/EPA scientists analyzed San Francisco Bay seal blubber samples that had been collected and archived from stranded, dead harbor seals from 1989 to 1998, PBDE levels were among the highest ever reported for the species (She et al. 2002). Of greater concern, the levels increased dramatically over time, doubling every 1.8 years (Figure 12). These results were reported around the world and were important for making the case to ban two of three classes of PBDEs in California.

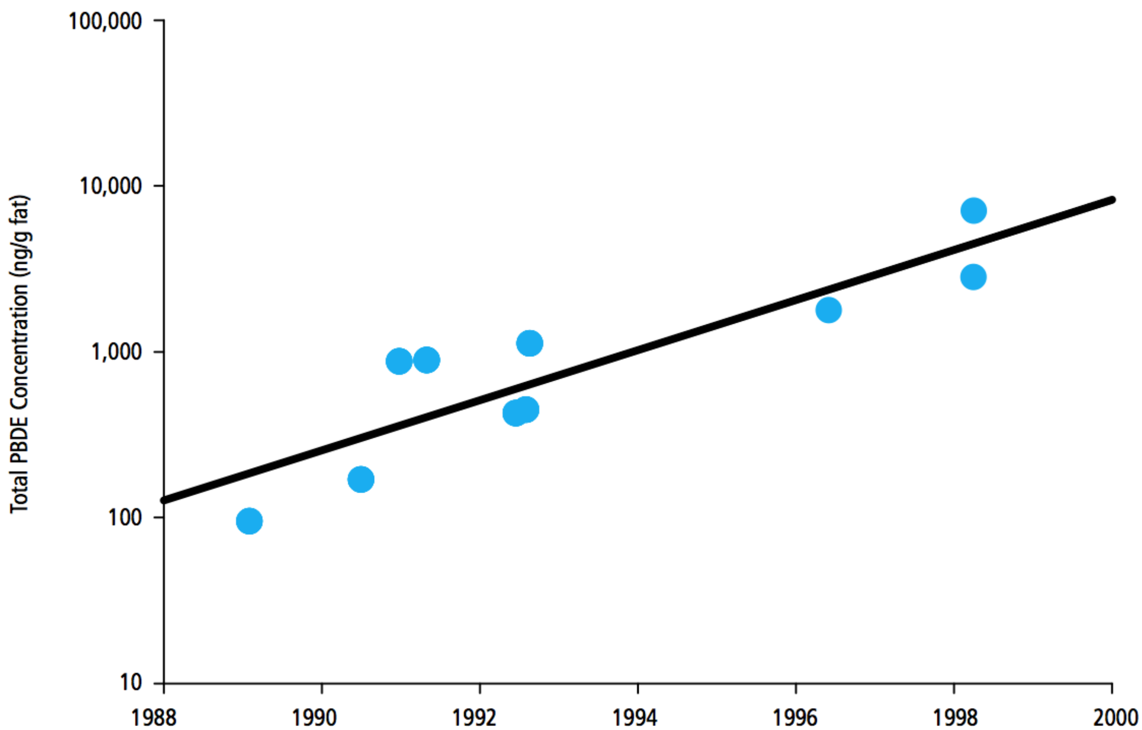

Figure 12. Concentrations of total PBDEs in San Francisco Bay harbor seals (from She et al. 2002).

A comparison of the PBDE levels measured in the blubber of the two adult harbor seals tested in 1998 (She et al. 2002) with two samples obtained by the RMP in 2006 and others collected from 2007 to 2008 and reported in the literature (Greig et al. 2011; Klosterhaus et al. 2012) suggests that the PBDE body burden for adults of this sentinel San Francisco Bay species may be declining (Table 5). These more recent measurements were generally comparable to those found in adult harbor seals from southern California and the northwest Atlantic (Shaw et al. 2008; Meng et al. 2009), and comparable or higher to those found in different regions of Great Britain (Hall et al. 2007).

Table 5. Recently collected total PBDE measurements in adult Bay harbor seals.

Year	1998[1]	2006[2]	2007-2008[3]	2007-2008[4]
Samples (n)	2	2	9	5
Maximum (ng/g lipid)	8325	1600	11000	5076
Minimum (ng/g lipid)	2985	550	300	530
Geometric mean (ng/g lipid)	4985	940	970	1076

[1] She et al. 2002
[2] The RMP
[3] Greig et al. 2011; seals from central California, including regions outside San Francisco Bay
[4] Klosterhaus et al. 2012

However, measurements in adult seals may not represent the levels of contamination experienced during younger and more vulnerable life stages. A recent study examined the effects of developmental stages on concentrations of PBDEs in very young central California harbor seals (Greig et al. 2011). Seal pups are exposed to organic contaminants through the placenta before birth and through milk during the three-to-five weeks nursing period after they are born. The study sampled blubber from 180 wild and stranded young-of-the-year animals, and categorized them by age and source of contamination (placenta, milk, or other diet).

The highest concentrations of PBDEs were found in blubber from pups that had been weaned in the wild, lost weight, then stranded and died. The blubber from one such pup had PBDE levels equal to the highest level measured in a Bay organism, 63,000 ng/g lipid (2002 Forster's tern egg sample; She et al. 2008). These results showed that harbor seals may be at particular risk during the post-weaning period, when contaminants move from blubber into blood. Continued monitoring of harbor seals for PBDEs, with a focus on vulnerable life stages, is warranted.

3.0 PBDE Contamination and Bay Impairment

The RMP launched its PBDE monitoring effort with the aim to answer the following management question: Are concentrations in the Estuary at levels of potential concern and are associated impacts likely?

3.1 Risks to Humans: PBDE Levels in Fish Are Safe for Human Consumption

In 2011, OEHHA established fish contaminant goals (FCGs) and advisory tissue levels (ATLs) for PBDEs (Klasing and Brodberg 2011). FCGs are estimates of contaminant levels in fish that pose no significant health risk to adults who consume sport fish at a rate of eight ounces per week (32 g/day), prior to cooking, over a lifetime. ATLs were calculated using the same formulas as those used to calculate FCGs, with some adjustments in order to incorporate the benefits of fish consumption. The FCGs provide a starting point for OEHHA to assist other agencies that wish to develop fish tissue-based criteria with a goal toward reducing contamination and protecting public health. The ATLs are used by OEHHA in developing consumption advisories.

FCGs are designed to prevent consumers from being exposed to more than the daily reference dose (RfD – USEPA's maximum acceptable oral dose of a toxic substance) for non-carcinogens, or to a risk level greater than $1x10^{-6}$ for carcinogens (not more than one additional cancer case in a population of 1,000,000 people consuming fish at the given rate over a lifetime). FCGs are based solely on public health considerations relating to exposure to each individual contaminant, and do not consider economic impacts, technological feasibility, or the counterbalancing health benefits of fish consumption. The most protective FCG, based on the daily reference dose for non-carcinogenic effects and assuming consumption of a single 8-ounce serving per week, is 310 ppb PBDEs.

ATLs provide a number of recommended fish servings that correspond to the range of contaminant concentrations found in fish. They are designed to prevent consumers from being exposed to more than the average daily RfD for non-carcinogens, or to a risk level greater than $1x10^{-4}$ for carcinogens (not more than one additional cancer case in a population of 10,000 people consuming fish at the given consumption rate over a lifetime). ATLs also confer no significant health risk to individuals consuming sport fish in the quantities shown over a lifetime. They encourage consumption of fish that can be eaten in amounts likely to provide health benefits and discourage consumption of fish that, because of contaminant concentrations, should not be eaten or cannot be recommended in amounts suggested for improving overall health. According to these ATLs, an adult can safely consume two servings of fish per week contaminated with more than 100 and up to 210 ppb PBDEs. Fish contaminated with more than 210 and up to 630 ppb PBDEs should generally only be consumed once a week. Fish with concentrations below 100 ppb can be consumed at a rate of three servings per week.

FCGs and ATLs were developed for 70 kg adults; adults weighing less should eat proportionately smaller amounts than the standard serving size of eight ounces. PBDE FCGs and ATLs were not designed for young children, who may be especially susceptible to the endocrine disrupting and developmentally neurotoxic effects of exposures to PBDEs (e.g., Eskenazi et al. 2013), and typically have higher PBDE body burdens than adults (Lunder et al. 2010).

PBDE concentrations in all fish samples obtained in 2009 were far below the lowest OEHHA threshold (the 100 ppb two servings per week ATL), indicating that PBDE concentrations in Bay sport fish are not currently a concern with regard to human health. A few fish samples collected in 2003 and 2006 exceeded 80 ppb, within 20% of this threshold. Continued monitoring of sport fish will be needed to determine whether the elimination of commercial PBDE production is indeed reducing concentrations in the Bay food web such that people can eat Bay fish without consuming harmful levels of these contaminants. Nevertheless, at the present time, PBDE contamination of the Bay does not appear to significantly increase risks to human health via fish consumption.

3.2 Risks to Wildlife

3.2.1 PBDEs Pose Possible Risks to Benthic Organisms

A study of polychaete larval settlement and growth found BDE-47 exposure triggered effects in three species at a sediment concentration of 3.0 ng/g dry weight, and no effect at a concentration of 0.5 ng/g (Lam et al. 2010). In Bay sediments, 37% of samples exceeded 0.5 ng/g BDE-47, and just one Bay sample and two Bay margin “hot spot” samples exceeded 3.0 ng/g BDE-47. Lam et al. (2010) did not specifically characterize 0.5 and 3.0 ng/g BDE-47 as a NOEC and LOEC, respectively; however, the high frequency of Bay sediment BDE-47 levels between these values suggests the potential for low level adverse effects to benthic organisms.

3.2.2 PBDEs Pose Possible Risks to Fish

In studies with fish, increased susceptibility to pathogenic microorganisms (Arkoosh et al. 2010) has been observed in subyearling Chinook salmon (*Oncorhynchus tshawytscha*) with PBDE concentrations comparable to those found in Bay fish, particularly samples of white sturgeon (*Acipenser transmontanus*) and anchovy (*Engraulidae*) collected in 2003 and white croaker (*Genyonemus lineatus*; analyzed with skin) collected in 2006. While all fish collected in 2009 had levels of PBDEs less than half the level associated with impaired immune function in this study, no specific toxicity thresholds (e.g., NOAEL or LOAEL) have been determined. It is possible that Bay fish may be susceptible to low level adverse effects at present.

Effects such as altered locomotion behavior (Chou et al. 2010) and thyroid disruption (Lema et al. 2008) have been documented in other studies of fish species, but have only been observed in fish with PBDE concentrations significantly higher than those found in Bay fish.

3.2.3 PBDEs Are Unlikely to Pose Risks to Birds

In birds, PBDEs have been associated with reproductive effects in a laboratory study of American kestrels (McKernan et al. 2009) and in wild populations ospreys (Henny et al. 2009) at concentrations within the range of those found in San Francisco Bay tern eggs (She et al. 2008), but higher than those observed in Bay cormorant eggs. Recent work sponsored by the RMP suggests that terns may not be as sensitive to exposure to PBDEs as kestrels and ospreys (Rattner et al. 2011, 2013). Terns may face the greatest risk among Bay bird species: they are the most highly exposed bird species studied in the Bay, and have exhibited some of the highest concentrations reported in any biota in the world (She et al. 2008).

In the RMP-sponsored study, 60 recently laid common tern (*Sterna hirundo*) eggs were collected from Poplar Island, Maryland (Rattner et al. 2011, 2013). Eggs from this area had relatively low levels of PBDEs and other organic contaminants. The eggs were artificially incubated, and on day 4 of development either a corn oil vehicle control or PentaBDE at doses of 0.2, 2, or 20 μg/g egg was injected into the air cell at constant volume (0.5 μL/g egg).

The terns were evaluated for embryonic survival, pipping and hatching success; embryos and hatchling terns were also examined for evidence of sublethal effects including deformities, growth patterns, hepatic, thyroid and immune organ histopathology, and biochemical effects. Exposure to PentaBDE produced no significant effects on survival to late incubation, pipping, or hatching (Rattner et al. 2011, 2013). However, when considering all PentaBDE treated eggs as a single group, the exposed eggs hatched 0.44 days later than those exposed to vehicle controls only ($p=0.0137$). No gross deformities were observed in tern embryos that failed to hatch or in tern hatchlings (Rattner et al. 2011, 2013). Crown-rump length and the weight of the hatchling, yolk sac, liver, bursa of Fabricius, thyroid, and organ to body weight ratios were not affected by PentaBDE, although spleen weight and spleen to body weight ratio of the 2 µg/g group alone were greater than controls ($p=0.05$ and 0.03). Skeletal and histopathological examinations as well as oxidative stress measurements in hatchling terns indicated no significant effects caused by PentaBDE exposure (Rattner et al. 2011, 2013).

As a positive control, a study was conducted in which American kestrel eggs either received corn oil vehicle or 20 µg PentaBDE per gram egg by injection into the air cell (Rattner et al. 2011, 2013). Although PentaBDE did not impair pipping and hatching success of kestrels, it did result in a delay in hatch, shorter humerus length, and lower total thyroid and total thyroid to body weight ratio. Concentrations of oxidized glutathione, reduced glutathione and thiobarbituric acid reactive substances were all greater in PentaBDE treated kestrels compared to controls.

The findings from this study suggest that common tern embryos, and likely those of other tern species, are probably less sensitive to PBDEs than American kestrel embryos (Rattner et al. 2011, 2013). Reproductive and developmental effects were not observed at injected concentrations approximating PBDE concentrations in Forster's tern eggs from San Francisco Bay. The chemical exposures that occur via egg injection are not equivalent to those that occur naturally via maternal transfer to the egg, a source of uncertainty that may affect the direct application of these findings to an assessment of risks posed to Bay birds. While no available studies assess the risks of PBDE exposure to Bay birds and bird eggs, this toxicity study suggests the risks may be low at current levels of exposure.

3.2.4 PBDEs Pose Possible Risks to Harbor Seals

Seals from the Bay have been found to exhibit a number of abnormal health parameters including low red blood cell counts and high white blood cell counts, and it has been hypothesized that environmental contaminants might play a role (Kopec and Harvey 1995). Seals from the central California coast have also been found to have considerably higher blood levels of PBDEs and other organic contaminants as compared to a reference population in Alaska (Neale 2004).

To probe the connection between PBDE exposure and the health of harbor seals, blood samples from 35 free-ranging Bay seals were examined as part of an integrated study of contaminant levels, immune function, and biological parameters (Neale et al. 2005). The 13 males and 22 females, including pups, yearlings, and adults, were captured from haul-out sites during the summers of 2001 and 2002; all seals were re-released to the wild after weighing, measuring, and drawing blood. The blood samples were analyzed for PBDEs and other contaminants as well as biological parameters.

Higher PBDE levels in blood samples were associated with higher white blood cell counts, suggesting that high levels of contaminants might be linked to increased rates of infection (Neale et al. 2005). In contrast, there was an inverse correlation between total PBDEs and red blood cells, though the relationship was not strong enough to support a clear connection to anemia.

Although the results of this study did not tie PBDEs directly to disease, the trends suggest contaminant-induced alterations in Bay harbor seals, especially in individuals with relatively high contaminant burdens (Neale et al. 2005). Further study to determine the contribution of PBDE contamination to the morbidity and mortality of the Bay harbor seal population is warranted. In particular, studies on exposure-related effects in young seals that lose weight during the post-weaning fast are needed, as this group contained the highest levels of PBDE contamination in blubber observed (Section 2.5; Greig et al. 2011). During the fasting period, contaminants like PBDEs are mobilized from blubber into the blood, where they may cause adverse health effects on various systems just as young seals are learning to forage and experiencing their first parasitic infections.

3.3 Potential for Impairment: Summary

The weight of the evidence suggests that for humans consuming Bay fish, current levels of PBDE contamination represent no impairment: "The available data demonstrate no negative effect on beneficial uses of the Bay, and there is sufficient information to make the finding." A standardized risk assessment based on multiple studies of toxicity and carcinogenicity produced thresholds of contamination that Bay fish do not exceed (Klasing and Brodberg 2011).

For benthic organisms exposed via sediment, there is evidence to indicate possible impairment: "There is some suggestion of impairment, but the uncertainties preclude making a definitive judgment." A study of polychaete larval settlement and growth found BDE-47 exposure caused effects in three species at a sediment concentration of 3.0 ng/g dry weight, and no effect at a concentration of 0.5 ng/g (Lam et al. 2010). The high frequency of Bay sediment BDE-47 levels between these values suggests the potential for low level adverse effects to benthic organisms.

For fish, there is evidence to indicate possible impairment. Increased susceptibility to pathogenic microorganisms (Arkoosh et al. 2010) was observed in subyearling Chinook salmon with PBDE concentrations comparable to those found in some Bay fish samples collected in 2003 and 2006. While all fish collected in 2009 had levels of PBDEs less than half the level associated with impaired immune function in this study, it is possible that Bay fish may be susceptible to low level adverse effects at present. Additional research is needed to identify appropriate toxicity thresholds for Bay fish.

For birds, the weight of the evidence suggests impairment unlikely: "The data indicate that PBDEs cause no impairment to the Bay. However, there is some uncertainty, due to lack of sufficient information or disagreement about how to interpret the data." A new, RMP-sponsored study of PentaBDE toxicity to tern eggs suggests current levels of contamination are not a cause for concern in a species thought to face relatively high exposure and risk (Rattner et al. 2011, 2013); however, studies probing more species and a broader array of health effects would be necessary to conclusively determine Bay birds are unaffected by current levels of these contaminants.

For harbor seals, there is evidence to indicate possible impairment. Higher blood levels of PBDEs appear to be associated with unhealthy alterations in red and white blood cell counts, though a causal connection cannot be substantiated at this time (Neale et al. 2005). Further study is needed to determine whether PBDE contamination levels in the Bay are impacting the health of harbor seals, especially the more highly exposed, weaning pups.

4.0 PBDE Pathways and Loads to San Francisco Bay

4.1 Pathways of PBDEs to the Bay: Stormwater and Large Tributary Inputs

PBDE contamination is primarily associated with proximity to urban landscapes. Like many other urban contaminants, PBDEs are expected to enter the Bay in large part through discharges of both treated wastewater and urban stormwater (Werme et al. 2007). Stormwater represents a particularly important pathway for the particle-bound, higher-brominated PBDEs like BDE-209 to move from the terrestrial landscape to the Bay.

Through funding from the RMP, SFEI has sampled ten mixed-use watersheds around the Bay Area for PBDEs in stormwater runoff (Table 6; McKee et al. *in prep*). Most of these watersheds have only been studied at a pilot level, with fewer than eight samples collected, whereas greater concentration and loading information exists for the Guadalupe River and Zone 4 Line A watersheds. The total PBDE mean of means measured across the ten San Francisco Bay sites was 41 ng/L; the mean proportion of BDE-47 was 8%, while for BDE-209 it was 58% (Table 7; McKee et al. *in prep*). In contrast, concentrations of total PBDEs measured in open Bay waters were ≤ 1 ng/L (Section 2.1.1).

Stormwater concentrations in Zone 4 Line A, a fully urban tributary in Hayward, showed a strong correlation with turbidity, for both the sum of PBDEs as well as the individual congeners BDE-47 and BDE-209 (r^2 = 0.88, 0.90, and 0.86, respectively; Gilbreath et al. 2012). In this watershed, an estimated 99% of the total PBDE load was transported during storm flow conditions, with 58% of the total load as BDE-209 and 6% as BDE-47. These observations are consistent with other local urbanized tributaries in the Bay Area (Oram et al. 2008).

Few data exist in the world literature on PBDE concentrations in stormwater (Table 6). Mean and median San Francisco Bay stormwater PBDE levels are all greater than those measured for urban areas in Washington and Oregon (Lubliner 2009; Morace 2012).

Likewise, concentrations in Bay Area tributaries are greater by approximately 5-7 times for most of the summary statistics provided in a study of monthly water samples collected from small tributaries in the urban e-waste "hot spot" Pearl River Delta region of China (Tables 6 and 7; Guan et al. 2007). However, lower measurements in the Pearl River Delta could be caused by a sampling regime that emphasized regular, monthly sample collection, as opposed to a focus on peak measurements obtained during storm events. SFEI samples of Zone 4 Line A, collected during both storm- and low-flow conditions, indicated average storm flow concentrations ten times greater than base-flow concentrations. Additional differences between the Bay and Pearl River Delta datasets are the relative contributions of BDE-47 and BDE-209, with BDE-47 having a much greater presence in San Francisco samples (Table 7). These differing congener profiles would be expected given California's flame retardant standards.

Although stormwater data do not exist for completely homogenous land uses in the San Francisco region or elsewhere, SFEI preliminarily explored the relationship between contaminant concentrations and land use in Bay watersheds. This exploration yielded strong correlations with the combined sum of proportion of High Residential and Open Compacted (e.g., urban park) spaces (Figure 13; McKee et al. *in prep*). The linear trendline in these graphs excludes one high outlier watershed, Zone 5 Line M in Union City. The land uses for this watershed are approximately 31% residential, 11% transportation, 36% open, 15% commercial, and 7% industrial. The most elevated concentration at this location was unlike the other samples collected in the same watershed and unlike the rest of the Bay Area samples in that the ratio BDE-209:BDE-47 was 38, as opposed to the Bay Area average ratio of 10. Ninety percent of the sample was comprised of BDE206-209, indicating that DecaBDE was the dominant source. Further investigation could reveal significant source areas in this watershed.

Table 6. Total PBDE concentrations in stormwater based on review of peer-reviewed literature and locally collected data by the RMP (McKee et al. *in prep*). All watersheds include mixed-urban land uses.

		PBDE concentrations (ng/L)				
Specific Location	**n**	**Min**	**Max**	**Mean**	**Median**	**Reference**
Hengmen riverine outlet to Pearl River Estuary, China	12	2.3	16	9	9	Guan et al. 2007
Honqilimen riverine outlet to Pearl River Estuary	12	0.6	9	4	3	Guan et al. 2007
Humen riverine outlet to Pearl River Estuary	12	0.4	33	8	3	Guan et al. 2007
Hutiaomen riverine outlet to Pearl River Estuary	12	0.3	8	3	2	Guan et al. 2007
Jiaomen riverine outlet to Pearl River Estuary	12	1.0	9	4	4	Guan et al. 2007
Jitimen riverine outlet to Pearl River Estuary	12	1.5	11	5	6	Guan et al. 2007
Modaomen riverine outlet to Pearl River Estuary	12	0.8	10	3	3	Guan et al. 2007
Yamen riverine outlet to Pearl River Estuary	12	2.4	68	19	13	Guan et al. 2007
Spokane River, WA	14			7	5	Lubliner 2009
Columbia River, WA, OR	16	ND	53	9	0.2	Morace 2012
Borel Ck, Peninsula Bay Area, CA	3	9	20	14	12	McKee et al. 2012
Coyote Ck, Santa Clara County, CA	7	7	36	15	13	SFEI unpublished
Guadalupe River, San Jose, CA	13	15	369	88	38	SFEI unpublished; McKee et al. 2006
Lower Marsh Ck, Brentwood, CA	1	20	20	20	20	SFEI unpublished
Lower Penetencia Ck, Milpitas, CA	4	13	22	18	19	McKee et al. 2012
San Leandro Ck, San Leandro, CA	3	41	80	57	50	SFEI unpublished
Santa Fe Channel, Richmond, CA	2	24	30	27	27	McKee et al. 2012
Sunnyvale East Channel, Sunnyvale, CA	6	5	100	48	42	McKee et al. 2012; SFEI unpublished
Zone 4 Line A, Hayward, CA	38	0	430	47	27	Gilbreath et al. 2012
Zone 5 Line M, Union City, CA	4	34	128	75	69	McKee et al. 2012

Table 7. Summary table of PBDE concentrations in stormwater runoff data, Pearl River Delta, China (Guan et al. 2007) versus San Francisco Bay, Calif. (McKee et al. *in prep*).

	Pearl River Delta Data (n=8)	San Francisco Data (n=10)
Minimum of dataset (ng/L)	0.3	0.4
Maximum of dataset (ng/L)	68	430
Mean of the Means Total PBDEs (ng/L)	7	41
Mean of the Means BDE-47 (%)	1	8
Mean of the Means BDE-209 (%)	91	58
Mean of the Means Ratio BDE-209:BDE-47	150	10

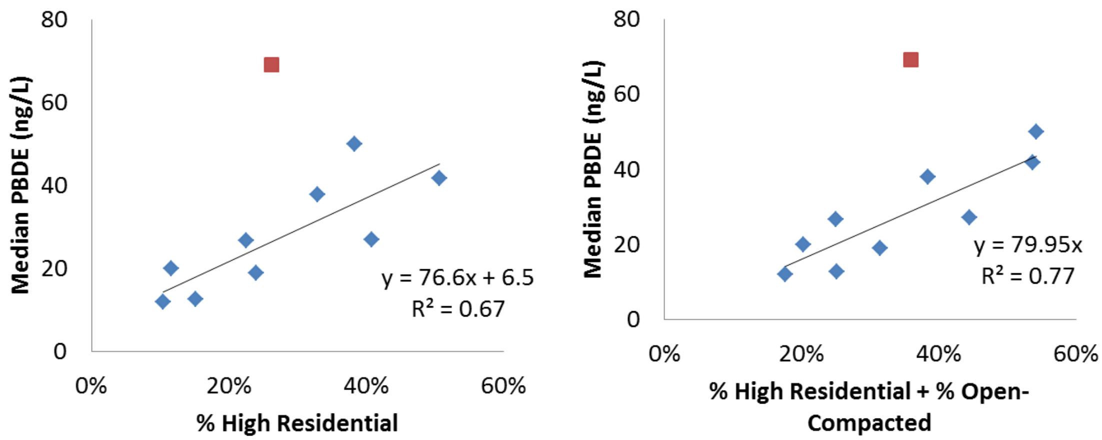

Figure 13. Median PBDE concentrations in relation to the percentage of high density residential and percentage of compacted open space in nine Bay Area watersheds (McKee et al. *in prep*). The linear trendline is related only to the nine watersheds represented by blue markers; the red marker is Zone 5 Line M.

In addition to the stormwater measurements made for small tributaries, the RMP examined PBDE levels in the Sacramento-San Joaquin River Delta at Mallard Island (David et al. 2012). The large tributary rivers feeding the Delta drain the Sacramento and San Joaquin watersheds, representing 154,000 km^2 of land, or about 37% of the state of California. Thirty-five samples of river water were analyzed for PBDEs during water years 2005 and 2006. However, because of blank contamination and recovery issues, BDE-209, which often represents a large proportion of the sum of PBDEs, could not be reported for many samples. The sampling program was designed to especially capture the highest flow events, which typically account for the majority of annual loads.

Total PBDE concentrations varied from 35 pg/L to 830 pg/L, with a calculated flow-weighted mean concentration (FWMC) of 480 pg/L (David et al. 2012). BDE-47 and BDE-209 were the dominant congeners in the PBDE mixture. BDE-47 concentrations ranged from 130 pg/L to 350 pg/L, with an average of 190 pg/L and a FWMC of 200 pg/L. Due to blank contamination, BDE-209 data were only available for water year 2005, and concentrations ranged from 110 pg/L to 400 pg/L, with an average of 190 pg/L and a FWMC of 190 pg/L.

Utilizing FWMCs, total PBDE loads of 13 and 8.7 kg were calculated for 2005 and 2006, respectively (David et al. 2012). However, the 2006 loads were calculated without BDE-209 being reported for all samples. Loads made on that basis are lower bound estimates. The FWMCs were diluted during wetter years; 670 and 270 pg/L for 2005 and 2006, respectively. This observation is consistent with a hypothesis that the main sources of PBDEs in the Sacramento-San Joaquin watersheds are from urban areas that contribute proportionally more runoff during low flow years compared to higher flow years. Cleaner runoff from the Sierra Nevada likely dilutes concentrations during high flows (Oram et al. 2008) and, if this is true, PBDE loads may be slightly underestimated because low flows were not sampled.

4.2 Loadings of PBDEs to the Bay

A 2008 RMP study presented the first estimates of PBDE loading to the Bay from multiple pathways (Oram et al. 2008). Water year 2005 discharge rates and flow-weighted mean concentrations of BDE-47 and BDE-209 from the Sacramento-San Joaquin River Delta were combined with those for both stormwater discharges from local tributaries (Guadalupe River and Coyote Creek) and treated wastewater discharges from local municipalities. Atmospheric deposition was estimated based on local measurements made by the CARB in 2003 and 2004 (CARB 2010). Finally, degradation rates and physical or chemical properties for BDE-47 and BDE-209 were taken from estimates or measurements found in the literature (Oram et al. 2008).

The resulting mass budget model estimated Bay inventories of BDE-47 and BDE-209 in 2006 to be 33 ± 3 kg and 153 ± 45 kg, respectively (Oram et al. 2008). Empirically derived estimates of annual inputs of BDE-47 and BDE-209 from all quantifiable external pathways ranged from 11 to 28 kg/yr and 22 to 24 kg/yr, respectively (Table 8). BDE-47 loads were dominated by treated wastewater, while runoff from local tributaries represented the largest contributor to BDE-209 loads. Presumably most of the BDE-209 entering wastewater treatment facilities settled out in the sewage sludge. The concentrations in treated wastewater and stormwater from small tributaries were about three orders of magnitude greater than concentrations sampled in Bay waters (Werme et al. 2007).

Table 8. Summary of estimated annual PBDE loads (kg) to San Francisco Bay (Oram et al. 2008).

Pathway	BDE-47	BDE-209
Sacramento-San Joaquin Delta[1]	3	3
Local tributaries[2]	3	17
Municipal wastewater	4-21	1-3
Atmospheric deposition	~1	~1
Total	11-28	22-24

[1] Determined using data from water year 2005; assumes water year 2005 is representative of average water year.
[2] Based on measurements from Guadalupe River and Coyote Creek.

Sensitivity of model results to changes in degradation rates for BDE-47 and BDE-209 was evaluated via hindcast estimates (Oram et al. 2008). While degradation rates for BDE-47 proved sufficient for this first-order mass budget, those for BDE-209 raised questions. For this congener, model results indicated that under a continuous external loading scenario of 80 kg/yr, there would be slightly more than 100 kg BDE-209 in the Bay after 30 years. Running the model with a continuous loading scenario of 140 kg/yr suggested there would be approximately 200 kg BDE-209 in the Bay after 30 years.

These loads are considerably higher than the range estimated from empirical data (22-24 kg/yr), indicating that either the BDE-209 degradation rates used are unrealistically fast, or that the actual BDE-209 load from all external pathways is in the range of 80 to 140 kg/yr. The agreement between model results and empirical inventory estimates of BDE-209 improved when the model was run with substantially slower degradation rates (half-lives of 13 yr for water and 50 yr for sediment).

Stormwater data from the fully urban Zone 4 Line A local tributary were not available at the time that this PBDE mass budget was developed (Oram et al. 2008), and can now be used to further refine the previous regional loadings estimated in that study. Annual BDE-209 yield from this urban stormwater pathway was 5.6 μg/m^2, which extrapolated to the entire Bay Area conurbation (excluding areas upstream from reservoirs = 5,050 km^2), yields an estimated total annual BDE-209 load to the Bay from local tributaries of 28.3 kg/yr, versus 17.3 kg/yr previously estimated (Gilbreath et al. 2012). Because it is a fully urbanized watershed, a local tributary loading based solely on Zone 4 Line A represents an upper bound for this value relative to the one based on the Guadalupe and Coyote Creek watersheds used to generate the original mass budget. The value calculated for this urban stormwater tributary supports the magnitude of the prior mass budget estimate, but indicates the total load might be slightly higher than previously estimated because many of the more highly urbanized watershed areas surrounding the Bay would be better characterized by yields estimated from Zone 4 Line A (Gilbreath et al. 2012). This potential increase in load would not be sufficient to account for the discrepancy between the original hindcast modeled BDE-209 loads and empirical data (Oram et al. 2008), and therefore suggests that degradation of BDE-209 in the Bay might be slower than suggested in the literature.

A contrasting concern, highly brominated congeners like BDE-209 can degrade to less brominated congeners through photolytic or biological processes (de Wit 2002), a conversion not accounted for in this mass budget. An initial investigation of the level of debromination occurring within the Bay is in press, and its findings indicate both processes are active in San Francisco Bay (Rodenburg et al. *in press*). Inclusion of terms to account for these processes could further refine calculations of the mass budget of PBDEs in the Bay ecosystem.

Nevertheless, as it stands the mass budget provides a useful framework for integrating future monitoring and modeling efforts. In particular, the mass budget can be useful for estimating reductions in PBDE loads over time under various management scenarios, as discussed in Section 5.3.

5.0 Past and Future Trends in Contamination

5.1 Declining Levels in San Francisco Bay Biota

As described in detail in Section 2.0, monitoring of wildlife for PBDEs suggests a decline in PBDE levels for all San Francisco Bay organisms under study. Bivalves collected during the three most recent samples years (2008, 2010, 2012) show lower levels of contamination than those collected when the RMP first began testing for PBDEs in 2002 (Figure 7). 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 (Figure 10). Cormorant eggs show reductions in PBDE contamination between 2009 and 2002 across all regions of the Bay (Figure 11), and Forster's tern eggs exhibited significantly less contamination in 2009 than they did when originally sampled by DTSC scientists in 2002 (Table 4; She et al. 2008). Finally, adult harbor seal blubber samples collected by the RMP and others (Greig et al. 2011; Klosterhaus et al. 2012) from 2006 to 2008 showed lower geometric means of PBDE contamination than those sampled in 1998 by DTSC (Table 5; She et al. 2002).

The recent decline in PBDE levels found in San Francisco Bay biota is likely a consequence of the voluntary production phase-outs and state bans of PentaBDE and OctaBDE, effective in 2006. While manufacturers voluntarily phased out production of the final commercial PBDE mixture, DecaBDE, by the end of 2013, it is unlikely that related changes in production would affect data collected through 2012. Chemical bans and phase-outs do not immediately remove all sources of contaminants to the environment, as the chemicals in question remain present in products in use or entering the wastestream. Nevertheless, these results suggest that management actions can be very successful in reducing contaminant concentrations in biota. In this case, noticeable changes occurred just a few years after bans were implemented.

RMP data provide the most abundant evidence to date of 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, including osprey eggs in the Pacific Northwest (Henny et al. 2009), sockeye salmon from the northeast Pacific Ocean (Ikonomou et al. 2011), and trout in the Great Lakes (Crimmins et al. 2012). The RMP's large bioaccumulation monitoring dataset, covering multiple species and collected consistently for many years, is essential to establishing the real environmental outcomes associated with management decisions. Continuing monitoring is needed to track the decline of PBDEs in Bay biota.

5.2 Some Decline in PBDEs Observed in Water and Sediment

In contrast to trends seen in Bay wildlife, concentrations in water and sediment have shown fewer distinct trends over the ten-year period of record (Section 2.0). While Bay-wide averages of the dominant congener in water, BDE-47, suggest a small, non-significant decline since 2004 (Figure 2), Bay-wide averages of the dominant congener in sediment, BDE-209, showed little change (Figure 4).

In contrast, Bay-wide averages of BDE-47 in sediment indicate a statistically significant declining trend over the last decade. Recent trends in sediment contamination may be obscured by mixing via bioturbation and wind wave resuspension, and by sample compositing; an RMP sediment sample consists of the top 5 cm of sediment, while the sediment accretion rate in most areas of the Bay is less than 0.5 cm/yr (Yee et al. 2011). The appearance of a statistically significant trend in Bay-wide averages of sediment BDE-47 levels despite this methodological constraint is noteworthy.

However, Bay-wide average values of water or sediment PBDEs may not reflect actual exposures experienced by Bay biota. Many small fish consumed by birds and sport fish forage in habitats on the margins of the Bay. These margin habitats are not typically sampled as part of RMP activities, and may be more PBDE-contaminated than open regions of the Bay.

A pilot study probing levels of another group of persistent contaminants, polychlorinated biphenyls (PCBs), in small fish in the Bay margins found average levels of contamination much higher than in sport fish (Greenfield and Allen 2013). PCB concentrations in the small fish were found to correlate well with PCB concentrations in nearby margin sediment samples, supporting this hypothesis. The high PCB uptake observed in small fish is an important element linking PCB sources and accumulation in the greater Bay food web.

In 2011, the RMP conducted sediment sampling of a few sites in the Bay margins and found that some of these locations hold PBDE concentrations far greater than any found in the greater Bay. Sediments in San Leandro Bay and Mission Creek contained BDE-209 concentrations at least four times greater than any other site sampled that year. A characterization of the fate of PBDEs in the margins of San Francisco Bay could prove useful to better predicting biotic and abiotic responses to management actions already underway (Jones et al. 2012). Investigation of potential contamination “hot spots” in the margins surrounding the Bay may prove useful in understanding the specific exposure pathways leading to PBDE declines in wildlife.

5.3 Anticipated Future Trends

Manufacture and use of PBDEs has changed dramatically over the past decade. In part as a result of the widely detected presence of PBDEs in the environment, the major manufacturer (Great Lakes Chemical Corporation, now Chemtura Corporation) of two of the three PBDE formulations (PentaBDE and OctaBDE) ceased production of these compounds at the end of 2004, and the California Legislature banned these compounds in 2006. Also in 2006, the USEPA issued a significant new use rule on these compounds, requiring that any use proposed in the future be reviewed for safety. Chemical manufacturers voluntarily phased out production of the DecaBDE formulation by the end of 2013. Finally, the state agency largely responsible for the widespread use of PBDEs and other chemical flame retardants has revised a key flammability standard, eliminating the incentive to incorporate flame retardants into upholstered furniture and many items for infants and young children (BEARHFTI 2013a). These management actions have a direct impact on anticipated future trends in PBDE contamination in San Francisco Bay.

5.3.1 PentaBDE and OctaBDE

Using the PBDE mass budget for the Bay, Oram et al. (2008) conducted forecast modeling to estimate the trajectory of Bay contaminant levels under different future scenarios. Running the model using a scenario of BDE-47 loads continuing at the upper end of available estimates of annual loading (approximately 30 kg/yr), a nearly 40% increase in the total BDE-47 inventory was considered likely. However, using a scenario at the lower end of current load estimates (approximately 10 kg/yr), a 50% decrease in the total inventory of BDE-47 in 40 years was predicted, with most of the decrease realized in the first 10 years. Important loss pathways of BDE-47 from the Bay were degradation in sediment and outflow.

The considerable difference between the 30 kg/yr and 10 kg/yr scenarios highlights the sensitivity of the Bay to changes in BDE-47 loads. If loads were reduced slightly from current levels, these model calculations suggest that the mass of BDE-47 in the Bay would decline appreciably. The recovery would be more rapid and more complete if loads were stopped altogether; a recovery of 90% in less than 10 years is possible. Given the state ban on PentaBDE, BDE-47 loads should decline, though they likely will not disappear entirely for some time, given the amount of BDE-47 that exists in products in use, in the wastestream, and in the watershed. Declines are already evident in wildlife, sediment, and perhaps Bay waters. Risks to Bay wildlife and human consumers of Bay fish should also decline.

Because the congeners making up OctaBDE represent a relatively small part of PBDE contamination observed in the Bay, mass budgets have not been developed for them. However, because OctaBDE has also been banned, its congeners are also likely to decline in the Bay.

5.3.2 DecaBDE

As with BDE-47, model results suggested high sensitivity of the Bay to loads of BDE-209, the dominant congener in DecaBDE (Oram et al. 2008). Using the degradation rates predicted in the literature and load estimates that produced the best agreement with empirical inventory estimates, the forecast model indicated that Bay inventories would either continue to increase or begin to decrease. Under this scenario, a total reduction of BDE-209 loads (0 kg/yr) resulted in a 90% decrease in Bay inventory in less than 10 years.

Alternatively, when using slower degradation rates that produced the best agreement between model and empirical data, a much slower recovery of the Bay was forecast: a total reduction of loads under this scenario resulted in a 50% reduction in Bay inventory in approximately 10 years. For both scenarios, important loss pathways of BDE-209 from the Bay were degradation in sediment and outflow, as with BDE-47. Given the uncertainty around the environmental degradation rate for BDE-209, the implications of reduced loads on the recovery of San Francisco Bay are uncertain. However, the model estimates do suggest a quick response in the inventory of BDE-209 in the Bay is plausible.

While bans of the other PBDE mixtures went into effect in 2006, the voluntary phase-out of DecaBDE production is only now complete. As a result, a significant reduction of BDE-209 contamination in the Bay may not be evident for some time. BDE-209 is the dominant congener in sediment and is often detected in water, but only rarely detected in San Francisco Bay aquatic biota because it does not bioaccumulate and has a relatively short half-life in these organisms. Sediment is likely to be the best matrix to monitor for evidence of a decline in response to the voluntary phase-out, though recent trends may be obscured through the act of sample compositing and by natural sediment mixing processes.

5.3.3 PBDE Alternatives

As PBDE flame retardants are removed from use through bans and phase-outs, manufacturers find different flame retardants to take their place. Many of these chemical alternatives have also found their way into Bay sediment and biota (Klosterhaus et al. 2012; Werme 2012).

There is little evidence to indicate that PBDEs and other flame retardants added to consumer goods actually produce fire safety benefits (Roe and Callahan 2012). These chemicals are typically added to furniture and electronics sold in California and across the U.S. in order to comply with flammability standards put forth by the California Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation. Should California's current flammability standards remain in place, an increase in contamination from non-PBDE flame retardants would be expected in San Francisco Bay. Any impacts associated with these non-PBDE contaminants could increase as well.

However, the Bureau is currently working to revise its standards, and has most recently revised its standard for upholstered furniture and consumer goods that are exempt (BEARHFTI 2013a). This revised standard eliminates the need for manufacturers to add chemical flame retardants to many consumer goods, and thus is likely to reduce the use of these substances. As a result, a decline in the levels of both PBDEs and PBDE alternatives is expected. Any associated exposure and risk should also decline.

6.0 Conclusions and Recommendations

PBDEs are widely detected in San Francisco Bay water and sediment, as well as small and large tributaries. These contaminants are also ubiquitous in Bay biota including bivalves, fish, bird eggs, and seals.

In part as a result of the widely detected presence of PBDEs in the environment, the major manufacturers of two of the three PBDE formulations (PentaBDE and OctaBDE) ceased production of these compounds at the end of 2004, and the California Legislature banned these commercial mixtures as of 2006. In addition, the USEPA issued a significant new use rule on these substances in 2006. Production of the DecaBDE formulation was phased out in 2013. Finally, the state agency largely responsible for the widespread use of PBDEs and other chemical flame retardants has revised a key flammability standard to eliminate the incentive to incorporate these substances into upholstered furniture and many items for infants and young children (BEARHFTI 2013a).

At present, PBDE contamination of the Bay does not impair the beneficial use of sport fish consumption based on comparison to thresholds developed by OEHHA (Klasing and Brodberg 2011). Contamination is also unlikely to impair reproduction and development of Bay birds, according to a recent study of the toxicity of PentaBDE to tern eggs (Rattner et al. 2011, 2013). It is possible that current levels of contamination may impair the health of Bay harbor seal populations (Neale et al. 2005), though further research is necessary to evaluate this risk. In addition, limited toxicity information suggests Bay fish and benthic organisms may also be susceptible to low level adverse effects.

Fortunately, bioaccumulation monitoring indicates a decline in PBDE levels for Bay organisms under regular study. This is consistent with management actions to eliminate new production and uses of PBDEs via bans and phase-outs. Declines in contamination, and in any potential impacts to Bay biota, are expected to continue. The RMP's mass budget model indicates rapid recovery is possible with the reduced contaminant loads that are likely to follow reduced use of these compounds (Oram et al. 2008).

Concentrations in abiotic Bay media such as water and sediment are beginning to show declines as well. Bay-wide averages from 2002 to 2012 indicate a statistically signficant trend of decreasing BDE-47 sediment contamination. In water, measurements suggest a small but steady decline of this congener since 2004, but the trend is not yet statistically significant. In contrast, sediment concentrations of BDE-209, the dominant congener for this matrix, showed little change. Because the phase-out of BDE-209 is more recent, and because natural mixing and sample compositing may cloud any signal of recent changes to sediment contaminant loads, it may be some time before a clear trend emerges from sediment monitoring.

Both the declining PBDE levels in biota and the outcome of mass budget forecast modeling (Oram et al. 2008) suggest that chemical bans and phase-outs should be sufficient to address the potential impacts of PBDE contamination of San Francisco Bay.

6.1 Recommendations for Future Monitoring

Review of this body of PBDE work suggests a few strategic modifications in future monitoring of PBDEs and other flame retardants:

A) <u>Continue Status and Trends monitoring of Bay matrices for PBDEs</u>

  a. Water – monitored with reduced frequency, for example, every four years. Existing water data do not suggest trends need to be examined on an annual or biennial basis.

  b. Sediment – monitored every two years. In particular, evidence of a decline in BDE-209 followings its phase-out in 2013 is anticipated.

  c. Bivalves – monitored every two years to track continued declines in PBDEs.

  d. Fish – monitored every five years to track anticipated declines in PBDEs.

  e. Bird eggs – monitored every three years to track anticipated declines in PBDEs.

  f. Harbor seals – monitored in collaboration with the Marine Mammal Center.

B) <u>Characterize PBDE contamination of Bay margins where fish and birds feed</u>

Limited sediment sampling of a few sites in the Bay margins suggests that some of these regions hold PBDE concentrations far greater than any found in the open Bay. Sediments in San Leandro Bay and Mission Creek in 2011 contained BDE-209 concentrations at least four times greater than any other site sampled that year. A characterization of the fate of PBDEs in the margins of San Francisco Bay could prove useful to better predicting biotic and abiotic responses to management actions already underway (Jones et al. 2012).

A recent study of PCB levels in small fish in the Bay margins found these organisms to average much higher levels of contamination than sport fish (Greenfield and Allen 2013). PCB concentrations in the small fish were found to correlate well with PCB concentrations in nearby sediment, supporting this hypothesis. The high PCB uptake observed in small fish is an important element of the linkage between PCB sources and accumulation in the Bay food web.

Research on PBDEs in margin habitats can be added to an existing proposal to perform a representative characterization of surficial sediment contamination and habitat ancillary characteristics in Bay shallow water and intertidal areas for sediment-associated contaminants. The addition of monitoring PBDEs in small fish co-located with sediment samples is recommended to more specifically address questions of PBDE movement through food webs. Because observation of temporal trends following management actions is the primary focus of PBDE monitoring in the Bay, sampling would need to be repeated after two to three years on a subset of sites, the number of which would be dictated by resource constraints.

C) <u>Expand monitoring of PBDE alternatives</u>

Initial studies indicate a number of flame retardants, some PBDE replacements, are present in Bay sediment and biota. Non-PBDE flame retardants detected in Bay wildlife include hexabromocyclododecane (HBCD), Dechlorane Plus (DP), pentabromoethylbenzene (PBEB), tris(1-chloropropyl) phosphate (TCPP), tris(2-chloroethyl) phosphate (TCEP), tris(2-butoxyethyl) phosphate (TBEP), and triphenyl phosphate (TPhP). Sediment samples contained measurable levels of these compounds as well as bis(2,4,6 tribromophenoxy) ethane (BTBPE) and tris(1,3-dichloro-2-propyl) phosphate (TDCPP). Brominated flame retardants that were analyzed but not detected in any Bay samples were EH-TBB and BEH-TEBP (the brominated components of the PentaBDE replacement commercial mixture, Firemaster 550), decabromodiphenylethane (DBDPE, a Deca-BDE replacement), and hexabromobenzene (HBB).

The phosphate flame retardants TDCPP, TCPP, and TPhP have been detected in Bay sediments at estimated concentrations that are comparable to the PBDE and PCB concentrations in the same samples. TCPP, TCEP, and TBEP were detected in cormorant eggs, while several other phosphate flame retardants were analyzed but were not detected (tripropyl phosphate, tris(2,3-dibromopropyl) phosphate, tributyl phosphate [TBP], tricresyl phosphate, 2-ethylhexyl-diphenyl phosphate, tris(2-bromo-4-methylphenyl) phosphate, tris(2-ethylhexyl)phosphate [TEHP]). It is hypothesized that some of these may be taken up by aquatic organisms (e.g., TDCPP) but are easily metabolized. In addition to quantitative measurements, passive water samplers (POCIS) deployed by SFEI as part of the NOAA Mussel Watch Contaminants of Emerging Concern (CECs) Early Warning Network: California Pilot Project indicated the presence of several organophosphate flame retardants in San Francisco Bay waters: TCPP, TDCPP, TCEP, TBP, and TPhP; TBEP TEHP were not detected. Dozens of additional flame retardants have never been the subject of Bay monitoring efforts.

Expanded monitoring of alternative flame retardants would be advisable. Selection of the flame retardants and matrices to investigate will be informed by a variety of factors, including chemical information on fate and transport, previous monitoring data, production and use trends, and availability of affordable analytical methods. A few potential candidates for study include:

a. TDCPP, TCPP, and TPhP in sediment – Previous monitoring has found levels comparable to PBDEs in sediment samples, suggesting periodic monitoring to assess trends in concentration with time would be appropriate. Lower detections in wildlife are consistent with the hypothesis that organisms are able metabolize and excrete these compounds; monitoring of biota is considered a lower priority.

b. PBEB, HBB, BTBPE, DBDPE in sediment, bivalves, seals – AXYS Analytical currently offers semi-quantitative measurements of these compounds as part of its regular PBDE analysis. Obtaining measurements of these alternative flame retardants on a subset of samples already intended for PBDE analysis may be particularly cost-effective. BTBPE and DBDPE were identified by Howard and

Muir (2010) as good candidates for environmental monitoring based on predicted persistence and bioaccumulative potential. However, in previous monitoring, DBDPE and HBB were not detected in Bay samples.

c. EH-TBB and BEH-TEBP (components of Firemaster 550) in sediment, bivalves, seals – These compounds were not detected in previous monitoring, but it was suggested that matrix interference compromised the measurements (Klosterhaus et al. 2012). Should analytical improvements be available, it would be useful to conduct a second round of monitoring.

d. Ethylene bis-tetrabromophthalidimide (EBTEBPI) in sediment, bivalves, seals – This compound was identified by Howard and Muir (2010) as a likely candidate for monitoring based on predictions of its persistence and bioaccumulative potential. It is a high production volume chemical and an alternative for DecaBDE, which was phased out of production in 2013. AXYS Analytical is developing capabilities for alternative flame retardant analysis, and has identified this chemical as a likely candidate for methodological development.

e. 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (DBE-DBCH or TBECH) in sediment, bivalves, seals – This flame retardant was also identified by Howard and Muir (2010) as a likely candidate for monitoring based on predictions of its persistence and bioaccumulative potential. It has been detected in Arctic wildlife (Tomy et al. 2008) and causes reproductive toxicity in American kestrels (Marteinson et al. 2012b). TBECH has also been identified as an androgen agonist (Larsson et al. 2006). However, no effects on plasma sex hormones were observed in exposed juvenile brown trout (Gemmill et al. 2011); instead, TBECH was found to modulate the thyroid axis in these fish at environmentally relevant concentrations (Park et al. 2011b). AXYS Analytical is developing capabilities for alternative flame retardant analysis, and has identified this chemical as a likely candidate for methodological development.

D) <u>Conduct collaborative research on PBDE exposure and health effects in harbor seals</u>
Further study is needed to determine whether PBDE contamination levels in the Bay are

impacting the health of harbor seals, especially the more highly exposed, weaning pups. Available research and monitoring data suggest PBDEs may be more likely to pose risks to this species relative to other Bay biota for which studies exist in the literature. Opening a dialogue with the Marine Mammal Center (Sausalito, Calif.) with the aim to design a joint study is recommended as soon as possible.

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